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New evidence for preservation of contemporary marine organic carbon by iron in Arctic shelf sediments

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E-mail: JFaust@marum.de**Keywords:** Barents Sea, OC-Fe, marine shelf sediments, radiocarbon, carbon isotopes, carbon sequestrationSupplementary material for this article is available [online](#)

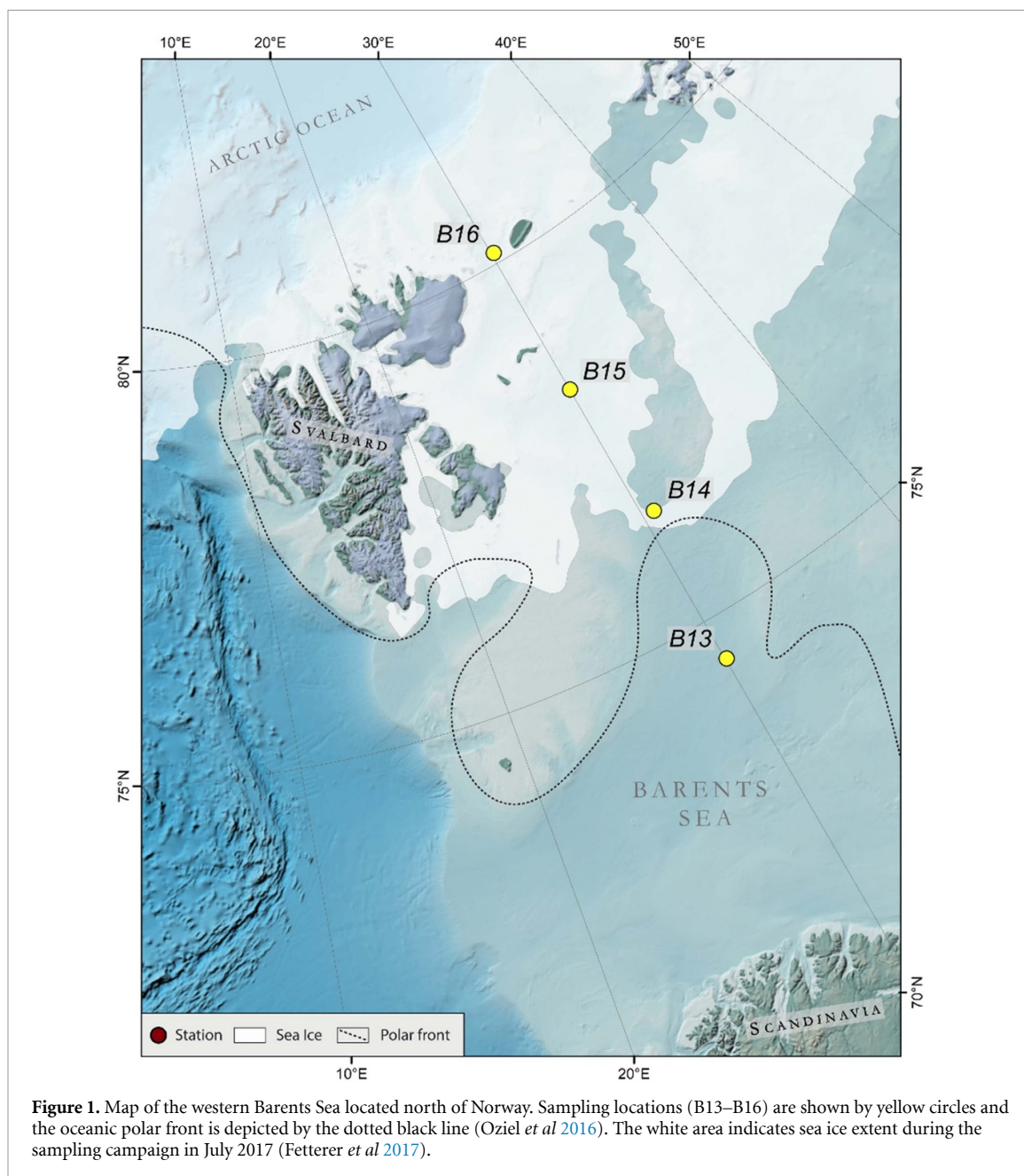
Abstract

The protection of organic carbon through association with iron minerals (Fe_R) is an important factor in its stabilisation, long-term storage, and burial efficiency in marine sediments. However, large uncertainties still exist concerning the sources, lability, age, and composition of the organic matter associated with Fe_R in natural sediments. Therefore, the timing and environmental setting of the carbon-iron bonding process remain elusive. Here we use radiocarbon ($\Delta^{14}\text{C}$) and stable isotopes ($\delta^{13}\text{C}$) of downcore bulk sedimentary organic matter, benthic foraminifera and the organic carbon fraction bound to Fe_R to interrogate the source and age of the organic carbon pool associated with Fe_R in Arctic marine sediments. In the Barents Sea, we find that the organic carbon associated with Fe_R is younger overall than the bulk organic matter and is probably marine derived. The comparison to other investigations of OC- Fe_R origins reveals that in large parts of Arctic shelf regions Fe_R associated organic carbon is radiocarbon enriched and has a higher $\delta^{13}\text{C}_{\text{org}}$ value compared to the bulk sediment, irrespective of sediment depth/age. Our findings suggest a rapid and preferential binding of fresh and marine organic matter with Fe_R . Hence, labile organic matter prone to decomposition is protected and stabilised, underlining the potential of the organic carbon-iron association as an efficient carbon burial mechanism.

1. Introduction

Organic carbon sequestration in marine sediments is a major control on atmospheric CO_2 and O_2 concentrations over geological time (Berner 2003), while being a poorly constrained pathway of contemporary carbon burial (Regnier *et al* 2022). The majority (approximately 90%) of organic carbon deposited at the global seafloor is buried in shelf and slope sediments (Hedges And Keil 1995, Smith *et al* 2015). A set of physical, biological and chemical processes combine to control organic carbon preservation, including sedimentation rate (Müller and Suess

1979, Ingall and Vancappellen 1990), the presence and absence of oxygen (Pedersen and Calvert 1990, Canfield 1994, Hartnett *et al* 1998), selective preservation of biochemically unreactive compounds (Hatcher *et al* 1983, Burdige 2007), and the protection of organic matter through interactions with a mineral matrix (Mayer 1994, Hedges and Keil 1995, Hemingway *et al* 2019). However, the relative importance of these factors remains poorly constrained. Moreover, sedimentary organic matter on marine shelves consists of a diverse mixture of terrestrial and marine components that exhibit different ages, degradation states and maturities. A major challenge



in evaluating the burial of organic carbon in marine sediments is the need to constrain degradation rates of these different organic components in relation to the environmental factors that control spatial and temporal changes in carbon sequestration (Arndt *et al* 2013).

Over the past four decades, enhanced atmospheric heat transport and inflow of Atlantic water have dramatically warmed the Arctic (e.g. Lind *et al* 2018). One of the most apparent signs of this warming trend and current global climate change is Arctic sea ice loss. For instance, the Barents Sea (figure 1) summer sea ice extent has drastically decreased by over 30% during the past decades (Meier *et al* 2014, Fetterer *et al* 2017). The ongoing transformation of the Arctic Ocean from an ‘icy land’ into an open ocean system forces the entire Arctic ecosystem to adapt

and restructure, changing the Arctic carbon cycle, i.e. atmospheric CO₂ uptake, pelagic-benthic coupling, organic matter sedimentation and long-term sequestration (Piepenburg 2005, Wassmann *et al* 2008, Arrigo and Van Dijken 2011, Wassmann 2011, Post *et al* 2013, Dalpadado *et al* 2014). However, future productivity and carbon burial in the Arctic and the Barents Sea remain uncertain, partly due to the challenges of linking of ongoing changes in the Arctic Ocean to organic carbon burial, sedimentary biogeochemical cycles and the marine ecosystems (Stein and Macdonald 2004, Wassmann 2011, Haug *et al* 2017).

Sedimentary organic matter can be protected and stabilised via association with inorganic components (Mayer 1994, Hedges and Keil 1995, Hemingway *et al* 2019). Clay minerals are viewed as a

major inorganic host for sedimentary organic matter, enhancing preservation (e.g. Mayer 1994, Kennedy *et al* 2002). However, as previously discovered in terrestrial soils, a chemical association between organic carbon and reactive iron oxides (nanoparticulate and amorphous phases of ferric (oxyhydr)oxides, e.g. ferrihydrite) could also play a central role in organic carbon preservation in marine sediments (Lalonde *et al* 2012). Organic carbon has a strong affinity to reactive iron phases (Fe_R), and the resultant association of organic carbon and iron (OC- Fe_R) is thought to promote long-term stabilisation and protection of sedimentary organic matter against microbial degradation (Lalonde *et al* 2012, Riedel *et al* 2013, Chen *et al* 2014, Chen and Sparks 2018). Investigations of global marine surface sediments revealed that the fraction of the total organic carbon bound to Fe_R (fOC- Fe_R) is on average 10%–20%, with values ranging from ~0.5% to 40% (Lalonde *et al* 2012, Salvadó *et al* 2015, Ma *et al* 2018, Zhao *et al* 2018, Wang *et al* 2019, Faust *et al* 2020) and even up to 80% (Longman *et al* 2021). Moreover, recent investigations of the association between organic carbon and Fe_R following sediment burial showed a millennial-scale OC- Fe_R persistence, underlining the importance of OC- Fe_R as an important carbon sequestration mechanism (Faust *et al* 2021). However, large uncertainties still remain concerning the sources, lability, age and composition of the organic matter (preferentially) associated with Fe_R in natural sediments. In particular, the timing and environmental setting of the carbon-iron bonding process remains elusive—information that is crucial to better quantify the role of OC- Fe_R in the global carbon cycle, both in the past and into the future.

The source and age of organic carbon at the seafloor can be recorded by radioactive and stable carbon isotopes (^{14}C and ^{13}C) of sedimentary organic matter (e.g. Eglinton *et al* 1997, Tesi *et al* 2011, Goñi *et al* 2013). The stable isotope composition of sedimentary fOC- Fe_R has refined our understanding about different sources and cycling of organic carbon in marine sediments (Lalonde *et al* 2012, Salvadó *et al* 2015, Shields *et al* 2016, Ma *et al* 2018, Zhao *et al* 2018, Wang *et al* 2019). However, the various modes of chemical binding and physical associations between organic carbon and reactive metal phases have mainly been investigated in the uppermost (0–3 cm) horizon of the seafloor (Faust *et al* 2021). Hence, longer-term OC- Fe_R burial mechanisms in natural marine sediments are not well characterized. Recent work on sediment cores from the western Barents Sea (figure 1) revealed that a substantial fraction of the OC- Fe_R pool is probably allochthonous, suggesting that the OC-Fe association is generated prior to deposition at the seafloor and not, for example, during authigenic precipitation of iron (oxyhydr)oxides at the $\text{Fe}(\text{II})/(\text{III})$ redox boundary in the sediments (Faust *et al* 2021).

To interrogate the source and age of the organic carbon pool associated with reactive iron in Arctic marine sediments, here we use radiocarbon and stable isotopes of downcore bulk sedimentary organic matter, carbonate (benthic foraminifera) and chemically extracted organic carbon bound to reactive iron.

2. Material and methods

2.1. Study area

The Barents Sea is located between 70 and 81° N off the northern Norwegian coast and is the largest of the six pan-Arctic shelf seas. It covers an area of 1.6 million square kilometres with an average water depth of 230 m (Carmack *et al* 2006). For a detailed descriptions about the modern climate setting and ecosystem of the Barents Sea, we refer to extensive overviews and reviews published during the past two decades (Loeng *et al* 1997, Wassmann *et al* 2006, Jakobsen and Ozhigin 2011, Smedsrud *et al* 2013, Dalpadado *et al* 2014, Jørgensen *et al* 2015). In brief, the oceanic circulation pattern of the western Barents Sea is dominated by the relatively warm northward-flowing North Atlantic Current (temperature 2 °C–8 °C, salinity >35‰) and 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 (figure 1) (Harris *et al* 1998) which is mainly determined by the shelf bathymetry and is, therefore, relatively stable from year to year (Drinkwater 2011). 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. Thus, sediment discharge through river inflow is low (e.g. Politova *et al* 2020) 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^{-1} since the last glacial period (Faust *et al* 2020), but can be much higher proximal to glacier outlets, for instance in places close to Svalbard. The present ecological setting, as in all Arctic shelf seas, is characterized by very pronounced seasonal fluctuations in insolation and primary production. 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 (Sakshaug 2004).

Throughout the western Barents Sea, oxygen penetration was repeatedly analysed by direct measurements and indirect indicators (e.g. pore water profiles), and was found to be between ~2 and 6 cm below the sediment–water interface (Vandieken *et al* 2006, Nickel *et al* 2008, Freitas *et al* 2020, Stevenson *et al* 2020, Faust *et al* 2021). In addition, ^{210}Pb profiles and direct measurements of benthic faunal activity show a distinct sediment mixed layer in the Barents Sea that extends to a sediment depth of approximately 2 cm (Carroll *et al* 2008, Solan *et al* 2020).

2.2. Sediment sampling

Four sediment cores were collected by using a multicorer along a south–north gradient in the western Barents Sea during the Changing Arctic Ocean Seafloor cruise (JR16006) in summer 2017 (figure 1). Sediment cores from station B13, B14, B15, B16 (supplementary table S1) were sliced in 0.5 cm intervals from 0 to 2 cm and in 1 cm intervals thereafter. Samples were stored in plastic bags at -20°C immediately after recovery on-board the Royal Research Ship James Clark Ross. Prior to any chemical sediment analysis, all samples were freeze-dried and homogenized by gentle grinding using an agate mortar and pestle. Between two and four downcore samples from each sediment core were selected for radioactive carbon-14 content ($\Delta^{14}\text{C}$) and stable isotopic $\delta^{13}\text{C}$ signature analysis (supplementary tables S2 and S3).

2.3. Organic carbon extraction and analysis

To quantify the amount of organic carbon bound to iron (oxyhydr)oxides in our samples, we applied a method described in detail by Lalonde *et al* (2012) and Salvadó *et al* (2015). Briefly, 0.25 g of sediment was transferred into 30 ml centrifuge tubes. Fifteen millilitre of a solution containing 0.27 M trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\cdot\text{H}_2\text{O}$) and 0.11 M sodium bicarbonate (NaHCO_3) was added, mixed and heated to 80°C in a water bath; 0.1 M sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$; 0.25 g) was added to the mixture, temperature was maintained at 80°C , and the tube was shaken every 5 min. After 15 min, the mixture was centrifuged for 10 min at 4000 rpm, the supernatant was decanted, and 200 μl of 12 N HCl were added to prevent Fe(III) precipitation. The remaining sediment samples were rinsed three times with artificial seawater and then freeze-dried. To quantify potential organic carbon loss unrelated to metal oxide dissolution, a control experiment was conducted: A 0.25 g aliquot of each sample was treated the same way as the reduction experiment, but the complexing and reducing agents (sodium citrate and sodium dithionite) 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.

Organic carbon 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 . Organic carbon content was determined with a LECO SC-144DR combustion analyser at the University of Leeds, UK (Faust *et al* 2021). 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 organic carbon analysis was $\pm 1.7\%$. To account for the mass loss during the extraction experiment we applied the mass balance calculation of Salvadó *et al* (2015).

The $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of organic carbon associated with reactive iron were determined by difference from the control and the reductive leach residue and compared to bulk untreated sediments (supplementary tables S2 and S3). In more detail, bulk sediment samples before and after the reduction and control experiments were moistened with a small amount of deionised water, covered by glass fibre filter papers and placed into a sealed glass desiccator vessel together with a beaker of concentrated hydrochloric acid to hydrolyse any carbonate in the sample over three days via acid fumigation at the Natural Environment Research Council Radiocarbon Facility. Decarbonated samples were freeze-dried before combustion to CO_2 in a sealed quartz tube. After combustion, sample CO_2 was cryogenically recovered on a vacuum line. An aliquot of recovered sample CO_2 was used to measure $\delta^{13}\text{C}$ on a dual inlet stable isotope mass spectrometer (Thermo Fisher Delta V). This value was used for normalisation of the measured sample $^{14}\text{C}/^{13}\text{C}$ ratio. A second aliquot of sample CO_2 was prepared to graphite and the sample $^{14}\text{C}/^{13}\text{C}$ ratio was measured by accelerator mass spectrometry at the Scottish Universities Environmental Research Centre AMS laboratory. The ^{14}C enrichment of organic carbon in each sample was calculated as $\Delta^{14}\text{C}_{\text{org}}$ based on the relative difference between the isotope ratio of the absolute international standard (relative to the year of measurement, 2021) and the age-corrected sample isotope ratio, where the latter was first normalised to -25% $\delta^{13}\text{C}$ Vienna Pee Dee Belemnite (VPDB), using the measured $\delta^{13}\text{C}_{\text{org}}$ value described above (Stuiver and Polach 1977). The fraction modern ($F^{14}\text{C}$) is also reported where $F^{14}\text{C} = (\Delta^{14}\text{C}_{\text{org}} + 1000)/991.448$ based on the correction factor for measurement in 2021. To quantify potential ^{14}C contamination from the organic carbon extraction process, three process standards, modern (TIRI Barley Mash; TBM), background (Anthracite) and carbon free silica sand, were separately processed alongside the natural sediment samples in both the control and the reaction experiment. The aliquots of Anthracite standard show slightly elevated values above the laboratory blank (i.e. ^{14}C added during

sample treatment), indicating an addition of a small amount of modern carbon during the extraction procedure. Accordingly, we applied a background correction to samples and TBM standards of a value of $F^{14}\text{C} = 0.006 \pm 0.001$. This value was obtained via the average of measured values for Anthracite processing blanks. This addition of a small quantity of carbon during processing is consistent with results for silica blanks, which showed a carbon content of 0.01%–0.02%.

$\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of the organic carbon bonded to reactive iron phases ($\delta^{13}\text{C}\text{-Fe}_\text{R}$; $\Delta^{14}\text{C}\text{-Fe}_\text{R}$; supplementary tables S2 and S3) were calculated assuming that the isotopic composition of the control sample ($\Delta^{14}\text{C}\text{-Fe}_\text{R}$ control) is comprised of a mixture of organic carbon from reactive iron (the unknown $\Delta^{14}\text{C}\text{-Fe}_\text{R}$) and carbon forming the residue after the reductive removal of reactive iron (measured $\Delta^{14}\text{C}\text{-Fe}_\text{R}$ reaction), such that mass balance leads to equations (1) and (2):

$$\Delta^{14}\text{C}\text{-Fe}_\text{R} = 1/\text{fOC}\text{-Fe}_\text{R} * (\Delta^{14}\text{C}\text{-Fe}_\text{R}\text{ control} - \Delta^{14}\text{C}\text{-Fe}_\text{R}\text{ reaction}) + \Delta^{14}\text{C}\text{-Fe}_\text{R}\text{ reaction} \quad (1)$$

$$\delta^{13}\text{C}\text{-Fe}_\text{R} = 1/\text{fOC}\text{-Fe}_\text{R} * (\delta^{13}\text{C}\text{-Fe}_\text{R}\text{ control} - \delta^{13}\text{C}\text{-Fe}_\text{R}\text{ reaction}) + \delta^{13}\text{C}\text{-Fe}_\text{R}\text{ reaction} \quad (2)$$

where $\text{fOC}\text{-Fe}_\text{R}$ is the fraction of total organic carbon bond to reactive iron from Faust *et al* (2021).

To determine the ^{14}C carbonate contents of benthic foraminifera, providing constraint on the ^{14}C activity of marine dissolved inorganic carbon (DIC) at time of deposition, aliquots of bulk sediment samples were washed through a 63 μm sieve before being dried at 50°C, and microfossils were picked using a Leica MZ12 binocular microscope. All benthic foraminifera used for radiocarbon analyses were a mixture epifaunal or shallow infaunal species, dominated by rotaliids (>90%). *Pyrgo* and other miliolid species, which have previously been associated with anomalous radiocarbon measurements in the Arctic (Ezat *et al* 2017), were not analysed. The radiocarbon activities of the carbonate microfossils were obtained via the Mini Carbon Dating System at the Bristol Radiocarbon Accelerator Mass Spectrometry facility. Carbonate specimens were acidified to release CO_2 (<100 μgC), which was measured directly without graphitisation (Tuna *et al* 2018).

3. Results and discussion

To evaluate the age and origin of the organic carbon bound to reactive iron phases (OC- Fe_R) over long time scales of about 6 kyr before present (BP) (figure 2), we analysed $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures in sediment samples ($\Delta^{14}\text{C}_\text{org}$ and $\delta^{13}\text{C}_\text{org}$) and in the organic carbon fraction bound to Fe_R ($\Delta^{14}\text{C}\text{-Fe}_\text{R}$ and $\delta^{13}\text{C}\text{-Fe}_\text{R}$). To place these in the context of the radiocarbon activity of the marine dissolved inorganic carbon reservoir at the time of deposition, we compare the organic matter to the $\Delta^{14}\text{C}$ content of benthic foraminifera (carbonate). In summary, we first discuss the origin of the bulk organic matter and show that its mainly marine-derived, but is

significantly aged prior to deposition. We then compare our bulk $\Delta^{14}\text{C}_\text{org}$ and $\delta^{13}\text{C}_\text{org}$ signatures with $\Delta^{14}\text{C}\text{-Fe}_\text{R}$, $\delta^{13}\text{C}\text{-Fe}_\text{R}$ and $\Delta^{14}\text{C}$ carbonate, finding that OC- Fe_R in the Barents Sea is younger overall than the bulk organic matter and probably marine derived. Finally, we relate our findings to other investigations of OC- Fe_R origins and reveal that in large parts of Arctic shelf regions iron associated organic carbon is radiocarbon enriched and has a higher $\delta^{13}\text{C}_\text{org}$ value compared to the bulk sedimentary, irrespective of sediment depth/age, which indicates rapid sequestration of contemporary organic carbon.

3.1. Origin of the bulk organic matter

The stable carbon isotope signature of organic matter ($\delta^{13}\text{C}_\text{org}$) in marine sediments reflects the isotopic composition of the carbon source and the fractionation between ^{12}C and ^{13}C during photosynthesis (Hayes 1993). As the contribution of C_4 plant types is insignificant in the Arctic region (Collins and Jones 1986, Still *et al* 2003), $\delta^{13}\text{C}_\text{org}$ can be a reliable proxy to identify marine versus terrigenous organic matter in Barents Sea sediments (e.g. Schubert and Calvert 2001). Marine organic carbon is isotopically enriched in ^{13}C compared to terrestrial C_3 plant material (Arthur *et al* 1985) and typical endmember values are -20.1‰ and -26.1‰ for marine and terrigenous organic matter, respectively, in the Barents Sea region (Knies and Martinez 2009, Pathirana *et al* 2014). Our results show that $\delta^{13}\text{C}_\text{org}$ signatures of all bulk untreated surface sediment samples vary between -22.1‰ and -23.7‰ (average -22.5‰) suggesting a bulk organic matter pool more dominated by marine organic matter (Martens *et al* 2021 and ref. therein). The $\delta^{13}\text{C}_\text{org}$ values show a slight decrease with sediment depth (figure 2 and supplementary figure 1). The decline in $\delta^{13}\text{C}_\text{org}$ is correlated with a $\Delta^{14}\text{C}_\text{org}$ decrease ($r = 0.8$; supplementary

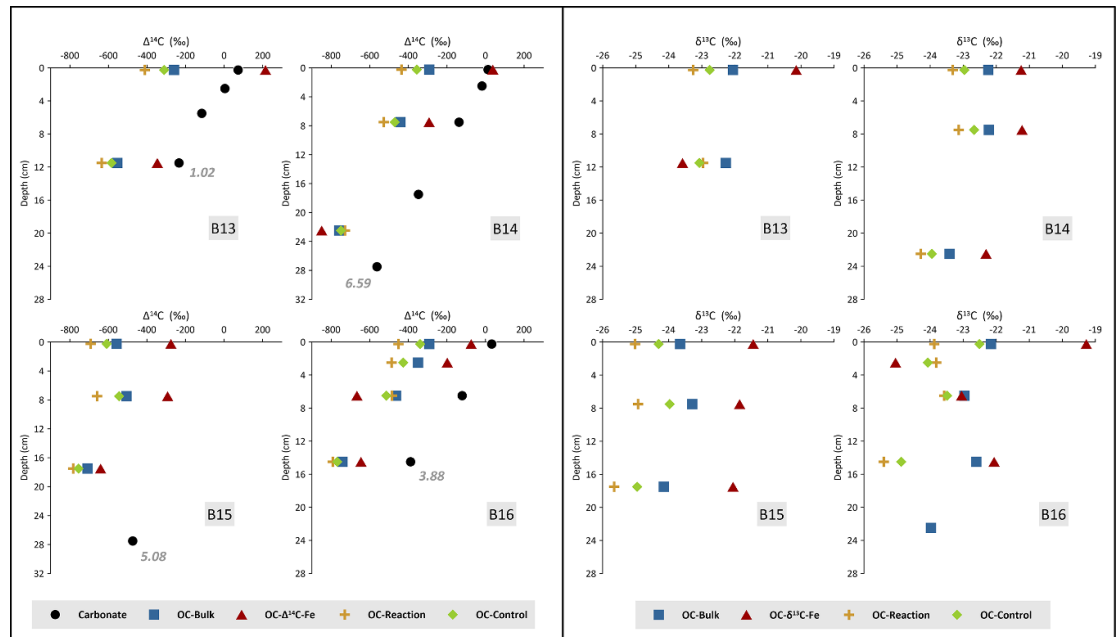


Figure 2. Downcore $\Delta^{14}\text{C}_{\text{org}}$ (left) and $\delta^{13}\text{C}_{\text{org}}$ (right) values in the sediment residuals of the control and extraction experiment and bulk sediment. These are shown relative to the $\Delta^{14}\text{C}$ content of benthic foraminifera (carbonate). The isotopic signatures of the organic carbon fraction bond to Fe_R ($\Delta^{14}\text{C}\text{-Fe}_\text{R}$ and $\delta^{13}\text{C}\text{-Fe}_\text{R}$) are calculated by mass balance (equations (1) and (2)). Grey numbers indicate uncalibrated radiocarbon dates of the lowest biogenic carbonate measurement in kyr BP.

figure S2) which occurs as total organic carbon contents and related biomarker records documenting relatively steady first-order organic matter decay with depth (Stevenson *et al* 2020, Faust *et al* 2021). This indicates no significant changes in the type of organic matter deposited at the seafloor, hence, we attribute these changes to a preferential degradation of labile marine organic matter, and not to a gradual change in organic carbon sources over time.

^{14}C is commonly utilized for age determination of the carbon-bearing component. The ^{14}C signature of marine organic matter ($\Delta^{14}\text{C}_{\text{org}}$) is a marker for modern, pre-aged or fossil carbon and, therefore, provides some information about the organic matter source, especially if combined with $\delta^{13}\text{C}_{\text{org}}$ signatures. Marine surface sediments from circum-Arctic shelf regions reveal a substantial range of published $\Delta^{14}\text{C}_{\text{org}}$ values, outlining large-scale differences in organic carbon sources to the present seafloor (Martens *et al* 2021). The Laptev and East Siberian Seas receive substantial carbon contributions from remobilization of thawing permafrost or other older deposits. In contrast, terrigenous organic carbon input in the Kara Sea is mainly contemporary (i.e. recent plant cover), and Barents and Chukchi Sea sediments are dominated by modern carbon derived from marine primary producers (Martens *et al* 2021).

The organic carbon $\Delta^{14}\text{C}_{\text{org}}$ signatures of our bulk untreated Barents Sea sediment samples vary between -260‰ and -760‰ and decrease with sediment depth due to the time-dependant decay of ^{14}C (figure 2, supplementary figure S1). Bulk $\Delta^{14}\text{C}_{\text{org}}$ values in the first centimetre of each core are in

accordance with published $\Delta^{14}\text{C}_{\text{org}}$ data of bulk surface sediments from the western Barents Sea, which range from -245‰ to -504‰ ($n = 11$) (Martens *et al* 2021). Sediment cores from stations B13, B14 and B16 show very similar $\Delta^{14}\text{C}_{\text{org}}$ values (-260‰ , -292‰ , -291‰) in the first centimetre. At station B15, $\Delta^{14}\text{C}_{\text{org}}$ is lower (-558‰) as is $\delta^{13}\text{C}_{\text{org}}$. Due to a very shallow mean bioturbation depth ($<2\text{ cm}$) at all investigated stations (Carroll *et al* 2008, Solan *et al* 2020), the presence of old bulk organic matter at the seafloor can be explained by a combination of generally low sedimentation rates in the Barents Sea (figure 2), leading to long residence times of material at the seafloor (Griffith *et al* 2010), and the lateral transport of material across the shelf, which could include pre-aged organic matter from terrestrial or marine sources (e.g. Vonk *et al* 2014).

3.2. Evidence for young and marine OC- Fe_R in Barents Sea sediments

Dissimilatory iron reduction is an important process in the anaerobic degradation of organic matter in marine sediments. Iron (oxyhydr)oxides are reduced, and Fe^{2+} is released into the pore waters (Burdige 1993). Following upward diffusion out of the iron reduction zone, this Fe^{2+} is oxidised mainly by molecular O_2 , but also by NO_3^- and solid Mn (oxyhydr)oxides (Burdige 1993). This oxidation usually occurs in the upper centimetres of a shelf sediment profile below the oxygenated, strongly bioturbated surface sediment layer, and leads to an authigenic enrichment of sedimentary Fe_R (Froelich *et al* 1978) below the sediment-water interface. Organic carbon

has a strong affinity to such freshly precipitating Fe(III) phases (e.g. ferrihydrite), and it has therefore been proposed that coprecipitation of organic carbon with or adsorption to, this authigenic Fe_R within the sediment is the main OC- Fe_R coupling process that promotes the stabilization of sedimentary organic matter (Lalonde *et al* 2012, Riedel *et al* 2013, Chen *et al* 2014, Barber *et al* 2017, Chen and Sparks 2018). However, several recent investigations indicate that the fraction of the total organic carbon content bound to Fe_R (FOC- Fe_R) is not generally controlled by Fe_R availability (Sirois *et al* 2018, Faust *et al* 2020, 2021). Downcore FOC- Fe_R profiles in combination with pore water composition and sedimentary Fe_R contents reveal that iron redox cycling and associated authigenic Fe_R formation within the sediment are less important for the coupling of Fe_R to organic carbon than assumed (Faust *et al* 2021). Indeed, substantial amounts (>10%) of the total organic carbon content is bound to Fe_R at the sediment-water interface above the zone of authigenic Fe_R precipitation. This raises the question of how much of the OC- Fe_R is allochthonous, i.e. formed in the overlying water column, in sea ice, or on land; and how much is autochthonous, i.e. formed by biogeochemical processes within the sediments.

To further validate and characterise a potential allochthonous OC- Fe_R source in Arctic marine sediments, we compare our bulk $\Delta^{14}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{org}}$ signatures with those of $\Delta^{14}\text{C-Fe}_R$ and $\delta^{13}\text{C-Fe}_R$ as well as $\Delta^{14}\text{C}$ content of benthic foraminifera. To identify the type and amount of organic carbon bound to Fe_R we conducted an iron oxide extraction (reaction experiment) based on the method originally developed by Mehra and Jackson (1958), modified for marine sediments by Lalonde *et al* (2012). To account for organic carbon released during the reaction experiment that was not related to iron phases, we conducted a sodium chloride extraction (control experiment) without the complexing and reducing agents trisodium citrate and sodium dithionate. The comparison of the $\delta^{13}\text{C}_{\text{org}}$ and $\Delta^{14}\text{C}_{\text{org}}$ values between the reaction experiment and control experiment reveal slightly more depleted values in the control experiment at station B13 (11.5 cm), B14 (22.5 cm) and B16 (2.5 cm, 6.5 cm; figure 2). Such differences have been reported before (e.g. Salvadó *et al* 2015) and they indicate that in some cases the sodium chloride treatment, washed out labile unbound organic matter. This could be an effect of different organic matter sources, degradation state or liberation of very labile OC- Fe_R during sodium chloride treatment (Fisher *et al* 2020). Nevertheless, following extraction treatment of our sediment samples, the isotopic signatures of $\Delta^{14}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{org}}$ in the solid residues of the control versus reaction experiments show clear differences from the bulk sediment samples at all stations (figure 2). The reaction and control experiment residues have mostly lower (more negative) $\Delta^{14}\text{C}_{\text{org}}$

and $\delta^{13}\text{C}_{\text{org}}$ values. It follows that the treatment liberated organic carbon that was relatively enriched in ^{13}C and ^{14}C from the sediments and selectively liberated organic matter with a more marine and younger isotopic signature. When we calculate the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures of the organic carbon bound to reactive iron phases ($\delta^{13}\text{C-Fe}_R$; $\Delta^{14}\text{C-Fe}_R$, equations (1) and (2)), we find they are considerably higher than the respective values in most of the studied bulk samples (figure 2). To further investigate these isotopic disequilibria between organic carbon fractions of the bulk, control and reaction residues, we calculate the respective 'fraction modern' (F^{14}C) offsets (see Soulet *et al* 2016 for details) of the contemporaneous carbon reservoirs of $\text{F}^{14}\text{C-Fe}_R$, bulk organic carbon and carbonate (benthic foraminifera; figure 3).

Benthic calcareous fossils (e.g. foraminifera) are commonly used to derive age-depth relationships for marine sediments over the last ~50 ka. In comparison to bulk organic carbon, which represents a mixture of organic carbon from various sources, of various ages and different degradation states, the calcareous material of benthic organisms reflects bottom-water radiocarbon activity (i.e. a single carbon source) that is not significantly influenced by processes within the sediment. Thus, radiocarbon ages based on $\Delta^{14}\text{C}$ content of benthic calcareous fossils are assumed to reveal the most accurate ages of sediment deposition (e.g. Skinner and Bard 2022). The ^{14}C offsets of $\text{F}^{14}\text{C-Fe}_R$ and benthic foraminifera (carbonate) in relation to bulk organic carbon show that over time (downcore), the offsets between carbonate and bulk organic carbon show an increasing trend (figure 3). As bioturbation activity is low at all investigated stations (Solan *et al* 2020, Faust *et al* 2021), we assume that this is a function of decomposition and preferential degradation of fresh and young marine organic matter in the bulk sediment. However, we cannot completely exclude the possibility that the observed offset change is caused by a variation in local ^{14}C reservoir effect i.e. bottom water dissolved inorganic carbon age changes e.g. due to oceanographic variability. The $\text{F}^{14}\text{C-Fe}_R$ offset is (apart from sample B16; 6.5 cm) always >1 and is relatively stable, ranging between 1.23 and 1.64. Thus, the organic carbon bound to iron is considerably younger than the bulk organic carbon. Moreover, the $\text{F}^{14}\text{C-Fe}_R$ offset relative to biogenic carbonate shows that $\text{F}^{14}\text{C-Fe}_R$ at the top of the sediment cores is of similar age, or even younger, than carbonate. The downcore decrease in the Fe_R -carbonate offset could be related to the loss of some fresh and labile organic carbon bound to iron. Alternatively, the type/source of the organic carbon bound to Fe_R could have changed in the past. But irrespective of the reason, our $\text{F}^{14}\text{C-Fe}_R$ data show that the organic carbon bound to iron is young in all samples, indicating rapid and lasting sequestration of CO_2 and a direct link to

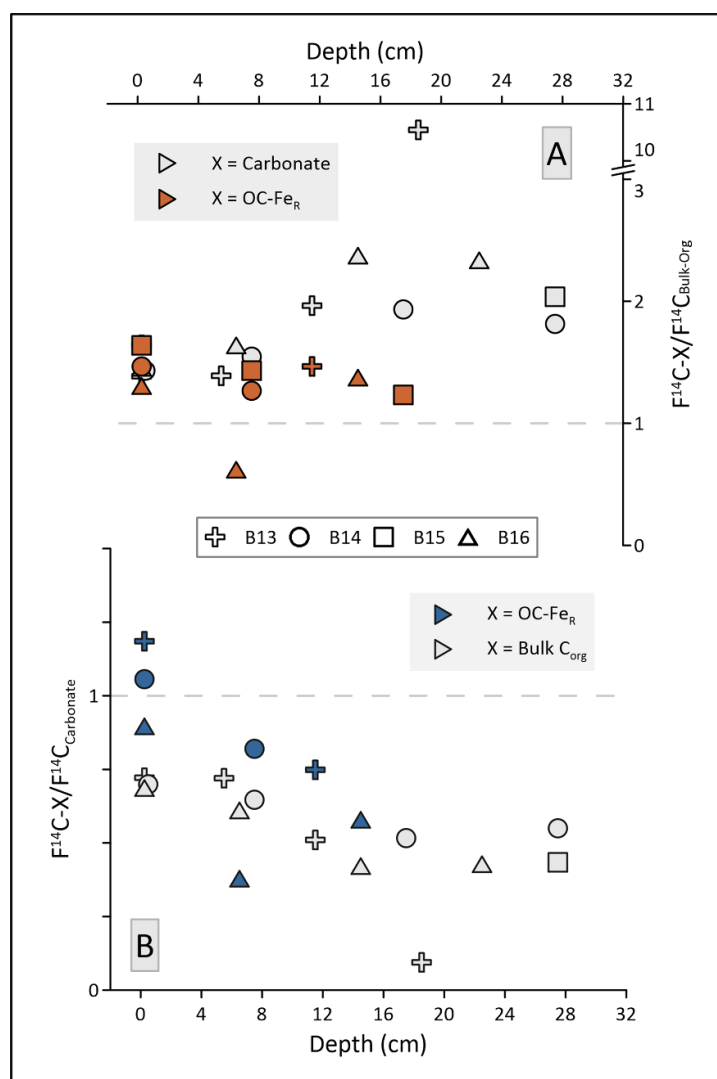


Figure 3. Comparison of fraction modern values ($F^{14}C$) between carbon phases measured at the same sediment depth for each station. (A) $F^{14}C$ of benthic foraminifera (carbonate) and $F^{14}C$ of OC associated to reactive iron (equation (1)), OC-Fe_R, relative to the $F^{14}C$ values of bulk organic carbon. Values >1 are younger (^{14}C -enriched) than the bulk organic matter. (B) $F^{14}C$ values of OC-Fe_R and bulk organic carbon relative to the $F^{14}C$ of carbonate. Values <1 show older (^{14}C -depleted) signatures compared to the benthic foraminifera phase.

contemporaneous terrestrial and/or marine primary productivity.

3.3. Wider evidence for contemporary iron associated organic carbon

Previous work on OC-Fe_R coupling in marine sediments further afield, has focused primarily on bulk carbon content, and/or $\delta^{13}C_{org}$ ($\delta^{13}C_{org-FeR}$) in surface sediments (Lalonde *et al* 2012, Barber *et al* 2014, Ma *et al* 2018, Zhao *et al* 2018, Wang *et al* 2019). In accordance with our bulk $\delta^{13}C_{org}$ and $\delta^{13}C_{org-FeR}$ findings, a global data set of sediment from various depositional environments, including freshwaters, estuaries, river deltas, shelf sediments and the deep sea, shows that, in most cases, $\delta^{13}C_{org-FeR}$ is enriched in ^{13}C relative to the bulk organic matter (Lalonde *et al* 2012). The authors attributed the isotopic shift towards higher values to selective association of certain types of organic matter rich

in proteins and carbohydrates, as these are more likely to establish protective inner-sphere complexes with reactive iron phases. Follow-up studies on surface sediments from the shelf areas of China indicated more complex $\delta^{13}C_{org-FeR}$ signatures with values ranging from -49‰ to -4‰ (mean -23‰) (Zhao *et al* 2018, Wang *et al* 2019). Their finding of larger regions with substantially enriched and/or depleted $\delta^{13}C_{org-FeR}$ values relative to bulk organic matter, and a trend of more enriched values towards the continental margin, indicated a preference for terrigenous organic carbon binding with iron. Presuming that the organic carbon-Fe_R bonding occurs mainly in the sediment, the authors suggested that the observed $\delta^{13}C_{org-FeR}$ variability was caused by selective sequestration and release of ^{13}C -depleted organic carbon either during the OC-Fe_R binding process or by its reduction under anoxic conditions (Wang *et al* 2019). Our downcore $\delta^{13}C_{org-FeR}$ signatures from

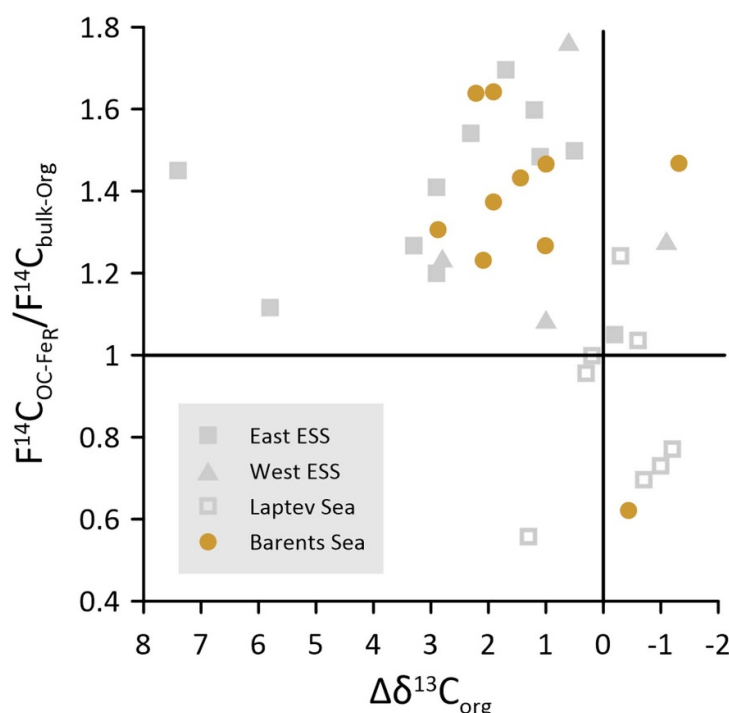


Figure 4. Difference between $\delta^{13}\text{C-FeR}$ and $\delta^{13}\text{C}_{\text{org}}$ bulk ($\Delta\delta^{13}\text{C}_{\text{org}}$ ‰) versus fraction modern ratio between OC-FeR and bulk organic carbon ($F^{14}\text{C}_{\text{OC-FeR}}/F^{14}\text{C}_{\text{bulk-ORG}}$). The comparison of the results from this study (yellow marks) with findings from the Laptev Sea, West- and East-Siberian Sea (grey filled/open squares and triangles; (Salvadó *et al* 2015)) shows that, apart from the Barents Sea samples B13: 11.5 cm and B16: 6.5 cm and samples taken close to the Lena River delta (Laptev Sea), the majority of these Arctic shelf regions iron associated organic carbon is radiocarbon enriched and has a higher $\delta^{13}\text{C}_{\text{org}}$ value compared to the bulk sedimentary organic matter.

the Barents Sea do not support the assumption of preferential binding of terrigenous organic carbon in the oxic part of the core, although the slight down-core decrease (^{13}C depletion) might indeed be related to selective release of ^{13}C -enriched organic carbon. But the driving force(s) for the OC-FeR binding is still not known and it could be physical, chemical and/or biological mechanisms that initiate an isotopic fractionation. This hinders the assignment of the $\delta^{13}\text{C}_{\text{org}}$ as organic carbon source indicator.

A more robust attempt to identify the type and origin of the organic carbon bound to FeR in marine sediment is a dual-carbon isotope approach similar to ours. To the best of our knowledge, only one study used both $\delta^{13}\text{C}_{\text{org}}$ and $\Delta^{14}\text{C}_{\text{org}}$ to evaluate the origin of the OC-FeR in marine sediments (Salvadó *et al* 2015). They showed that along the Eurasian Arctic shelf, $\delta^{13}\text{C}_{\text{org-FeR}}$ and $\Delta^{14}\text{C}_{\text{org-FeR}}$ signatures point towards an older and more terrestrial source in the Laptev Sea, probably related to coastal erosion and thawing permafrost. However, in areas where marine phytoplankton is an important sedimentary organic carbon source, e.g. in the East Siberian Sea and towards the outer shelf areas, their data imply a younger and marine plankton-dominated source of the organic carbon bound to FeR. Thus, the $\delta^{13}\text{C}_{\text{org-FeR}}$ and $\Delta^{14}\text{C}_{\text{org-FeR}}$ spatial variability in Chinese and Eurasian shelf sediments implies that the origin of the organic carbon varies distinctly with proximity

to land and is related to the dominant organic matter source (marine versus terrigenous), of the bulk sedimentary composition.

Remarkable though is that, disregarding the spatial variability of the $\delta^{13}\text{C}_{\text{org-FeR}}$ and $\Delta^{14}\text{C}_{\text{org-FeR}}$ signatures in Eurasian Arctic shelf surface sediments, a re-examination of these data reveals that the $\delta^{13}\text{C}_{\text{org}}$ and $\Delta^{14}\text{C}_{\text{org}}$ offsets between bulk and FeR-bound organic carbon show $F^{14}\text{C}$ offsets >1 and enriched $\delta^{13}\text{C}_{\text{org}}$ values compared to the bulk sediment composition the East- and West-East Siberian Sea (figure 4). In a similar way, the four sediment cores from the Barents Sea have organic carbon bound to FeR that is enriched in ^{13}C and ^{14}C compared to the bulk organic carbon content, irrespective of sediment depth/age. These findings indicate a rapid and preferential binding of fresh and marine organic matter with FeR. Thus, FeR not only protects organic matter from degradation in marine sediments over millennial time scales (Faust *et al* 2021), FeR also sequestered contemporary carbon across the Arctic Shelf which further highlights the potential efficiency of this ‘rusty carbon sink’.

4. Implications and concluding remarks

To better understand the sources and overall fate of organic carbon in the marine realm, both the composition and mode of binding of organic carbon that

accumulates in sediments must be determined. The previous findings of the occurrence of large fractions of total organic carbon bound to Fe_R (>10%) at the sediment-water interface (above the iron redox zone) in the Barents Sea (Faust *et al* 2021), as well as possibly in the surface sediments from the Eurasian Arctic and Chinese shelf seas, suggests the important role of allochthonous OC- Fe_R source. Based on the new data of this study and in concert with the findings from the Eurasian Arctic and the Chinese shelves, we propose that areas dominated by a marine carbon pool see a coupling of Fe_R to relatively fresh and young organic carbon. Furthermore, these investigations combined indicate that the origin of OC- Fe_R varies distinctly with proximity to land, indicating that Fe_R tends to associate with the pervasive type of organic carbon available. Nevertheless, enriched $^{13}\text{C}\text{-Fe}_R$ and $^{14}\text{C}\text{-Fe}_R$ signatures compared to the bulk organic carbon content indicate a rapid and preferential binding of fresh and marine organic matter with Fe_R even in Arctic shelf areas containing larger fractions of terrigenous organic carbon. Hence, labile organic matter prone to decomposition seems to be protected and stabilised, underlining the potential of OC- Fe_R as an efficient carbon burial mechanism. Additionally, young and marine $\Delta^{14}\text{C}_{\text{org}}\text{-Fe}_R$ and $\delta^{13}\text{C}_{\text{org}}\text{-Fe}_R$ signatures imply a binding process in the water column, for example, during the formation of particulate iron-oxyhydroxides formed by oxidation of dissolved Fe(II) in the euphotic zone (Gelting *et al* 2010). To better understand the formation and source of OC- Fe_R in the marine environment further investigations of the organic carbon type and source as well as a possible allochthonous OC- Fe_R binding process, prior organic carbon and Fe_R sedimentation, needs to be investigated. This is crucial for a better estimation of the efficiency of the ‘rusty carbon sink’, its contribution to the global cycles of carbon and oxygen and its carbon burial function in warming Arctic Ocean.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflict of interest

The authors declare no competing interests.

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