Research

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Benthic phosphorus cycling within the Eurasian marginal sea ice zone

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The Arctic Ocean region is currently undergoing dramatic changes, which will likely alter the nutrient cycles that underpin Arctic marine ecosystems. Phosphate is a key limiting nutrient for marine life but gaps in our understanding of the Arctic phosphorus (P) cycle persist. In this study, we investigate the benthic burial and recycling of phosphorus using sediments and pore waters from the Eurasian Arctic margin, including the Barents Sea slope and the Yermak Plateau. Our results highlight that P is generally lost from sediments with depth during organic matter respiration. On the Yermak Plateau, remobilization of P results in a diffusive flux of P to the seafloor of between 96 and 261 $\mu\text{mol m}^{-2} \text{yr}^{-1}$. On the Barents Sea slope, diffusive fluxes of P are much larger (1736–2449 $\mu\text{mol m}^{-2} \text{yr}^{-1}$), but these fluxes are into near-surface sediments rather than to the bottom waters. The difference in cycling on the Barents Sea slope is controlled by higher fluxes of fresh organic matter and active iron cycling. As changes in primary productivity, ocean circulation and glacial melt continue, benthic P cycling is likely to be altered with implications for P imported into the Arctic Ocean Basin.

1. Introduction

The Arctic Ocean is experiencing some of the fastest and most drastic changes on Earth in response to anthropogenic climate change, including rapid reduction of sea ice cover and thickness [1], retreat of marine-terminating glaciers, changing ocean circulation patterns [2,3] and ocean warming [4]. These changes are affecting the entire Arctic marine ecosystem, including the primary producers at the base of the food web. Primary productivity in the Arctic can be either light or/and nutrient-limited [5,6]. As sea ice continues to retreat, light limitations will be reduced followed by the anticipated increase of primary production [7]. Nutrient availability is likely to change in response to enhanced utilization from primary productivity as sea ice retreats and to changes in nutrient inputs due to changes in ocean circulation patterns, stratification and meltwater fluxes from land [6].

An understanding of the evolving sources and sinks of phosphate is necessary for predicting future changes in the Arctic primary productivity, which underpins the health of the entire Arctic ecosystem and can drive climate feedbacks associated with carbon burial. Phosphate plays a key role in marine environments [8,9], however, gaps in our understanding of the marine phosphate cycle persist [10]. Phosphate is commonly considered to be the 'ultimate' limiting nutrient in the ocean over long timescales [8] due to its long residence times and the possibility that N deficits can be offset by N fixation. The specific ratios of available nutrients can also affect the distribution and biogeochemical roles of plankton, as many planktons are adapted to relative differences in P and N availability [10,11].

Dissolved P is delivered to the oceans from the land by rivers, dust and ice-rafted debris and removed from seawater through sedimentary burial [12,13]. Mass balanced transport estimates of phosphate for the entire Arctic Ocean indicate that the Arctic is a net exporter of dissolved inorganic phosphorus to the North Atlantic [14]. Riverine inputs of phosphate to the Arctic cannot explain the missing source of phosphate, demonstrating that the P cycle within the Arctic remains poorly understood [15]. One possible source of P is glacial melt. Recent work from Greenland indicates that glacial melt represents a significant source of this missing P [16].

Phosphorus cycling in the benthic environment is also important because phosphorus can be sequestered in sediments or recycled back into the water column. As organic matter is remineralized within sediments, dissolved inorganic and organic phosphorus is released into sediment pore waters. These dissolved phosphorus phases may be released to bottom waters by diffusive fluxes from the seafloor or sequestered via sorption on minerals such as Fe and Mn oxides or authigenic mineral formation such as carbonate fluorapatite (CFA) and vivianite [17–19]. Adsorption and co-precipitation with Fe oxides may be especially important in polar continental margins, which may have large fluxes of reactive Fe from terrestrial glacial melt [20–23].

Here, we focus on cores collected on the Arctic Margin north of Svalbard, including the Barents Sea slope, the Sofia Basin and the Yermak Plateau, to investigate benthic controls on phosphate cycling. Our main aim was to investigate the benthic burial and recycling of P in the Arctic Ocean. We present paired pore water and sediment data to investigate the controls on phosphorus fluxes from the seafloor to the water column. Phosphorus speciation data is also paired with Fe speciation results to evaluate the relationship between Fe minerals and phosphate sequestration in the sediments.

2. Study site

This study focuses on the marginal sea ice zone north of the Svalbard archipelago (figure 1). Study locations from the Barents Sea slope, north of Spitsbergen, range from 481 to 1852 m water

Figure 1. Map of the Barents Sea and Eurasian Arctic margin (adapted from [24]). Cores are indicated with circles (the Yermak Plateau core in yellow, Sofia Basin core in orange and the Barents Sea slope cores in red). Median sea ice extent from 1981–2010 for March (dashed) and September (solid) are indicated in yellow (data from the National Snow and Ice Data Center, www.nsidc.org). Bathymetry is indicated by shades of blue [25]. The WSC is indicated in red. (Online version in colour.)

depth. The Yermak Plateau is a bathymetric feature to the northeast of Svalbard and is separated from the northern Barents Sea slope by the Sofia Basin. Estimates of recent sedimentation rates are generally low and similar in both the northern Barents Sea ($0.5\text{--}1.0\text{ mm yr}^{-1}$; [26]) and the Yermak Plateau (0.7 mm yr^{-1} ; [27]). Study locations from the Yermak Plateau range from 817 to 1523 m water depth, and the study location from the Sofia Basin is 2175 m. The region is situated at the entrance of the Arctic Ocean, where Atlantic water flows into the Central Arctic Basin. The West Spitsbergen Current (WSC) carries nutrient-rich, warm, saline ($T \geq 2^\circ\text{C}$, $S \geq 34.88\text{ psu}$) [28] Atlantic waters northwards in the eastern Fram Strait. Between 78° and 80° N , the WSC splits, with the main branch flowing along the western and then northern continental margin of Spitsbergen [29–33]. During transit northwards, water temperatures and salinities in the WSC decrease by $0.20^\circ\text{C}/100\text{ km}$ and $0.010\text{ psu}/100\text{ km}$ [34]. This current continues along the eastern margin of the Eurasian Basin.

The study area is sea ice covered during the winter with the sea ice maximum being reached in March (figure 1). In the spring, the sea ice begins to melt, and during the summer the region is located within the marginal sea ice zone, which is the transition between the open ocean and sea ice. The sea ice minimum is reached in September. Sedimentary Fe cycling was previously examined at these core locations [24]. This study highlighted that in the Barents Sea slope region, reactive Fe was remobilized within the sediments and shuttled away region. On the Yermak Plateau and Sofia Basin, reactive Fe accumulated in sediments with no evidence for remobilization. The main driver of these differences was higher oxidant demand within Barents Sea slope sediments associated with higher fluxes of organic carbon to the seafloor, which fuelled more Fe reduction and remobilization, resulting in near-surface accumulation or sediment loss.

Table 1. Locations of cores in this study. Full site names are given here and shortened in the text to the station name (i.e. ‘19’ for the first core in table below) and deployment number (i.e. ‘19’ for the first core in table below).

core	water depth (m)	latitude	longitude
<i>Barents Sea slope</i>			
PS92/019-19-MC	481	81°13.79' N	18°33.04' E
PS92/027-15-MC	795	81°19.55' N	17°16.87' E
PS92/031-13-MC	1852	81°30.20' N	18°31.72' E
<i>Sofia Basin</i>			
PS92/047-20-MC	2175	81°20.68' N	13°39.94' E
<i>Yermak Plateau (eastern flank)</i>			
PS92/039-05-MC	1523	81°55.50' N	13°37.98' E
PS92/040-01-MC	1158	81°49.04' N	10°52.06' E
PS92/046-15-MC	886	81°50.62' N	09°45.48' E
PS92/056-05-MC	854	81°0.94' N	08°17.05' E
<i>Yermak Plateau (western flank)</i>			
PS92/043-20-MC	817	82°10.45' N	07°0.53' E

Conversely, low oxidant demand within the Yermak Plateau and Sofia Basin sediments resulted in enrichments of reactive Fe within the upper 30 cm.

3. Material and methods

Sediment samples were collected with the RV *Polarstern* using a multicorer during spring 2015, May/June, as part of the Transitions in the Seasonal Sea Ice Zone (TRANSSIZ) expedition PS92 ([35]; figure 1). Core top results from nine locations are presented in table 1. Downcore results were additionally produced on representative cores taken from five sites on the Barents Sea slope and Yermak Plateau (PS92/019-19, 27-15, 39-5, 46-16 and 56-5; table 1). Cores were sliced onboard at 1 cm resolution and frozen at –20°C. Samples were subsequently freeze-dried and powdered in an agate mortar and pestle in the laboratory.

A sample split from cores 19-19, 27-15, 39-05, 46-15 and 56-05 was prepared for wavelength-dispersive X-ray fluorescence (XRF) by borate glass bead fusion. The XRF analyses of total Fe, Al and P were performed using a Philips PW-2400 WD-XRF spectrometer calibrated with 53 geostandards at the University of Oldenburg (for detailed method description, see [36]). A sediment split from all cores was analysed for Fe-bound phosphorus after extraction by citrate-dithionite-bicarbonate (CDB; pH=8.0) for 8 h at room temperature [37]. Extracted P concentrations were determined by inductively coupled plasma-optical emission spectrometry (Thermo iCAP 7400 ICP-OES) at the University of Leeds (for detailed method description, see [38]). The most reactive Fe oxyhydroxides (OHO; i.e. ferrihydrite) have been previously extracted and measured [24] using an ascorbate extraction [39].

Carbon concentrations were measured on an LECO CS244 carbon analyser at the University of Newcastle for all cores. Total organic and inorganic carbon were determined using paired acidified (organic) and unacidified (total) carbon measurements. In preparation for analysis of total organic carbon (TOC), samples were acidified in 5% HCl until all the carbonate was removed. Dried, acidified samples were powdered and homogenized in an agate mortar and pestle prior to analysis. Chlorophyll *a* (Chl *a*) concentrations were analysed on samples from all cores except 40-01 and 56-05 fluorometrically following methods described in [40] and results for most locations were previously published in [41].

Pore waters were extracted onboard using Rhizon samplers (Rhizosphere; 0.15 µm pore size) with vacuum applied by plastic syringes with wooden stoppers [42]. Samples were collected from all cores at resolutions between 1 and 5 cm, with decreasing resolution downcore. Bottom waters were sampled from the water overlying the sediments within the multicorer. Pore waters were acidified with ultrapure HCl and stored at 4°C. Pore waters were then diluted 1:1 with MQ water and analysed for major element composition, including Fe and P, by inductively coupled plasma-optical emission spectrometry (Thermo iCAP 7400 ICP-OES) at the University of Leeds. An internal standard spiked with Y was added to each sample to monitor the precision of Fe and P measurements via ICP-OES. Analytical precision (two standard deviations of the measured value/reported value) for Fe and P were ± 1.91 and ± 2.53 , respectively.

Diffusive fluxes were calculated using Fick's first law of diffusion (equation (3.1)) assuming steady-state conditions from pore water P results under the assumption that the P pool was all in the species HPO_4^{2-} . The concentration gradient was determined from the sediments to the bottom waters with the exception of cores that have no gradient across the sediment water interface. For these cores (19-19, 27-15 and 31-13), a diffusive flux of P is calculated into the oxic layer:

$$J = \Phi \times D_s \times \frac{\partial C}{\partial x}, \quad (3.1)$$

where J is the diffusive flux, D_s is the sedimentary diffusion constant, Φ is the porosity and $\partial C/\partial x$ is the concentration gradient. Without direct measurements for porosity, a conservative value of 0.8 was chosen following [43].

The sediment diffusion constant is calculated with the empirical equation of Ullman and Aller [44] (equation (3.2)), which takes into consideration sediment tortuosity. A diffusive molecular coefficient, D_m , of $0.0134 \text{ m}^2 \text{ yr}^{-1}$ is used for HPO_4^{2-} at 4°C:

$$D_s = \Phi^{n-1} \times D_m, \quad (3.2)$$

where D_s is the sedimentary molecular diffusion constant, Φ is the porosity and n is a correction factor (such that $n = 2$ when porosity is greater than 0.7).

4. Results

On the shallowest core location on the Barents Sea slope (19-19), P/Al (presented as wt% ratios) is elevated within the top 7 cm (up to 0.034) with values of 0.010 for the rest of the core (figure 2). In a deeper Barents Sea slope core (27-15), P/Al decreases from 0.015 at the sediment water interface to 0.012 at 8.5 cm. Below this, P/Al increases to 0.014 and then decreases to the base of the core (0.012). In cores from the Yermak Plateau 39-5 and 46-15, P/Al decreases from 0.014 to 0.012. The P/Al ratio also decreases in the other Yermak Plateau core (56-5) from 0.013 to 0.007 with the exception of an increase in the relative P concentration at 1.5 cm. The trends in P/Fe are generally similar to P/Al with values ranging between 0.015 and 0.044 (figure 2). Total Fe and P concentrations are plotted in Supplementary Figure 1.

Core top TOC values range from 0.53% to 1.61%. In the five cores with downcore TOC records, TOC decreases with depth (figure 3). Organic carbon to phosphorus (C_{org}/P) ratios (presented as wt% ratios) broadly decrease with depth in all cores except 19-19, with core top values from 10.0 to 12.9 and values below the surface sediments as low as 5.2 (figure 3). In core 19-19, C_{org}/P values decrease from the surface (13.1) to minimum values at 2.5 cm (6) below the sediment water interface coincident with the maximum P/Al values before increasing again to an average value of 17.6. Concentrations of Chl *a* in the surface sediments range from 0.04 to $0.71 \mu\text{g g}^{-1}$, with higher concentrations of the Barents Sea slope (table 2). Iron bound phosphorus ranges between 0.003% and 0.034% (table 2 and figure 4) with the highest concentrations in the top 5 cm of core 19-19 and the lowest concentrations in sediments below 5 cm in core 19-19 and in the other Barents Sea slope cores (27-15 and 31-13). The Fe-bound P represents between 3% and 14% of the P pool.

In the Yermak Plateau cores (39-5, 46-15 and 56-5), pore water P increases downcore with maximum concentrations of $5.39 \mu\text{mol}$, $4.06 \mu\text{mol}$ and $4.84 \mu\text{mol}$, respectively (figure 5). In the

Figure 2. Downcore records of (a) P/Al (%%) and (b) P/Fe (%%) from XRF analysis. Dashed lines indicate the average shale ratio of 0.008. The Barents Sea slope sites (19-19 and 27-15) are in red and the Yermak Plateau sites (39-5, 46-15 and 56-5) are in yellow. (Online version in colour.)

Figure 3. Downcore records of (a) organic carbon to phosphorus (C/P) ratios (%%) and (b) TOC. The Barents Sea slope sites (19-19 and 27-15) are in red and the Yermak Plateau sites (39-5, 46-15 and 56-5) are in yellow. (Online version in colour.)

Figure 4. Cross plot of Ascorbic extractable Fe (from [24]) versus Fe-bound P. Sediments from the Barents Sea slope are in red, Sofia Basin are in orange and the Yermak Plateau are in yellow. Slope lines for the Barents Sea slope cores and the Yermak Plateau cores are included as dashed lines. The slope for the Sofia Basin core (47-20) is similar to the Yermak Plateau slope but not shown. (Online version in colour.)

Table 2. Concentrations of (a) Chl *a* ($\mu\text{g g}^{-1}$) in the upper 2 cm of sediment, (b) maximum Fe-bound P (wt%) and (c) maximum Fe-bound P/total P. Dashes are used to indicate no existing data.

core	chl <i>a</i>	max P _{Fe} (wt%)	P _{Fe} /P _{Tot} (%)
<i>Barents Sea slope</i>			
19-19	0.71	0.034	13.7
27-15	0.64	0.005	7.4
31-13	0.27	0.004	—
<i>Sofia Basin</i>			
47-20	0.10	0.008	—
<i>Yermak Plateau (eastern flank)</i>			
39-5	0.09	0.007	7.6
40-1	—	0.008	—
46-15	0.08	0.007	7.2
56-5	—	0.007	7.6
<i>Yermak Plateau (western flank)</i>			
43-20	0.04	0.008	—

Barents Sea slope cores (19-19 and 27-15), the concentration of pore water P in the top 2 cm is less than or equal to seawater P (0.00 and 0.85 μmol , respectively). In both Barents Sea Slope cores, pore water P increases sharply at 2 cm before stabilizing to average concentrations of 31.79 and

Figure 5. Records of (a) pore water phosphorus and (b) pore water iron to phosphorus ratios. Barents Sea slope sites (19-19 and 27-15) are in red and Yermak Plateau sites (39-5, 46-15 and 56-5) are in orange. Blue squares represent bottom water samples. Orange horizontal lines represent transition pore water iron reduction and precipitation [24]. (Online version in colour.)

$3.56 \mu\text{mol}$. Pore water Fe/P (weight:weight) ratios are plotted in figure 5. Most samples have values of less than 3.3, with the exception of samples from core 19-19, which has values up to 25.2. Calculated diffusive fluxes range from 117 to $2449 \mu\text{mol m}^{-2} \text{yr}^{-1}$ (table 3). At all core sites on the Yermak Plateau (39-5, 40-01, 43-20, 46-15 and 56-5) and Sofia Basin (47-20), there is a flux of P from the sediments into the bottom waters across the sediment water interface. Conversely, at the Barents Sea slope core sites (19-19, 27-15 and 31-13), there is no flux of P across the sediment water interface, but a flux from deeper sediments into a near-surface layer (0–3 cm). The flux of P into the bottom waters on the Yermak Plateau and Sofia Basin are an order of magnitude lower than the Barents Sea slope fluxes from deeper sediments into a near-surface layer. Porewater Fe concentrations are plotted in Supplementary Figure 2.

5. Discussion

At all core locations, P decreases with depth as compared to both Al and Fe, indicating that relatively less P is preserved at depth than is originally deposited at the seafloor (figure 2). TOC within sediments also decreases downcore, indicating that the patterns of P loss are controlled by the remineralization of organic matter. This would result in a loss of both P and C from the sediments and release of dissolved P to the pore waters [45–47]. Ratios of C_{org}/P decrease downcore, illustrating that P losses are smaller relative to organic carbon with increasing depth. Organic matter respiration appears to have a more significant effect on the organic C pool than the P pool. This is to be expected since organic bound P represents a small portion of the total P pool, unlike the measured organic carbon. The preferential loss of organic C relative to P may also suggest that P released to the pore waters is being adsorbed onto mineral phases and/or precipitating as authigenic minerals rather than being lost from the sediments [17–19] or that utilization by benthic organisms affects the C and P pools differently.

Table 3. Calculated diffusive fluxes for the studied cores. Fluxes into bottom waters are bolded and fluxes into a near-surface sediment layer are italicized.

core	water depth (m)	diffusive flux ($\mu\text{mol m}^{-2} \text{yr}^{-1}$)
<i>Barents Sea slope</i>		
PS92/019-19-MC	481	<i>2449</i>
PS92/027-15-MC	795	<i>1996</i>
PS92/031-13-MC	1852	<i>1736</i>
<i>Sofia Basin</i>		
PS92/047-20-MC	2175	117
<i>Yermak Plateau (eastern flank)</i>		
PS92/039-05-MC	1523	189
PS92/040-01-MC	1158	141
PS92/046-15-MC	886	96
PS92/056-05-MC	854	261
<i>Yermak Plateau (western flank)</i>		
PS92/043-20-MC	817	151

Pore water P concentrations are, generally, elevated in the sediments relative to bottom waters (figure 5). On the Yermak Plateau, P/Al ratios generally decrease from the surface to the deeper sediments (figure 2), coincident with a gradual increase in pore water P concentrations (figure 5), supporting that P is being lost from the solid phase and released to pore waters. The gradient of pore water P crosses the sediment water interface, indicating a diffusive flux of P from the sediments to the bottom waters. Pore water P continues to increase in the core with depth, suggesting the continued release of dissolved P. Sequestration of P as authigenic CFA has been observed in many continental margin settings [48]. While this process may be occurring on the Yermak Plateau, CFA precipitation does not appear to keep pace with P release.

Conversely, on the shallow Barents Sea slope, P/Al ratios are elevated within a near-surface sediment layer between 0 and 5 cm. Pore water P profiles on the Barents Sea slope (19-19) are characterized by zero to low concentrations in the upper 2 cm and a rapid increase in P concentrations below this depth. These profiles indicate that P is released to pore waters within sediments deeper than 5 cm and pore water P is sequestered in near-surface sediments. Benthic P cycling on the deeper Barents Sea Slope is intermediate to the Yermak Plateau and the shallow Barents Sea slope. The pore water results from the deeper Barents Sea slope (27-15) are similar to core 19-19, despite the lack of sedimentary evidence for an Fe- and P-rich near-surface layer, perhaps suggesting that Fe and P accumulated near the surface but were later physically and/or biogeochemically remobilized. Elevated but stable concentrations of pore water P at both sites below 10 cm may indicate CFA precipitation within sediments but further P extractions and pore water results (F concentrations) would be required to directly test this. Diffusive fluxes of P were calculated based on pore water total dissolved P profiles. The calculated benthic fluxes illustrate that the flux of P into the near-surface sediment layers on the Barents Sea slope is an order of magnitude higher than the flux of P to bottom waters in the Yermak Plateau sites (figure 6).

The accumulation of P in the near-surface oxic layer in core 19-19 co-occurs with Fe-rich sediments at this location [24] suggesting that P is sorbing onto Fe oxide and oxyhydroxide minerals (Fe OHO) within near-surface sediments. The role of Fe in binding sedimentary P has been well-established based on the observation that pore water P can be trapped within sediments through sorption to Fe OHO surfaces and/or co-precipitation with dissolved Fe^{2+} [49–52].

Figure 6. Geochemical results from the Eurasian Arctic Margin including (a) surface chl *a* values in core top sediments, (b) TOC in core top sediments, (c) diffusive flux of P and (d) ratio of Fe-bound P and ascorbate extractable Fe in core top sediments. (Online version in colour.)

To evaluate the relationship between benthic Fe and P cycling, the amount of P bound to Fe was quantified (figure 4) and compared to the concentration of the most reactive Fe OHO, ferrihydrite. Ferrihydrite has the highest P adsorption potential and fastest adsorption rates compared to other Fe minerals because it is poorly crystalline and has a higher surface site density [53]. All samples contained Fe-bound P, indicating that some P is sorbed to Fe minerals in all locations and at all depths. In most samples, Fe-bound P represented less than 10% of the total P pool (table 2). Higher concentrations (up to 15% of the P pool) were measured within the Fe-rich, near-surface sediments of core 19-19 [24].

Within every core, the concentration of Fe-bound P and ascorbate extractable Fe covary is shown in figure 4. However, different relationships exist spatially between these cores. On the Barents Sea slope, higher concentrations of Fe-bound P are associated with relatively lower concentrations of Fe OHO (figure 4). This relationship indicates that P sequestration is more efficient on the Barents Sea slope, where cycling of Fe and P are more active (figure 5; [24]). The efficiency of P sequestration on the Barents Sea slope prevents any flux of P to the bottom waters. Conversely, the less efficient P sequestration by Fe minerals on the Yermak Plateau results in a loss of dissolved P from the sediments to the bottom waters, regardless of higher concentrations of reactive Fe in many of the sediments.

The difference in benthic Fe and P cycling between the shallow Barents Sea slope and the Yermak Plateau is likely associated with differences in fluxes of fresh organic matter [54]. Higher fluxes of fresh organic matter might be expected on the Barents Sea slope which is located in the productive marginal sea ice zone, while the Yermak Plateau is covered with sea ice longer during

the year. In addition, the Barents Sea slope is influenced by the core of the Atlantic water inflow ([55] and references therein), which generally supports higher primary production in this region [56,57]. Within the studied cores, surface Chl *a* concentrations indicate that the Yermak Plateau sediments have a lower concentration of fresh organic matter than the Barents Sea slope ([35,58]; figure 6). Sediments from core 19-19 also have the highest TOC concentrations (up to 1.6%). However, in the neighbouring core 27-15, some of the lowest TOC concentrations (less than 1%) are found (figure 6). This may indicate that the deep Barents Sea slope has been organic carbon starved but is now receiving large fluxes of fresh organic matter. Conversely, it may suggest that because TOC includes OC from multiple sources, it is a poor proxy for the flux of labile organic matter.

The higher fluxes of labile organic matter to the seafloor on the Barents Sea slope would lead to higher levels of organic matter respiration within the sediments and a richer benthic community that would likely enhance OM usage, respiration and remineralization. Higher rates of respiration will result in higher fluxes of nutrients to the pore waters from respired organic matter. Additionally, respiration consumes oxygen within the pore waters. Once most of the oxygen is consumed, microbial metabolisms that use other electron acceptors (e.g. Fe^{3+}) dominate [59]. Fe^{2+} from these anaerobic sediments diffuse upwards from below, providing a source of Fe for co-precipitation with P. Orange lines in figure 5 indicate the depth at which Fe precipitates in the sediments from Fe^{2+} diffusing upwards.

On the Barents Sea slope, the transition depth from Fe reduction to Fe OHO precipitation is coincident with elevated dissolved P concentrations (figure 5). Conversely, on the Yermak Plateau, there is no evidence for Fe reduction within the sediment cores. In summary, the higher fluxes of labile organic matter to the Barents Sea slope, fuels both the higher release of P to pore waters and the active redox cycling that result in the trapping of this P in surface sediments.

The importance of the active reduction and reprecipitation of Fe is highlighted by the Yermak Plateau sediments. While these sediments also contain significant amounts of reactive Fe ([24]; figure 4), P does not sorb efficiently enough to these mineral surfaces to stop the flux of P from the seafloor. This may be due to the importance of co-precipitation of P with Fe, rather than sorption of pore water P on pre-existing Fe OHO. One explanation for the low efficiency of P sorption in the Yermak Plateau is that these 'preformed' Fe OHO may have decreased adsorption capacity due to pre-sorbed organic matter blocking the mineral surfaces [60].

Ratios of pore water Fe:P can be used to investigate whether pore water conditions are appropriate for P binding. The predominant surface complexation ratio of Fe:P on Fe OHO is 2 mol:mol, which corresponds to a mass ratio of 3.6 [61–63]. It has been proposed that if the pore water Fe^{2+} :P ratio is less than 3.6, the recently formed Fe OHO is not sufficient to bind all the diffusing P resulting in a flux of P to the bottom waters [64]. The pore waters in core 19-19 have high Fe:P ratios (up to 25), which supports the argument that a sufficient flux of Fe is diffusing into the surface layer to trap all P. In core 27-15, the values of Fe:P are low; however, significant data are lacking because Fe in pore waters was below detection limits. Within the Yermak Plateau sediments, Fe:P ratios are also below 3.6, indicating that the flux of Fe is too low for efficient P binding, despite the abundance of reactive Fe minerals within the sediments.

As a whole, our results indicate that locations underlying more productive surface waters, such as the Barents Sea slope, are characterized by active sedimentary biogeochemical cycling, which results in accumulation of P within near-surface sediments. While P is currently sequestered in Barents Sea slope sediments, it is also important to note that our pore water results capture transient conditions that may not persist over longer timescales, especially as the Arctic is currently undergoing rapid changes, which are likely to affect P cycling in the region. The delivery of reactive organic matter to the seafloor acts as a control on benthic phosphorus cycling both by delivering organic bound phosphorus and by increasing the oxidant demand within sediments, fuelling reduction and remobilization of reactive Fe. Changes in sea ice extent and nutrient availability are likely to alter the surface primary productivity and, subsequently, the flux of fresh organic matter to the seafloor. Currently, Chl *a* derived primary productivity is increasing in the Barents Sea and Eurasian Arctic [7] and this region is arguably experiencing the most rapid

increases in Chl *a* derived primary productivity [65]. Models suggest that some of the largest increases in primary productivity in the future will occur on the Eurasian perimeter, including the northern Barents Sea [66,67]. If these predictions are proven correct, it would be expected that the flux of P to the seafloor would increase in this region, as the depth of Fe reduction shoals within the sediments remobilizing sorbed P. The availability of reactive Fe is the main control on benthic P recycling, and therefore, changes in the delivery of reactive Fe to the seafloor will impact benthic P cycling. Within the polar region, glacial melt [20–23] and ice-rafted debris [68] act as sources of reactive Fe. Therefore, future changes in meltwater and ice rafting are likely to impact both benthic Fe and P cycling.

6. Conclusion

This study investigated benthic cycling of P on the Eurasian Arctic margin. Combined sediment and pore water geochemical data shed light on the controls of P burial and recycling in the Barents Sea slope and Yermak Plateau sediments. These results indicate that fluxes of P are controlled by delivery of fresh organic matter and the precipitation of fresh Fe minerals within sediments. Pore water results from the Barents Sea slope cores indicate high P fluxes into near-surface (0–5 cm) sediment layers. On the shallow slope, this pattern can be clearly explained by the co-precipitation of P with Fe OHO minerals in Fe-rich, near-surface sediments. Results from the deeper slope are more ambiguous since pore waters indicate P trapping in the upper 2 cm of sediments, but an obvious Fe- and P-rich oxic layer is not observed. However, the ratio of Fe_{asc} to Fe-bound P still hints at P trapping within this layer.

By contrast, the Yermak Plateau cores exhibit the trends characteristic of P loss due to organic matter remineralization resulting in a small flux of P from the seafloor into the bottom waters. While these cores all contain reactive Fe and Fe-bound P, P sequestration is not efficient. In all of the Yermak Plateau cores, pore water Fe/P ratios are lower than 3.6, suggesting that dissolved Fe concentrations are insufficient to bind dissolved P. This result highlights that the presence alone of reactive Fe oxide minerals is not sufficient to sequester P and that efficient binding of P requires co-precipitation of Fe and P.

In response to anthropogenic warming, sea ice is expected to retreat further and patterns of surface ocean primary productivity are expected to change, leading to changes in the patterns of P burial and recycling as well. Altered patterns of the delivery and recycling of reactive Fe within sediments will be of primary importance to future benthic P cycling. Increased delivery of labile organic matter in response to elevated surface productivity will increase the oxidant demand and Fe remobilization within sediments. These changes may result in conditions on the Yermak Plateau shifting towards those observed on the Barents Sea slope. Increased organic carbon fluxes on the Barents Sea slope may result in large fluxes sedimentary fluxes of P to bottom waters, as a large stock of P has been accumulated in near-surface sediments.

Data accessibility. The datasets supporting this article have been uploaded to Pangaea. Additional data used in this paper are found in [24,41].

Authors' contributions. A.T. and C.M. were responsible for the design of this project. C.M., M.K., N.M., M.N., J.M., M.O. and I.P. were involved in sample collection. A.T., C.M., M.K. and N.M. contributed to data production. All authors contributed to the data interpretation, drafting, revising and final approval of the manuscript.

Competing interests. We declare we have no competing interests.

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