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# Limited physical protection leads to high organic carbon reactivity in anoxic Baltic Sea sediments

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## Abstract

Marine sediments bury ~160 Tg organic carbon (OC) yr$^{-1}$ globally, with ~90% of the burial occurring in continental margin sediments. It is generally believed that OC is buried more efficiently in sediments underlying anoxic bottom waters. However, recent studies revealed that sediments in the central Baltic Sea exhibit very high OC mineralization rates and consequently low OC burial efficiencies (~5-10%), despite being overlaid by long-term anoxic bottom waters. Here, we investigate factors contributing to this unexpectedly high OC mineralization rates in the Western Gotland Basin (WGB), a sub-basin of the central Baltic Sea. We sampled five sites along a transect in the WGB, including two where organic carbon-iron (OC-Fe) associations were quantified. Sulphate reduction rate measurements indicated that OC reactivity ($k$) was much higher than expected for anoxic sediments. High OC loadings (i.e., OC concentrations normalized to sediment specific surface area) and low OC-Fe associations showed that physical protection of OC is limited. Overall, these results suggest that the WGB sediments receive large amounts of OC relative to the supply of mineral particles, far exceeding the potential for OC physical protection. As a result, a large fraction of OC is free from associations with mineral surfaces, thus the OC reactivity is high, despite anoxic bottom waters. Overall, our results demonstrate that anoxia does not always lead to lower OC mineralization rates and increased burial efficiencies in sediments.

## 1 Introduction

OC burial within marine sediments modulates atmospheric oxygen ($O_2$) and carbon dioxide ($CO_2$) concentrations over geological timescales. Marine sediments are the largest active OC sink with ~160 Tg OC buried annually on a global scale (Berner, 1982; Burdige, 2007; Hedges and Keil, 1995; LaRowe et al., 2020). OC burial efficiency, which corresponds to the percent of the OC deposition flux to the sediments that is eventually preserved (and therefore, not mineralized) is low globally, with on average ~10% of the OC settling at the sediment-water interface being buried (Burdige, 2007). However, this number can reach up to 80% in continental shelf and coastal sediment depocenters (Blair and Aller, 2012; Canfield, 1994; Henrichs, 1992; Ingall and Cappellen, 1990; Ståhl et al., 2004). Multiple factors influence the OC burial and mineralization rates (Arndt et al., 2013; LaRowe et al., 2020) and specifically, the availability of $O_2$ in the benthic environment has been suggested to play a pivotal role in regulating the sediment biogeochemistry and faunal community. However, the extent to which $O_2$ influences the OC burial efficiency remains a topic of debate (Canfield, 1994; Middelburg and Levin, 2009; van de Velde et al., 2023). It is often reported that anoxia promotes OC preservation, which has been suggested to be caused by a positive effect of $O_2$ on the OC mineralization due to (i) a higher free energy yield from aerobic respiration pathways (LaRowe and Van Cappellen, 2011), (ii) the fact that some complex organic molecules can be more readily degraded via aerobic than via anaerobic pathways (Megonigal et al., 2003), (iii) the existence of certain organic compounds that can only be degraded via oxidative enzymes (Burdige, 2007; Canfield, 1994), (iv) the presence of macrofauna in oxygenated sediments, which may (in)directly enhance mineralization rates (Kristensen et al., 1992; Papaspyrou et al., 2007; van de Velde et al., 2020) along with (v) prevention of the build-up of reduced toxic products such as $H_2S$ (Aller and Aller, 1998).

However, determining a clear relationship between burial efficiency and $O_2$ exposure is challenging, as the OC mineralization can be hindered by physical protection mechanisms, such as adsorption on – or coprecipitation with – organic and inorganic matrices, forming 'geomacromolecules' highly resistant to enzymatic hydrolysis and bacterial mineralization (Jørgensen, 2006). Examples of such processes are the formation of authigenic minerals, adsorption to mineral surfaces, encapsulation by refractory macromolecules or complexation with metals (Burdige, 2007; Henrichs, 1992; Lalonde et al., 2012). OC loading, defined as the ratio between OC content and specific surface area (SSA) of sediment, is commonly used as a proxy to understand the OC fate in sediments. Because of their high SSA and positive surface charge, which confer enhanced adsorption capacity, reactive iron oxides ($Fe_R$) have been recognized for their significant role in sorbing OC in soils and sediments (Barber et al., 2014; Faust et al., 2021; Lalonde et al., 2012; Mehra and Jackson, 1958; Placitu et al., 2024; Yao et al., 2023).

Recently, studies in the Baltic Sea suggested that the magnitude of the positive effect of $O_2$ level on OC mineralization rates has been overestimated (Nilsson et al., 2019; van de Velde et al., 2023). Extensive regions of the Baltic Sea suffer from prolonged periods of anoxia ($O_2$ <0.5 µM) due to eutrophication caused by intense land activities in the drainage area, strongly stratified waters induced by a permanent halocline around 60–80 m depth and limited water exchange with the North Sea, which lead to a relatively long water residence time of 25-35 years (Hall et al., 2017). Despite the absence of $O_2$ in bottom waters over a large area of the central Baltic Sea, carbon budget calculations indicate that ~22 Tg OC is mineralized and recycled back to the water column annually, while the long-term burial only involves 1.0 ± 0.3 Tg OC (Nilsson et al., 2019). This suggests that sedimentary OC in the Baltic Sea is more reactive than the environmental conditions would predict. van de Velde et al. (2023), combining *in situ* benthic chamber lander and core-based measurements, showed that the OC mineralization rates in anoxic sediments in the central Baltic Sea are much higher, and OC burial efficiencies much lower, than previously reported for sediments underlying anoxic bottom waters. Here, we evaluate how physical protection influences the mineralization and burial of OC by investigating five sites along a transect across the Western Gotland Basin (WGB) in the central Baltic Sea. We report OC decay rate constants ($k$) and OC loadings from five stations and quantify the OC-Fe associations (the so-called 'rusty carbon sink') at two stations representing contrasting redox conditions: one deep, persistently anoxic site and one comparatively shallow, hypoxic station.

## 2 Materials and Methods

### 2.1 Study area and sampling

The Baltic Sea is the largest brackish water body in the world (Björck, 1995), spanning from latitude 53°N to 66°N and longitude 10°E to 30°E, covering an area of approximately 370 000 km$^2$. Enclosed by the landmasses of Eastern and Central Europe and Scandinavia (Andrén et al., 2000) it connects to the North Sea via the Danish-Swedish straits, Öresund and Store Bælt. The vast drainage basin extends nearly 2 million km$^2$ and is home to approximately ~85 million people (Nilsson et al., 2021 and references therein).

During a cruise in August 2021 aboard the R/V Skagerak, five sites (named WGB1 to WGB5) were sampled along a transect in the WGB (Figure 1, Table 1). Bottom-water temperature, salinity and $O_2$ were recorded through a CTD instrument (SBE 911, Sea-Bird Scientific) equipped with a high-accuracy $O_2$ sensor (SBE 43, Sea-Bird Scientific). Sediment cores were retrieved using a GEMAX gravity corer (9 cm inner diameter). Two cores from each station were sectioned at 0.5 cm resolution from 0 to 2 cm depth, at 1 cm resolution between 2 and 6 cm depth, and in 2 cm slices from 6 to 20 cm depth in ambient air and samples were frozen until determination of the SSA of the sedimentary particles, particulate organic carbon (POC), nitrogen (N), and $\delta^{13}C$ signature. At stations WGB1 and WGB2, two extra sediment cores were collected for the determination of OC-Fe associations. These cores were processed within a glovebag (Captair Pyramid, Erlab, France) under $N_2$ atmosphere immediately after collection. Slicing was done at 1 cm intervals to a depth of 15 cm. Sediment sections were then transferred to 50 mL Falcon tubes (VWR, USA) and frozen until analysis.

Determination of porewater sulphate ($SO_4^{2-}$), sulphate reaction rates (SRR), porosity, and $^{210}Pb$ dating are detailed in van de Velde et al. (2023). Briefly, two cores at each station were sectioned under $N_2$ atmosphere in a portable glove bag (Captair Pyramid, Erlab, France) at the same resolution as the POC cores and porewater was collected using Rhizon samplers (pore size ~0.15 µm; Rhizosphere Research Products, The Netherlands). Porewater samples for $SO_4^{2-}$ analysis were stabilized using ZnAc (2.25 ml of a 10% ZnAc solution per 0.25 ml sample) and stored at 4°C. Two subcores (2.5 cm inner diameter) were collected from the GEMAX corer at each station for sulphate reduction rate (SRR) measurements using the $^{35}$S radiotracer method (Jørgensen, 1978). One core per station was collected for $^{210}$Pb dating at Linköping University, Sweden.

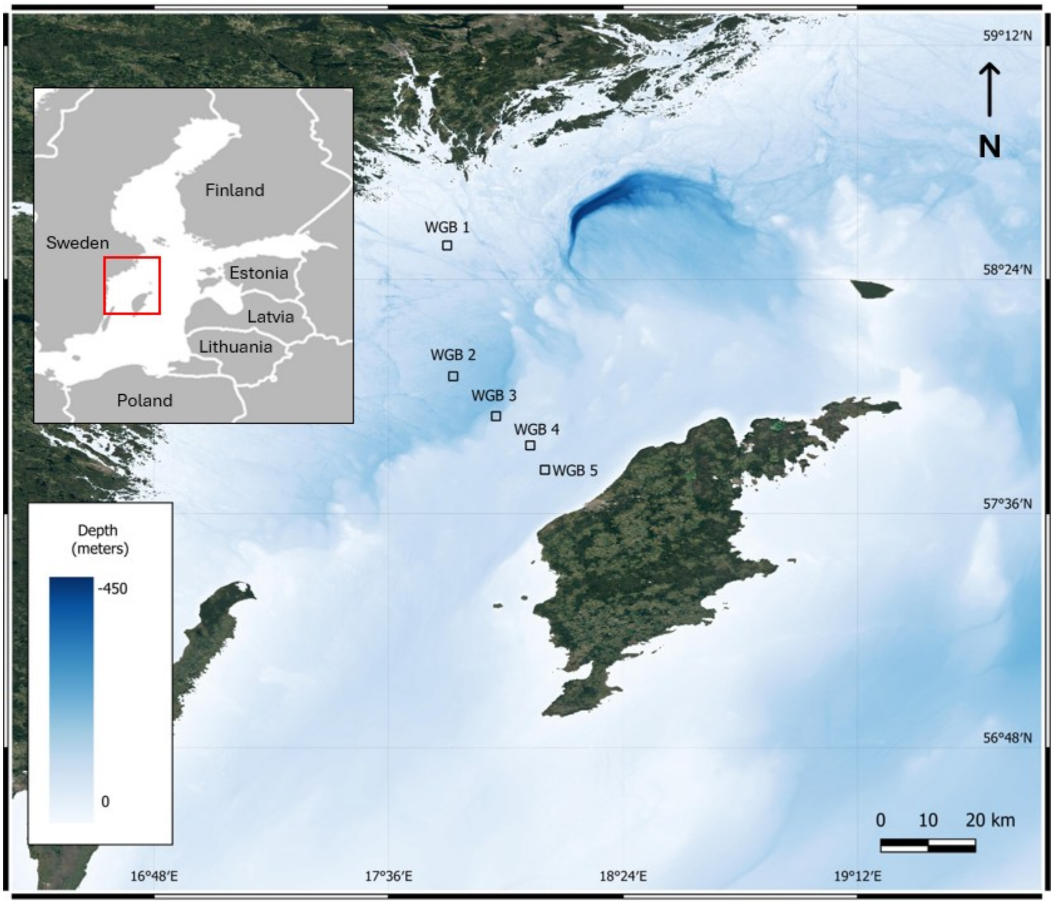

**Figure 1: Sampling locations in the West Gotland Basin, Baltic Sea. The bathymetry is from https://emodnet.ec.europa.eu/en**

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**Table 1: Sampling location and bottom water CTD data. Mass accumulation rates (MAR) are taken from van de Velde et al. (2023).**

| Station | Coord. | Water depth | Sal. | Temp. | $[O_2]$ BW | MAR |
|---|---|---|---|---|---|---|
| | | m | | °C | µM | g $m^{-2}yr^{-1}$ |
| **WGB 1** | N 58°31<br>E 17°48 | 75 | 10 | 5.7 | 0-20 | 108–285 |
| **WGB 2** | N 58°04<br>E 17°49 | 170 | 11 | 6.3 | anoxic | 59 – 285 |
| **WGB 3** | N 57°56<br>E 17°58 | 160 | 11 | 6.2 | anoxic | 84–226 |
| **WGB 4** | N 57°50<br>E 18°05 | 100 | 11 | 6.2 | anoxic | 70–230 |
| **WGB 5** | N 57°45<br>E 18°08 | 110 | 11 | 6.1 | anoxic | 60–180 |

## 2.2 POC, N, $\delta^{13}C$ signature and OC loadings

Prior to determination of POC, N, and isotopic signatures, sediments were freeze dried and homogenized by gentle grinding in an agate mortar, which was cleaned with acetone after each sample. Typically, 15 to 30 mg of dry sediment were weighed in a silver capsule and decarbonated via fumigation overnight in a desiccator using 37% HCl fuming acid after adding a drop of MilliQ water to the sediment (Harris et al., 2001). The samples were then dried with an infrared lamp and transferred into a tin capsule before being loaded into an elemental analyser coupled to an isotope ratio mass spectrometer (Sercon, UK). POC and N contents are expressed as % of sediment dry weight, and the $\delta^{13}C$ isotopic signature are reported as ‰ deviations from Vienna Pee Dee Belemnite (VPDB). Each batch analysed included certified reference material and blanks. The relative precision of the POC measurements was 5% or better.

The SSA of sediments was determined for certain sediment depths (Table SI 1) on an aliquot of the POC samples, using the 5-point BET method (BET, $N_2$ adsorption isotherm at 77K) via ASAP 2020 surface area analyser (Micromeritics, US). Prior to the SSA analysis, freeze-dried sediment samples were heated at 350°C for 24 h to remove OC following the method described by Cui et al. (2022). The OC loadings (mg C $m^{-2}$) are calculated as the ratio between OC content (mg C $g^{-1}$) and SSA ($m^2$ $g^{-1}$).

### 2.3 Extraction and calculation of OC-Fe

The OC-Fe associations were quantified in sediment cores from WGB1 (the shallowest station with hypoxic BW) and WGB2 (the deepest station with anoxic BW) using the citrate-bicarbonate-dithionite (CBD) extraction method adapted from Mehra and Jackson (1958) described in Lalonde et al. (2012) . This extraction method targets all reactive Fe ($Fe_R$), while leaving clay minerals unaffected (Lalonde et al., 2012).

In brief, 250 mg of freeze-dried sediment were weighed and placed into a 50 mL Falcon tube. Then, 15 mL of the extraction solution (0.27 M trisodium citrate and 0.11 M sodium bicarbonate) were added, and the tube was placed in a water bath at 80°C. Once the temperature was reached, 250 mg of sodium dithionite were introduced to the solution which was continuously agitated in the water bath to maintain a constant temperature. After 15 min, the extraction was stopped and the tube centrifuged (Eppendorf centrifuge 5804, Germany) at 3200 g for 10 min, after which the supernatant was filtered through a 0.22 µm PTFE filter and collected in 50 mL Falcon tubes. The sediment was subsequently rinsed with 10 mL of artificial seawater (0.235 M sodium chloride and 0.0245 M magnesium sulphate heptahydrate), centrifuged, and filtered. The rinsing step was repeated three times. The rinsing and the extraction solutions were combined and acidified with 100 µL trace-metal grade HCl (32%) to prevent Fe reoxidation.

Parallel to the CBD extraction, a control extraction was performed to discriminate the portion of OC not associated with $Fe_R$, but solubilized due to the high ionic strength of the solution (Fisher et al., 2020). In the control extraction, trisodium citrate was substituted with 1.6 M of sodium chloride, and the sodium dithionite was substituted with 220 mg of sodium chloride to maintain the same ionic strength as the CBD solution. The extraction protocol mirrored the CBD extraction, with all steps described in (Table S1 in Supplementary Information). The Fe concentrations in the supernatant solutions were determined by ICP-OES (Varian, VISTA-MPX CCD, US) with an analytical precision of 5%. Sediment leftovers from the extractions were frozen at -20°C and then freeze-dried prior to POC analyses as described above.

The percentage of bulk OC associated with $Fe_R$ ($\%OC\text{-}Fe_R$) is calculated as the difference between the %OC left after the control extraction ($\%OC_{Control}$) and the %OC residual post CBD extraction ($\%OC_{CBD}$), normalized to the total OC in the bulk sediment ($\%OC_{Bulk}$) before extractions as follow:

$$\%OC - Fe_R = \frac{\%OC_{Control} - \%OC_{CBD}}{\%OC_{Bulk}} 100 \qquad (1)$$

### 2.4 OC reactivity *k* and age

The OC reactivity, approximated by the first-order decay rate constant *k* ($yr^{-1}$), is derived from the volumetric SRR. The rate of OC mineralization $R_{min}$ (nmol $cm^{-3}$ $yr^{-1}$) at depth x (cm) can be calculated as:

$$R_{min\ (x)} = k_{(x)} C_{(x)} \qquad (2)$$

where $C_{(x)}$ represents the OC concentration (nmol $cm^{-3}$) at sediment depth x. These sediments are anoxic, unaffected by bioturbation, and $SO_4^{2-}$ is not depleted, so one can assume that all OC mineralization results from sulphate reduction:

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S \qquad (3)$$

The value of $R_{min(x)}$ can thus be approximated by the SRR, accounting for the 2 C for 1 S stoichiometry during sulphate reduction:

$$k_{(x)} = \frac{2SRR_{(x)}}{C_{(x)}} \qquad (4)$$

Since these WGB sediments are unbioturbated, the POC age (yr) can be approximated from the $^{210}$Pb dating of each sediment depth. However, as the $^{210}$Pb dating quantifies the time since deposition at the sediment surface, it underestimates the actual age of the POC (i.e., time since formation).

## 3 Results and Discussion

### 3.1 Organic carbon in WGB sediments is highly reactive

The sedimentary POC profiles (Figure 2, A-E) exhibit similar patterns across all five stations, with the highest concentrations found within the topmost 5 cm and steadily declining with depth to approximately stable concentrations of around 2 wt% between 5-10 cm depth. At stations WGB2 and WGB3, the deepest stations (Table 1), the POC content in the topmost layer of the sediments reaches up to 20 wt%. Elevated POC concentrations observed in the Baltic Sea stem from the occurrence of cyanobacteria, diatoms, and other phytoplankton blooms induced by high nutrients inputs, reflected in the $\delta^{13}C$ signature and C/N ratios of these sediments, highlighting the presence of 'fresh' material (see Figure S1 in Supplementary information). Due to increased nutrient loading since the mid 1900's, the OC input has increased considerably in the central Baltic Sea, while the construction of dams in the main Baltic rivers caused a decrease of the sediment input and low dilution of the autochthonous OC (Emeis et al., 2000; Leipe et al., 2011). Shuttling of POC from shallow bottoms also contributes to the higher sedimentary POC concentrations in deeper parts of the basin (Nilsson et al., 2021).

The SRR profiles with depth (Figure 2, F-J) show the same trends as for POC, with stations WGB2 and WGB3 exhibiting the highest rates. All profiles display the highest value in the topmost 5 cm and show a steep decline with sediment depth, reaching values close to zero in all locations except for station WGB2.

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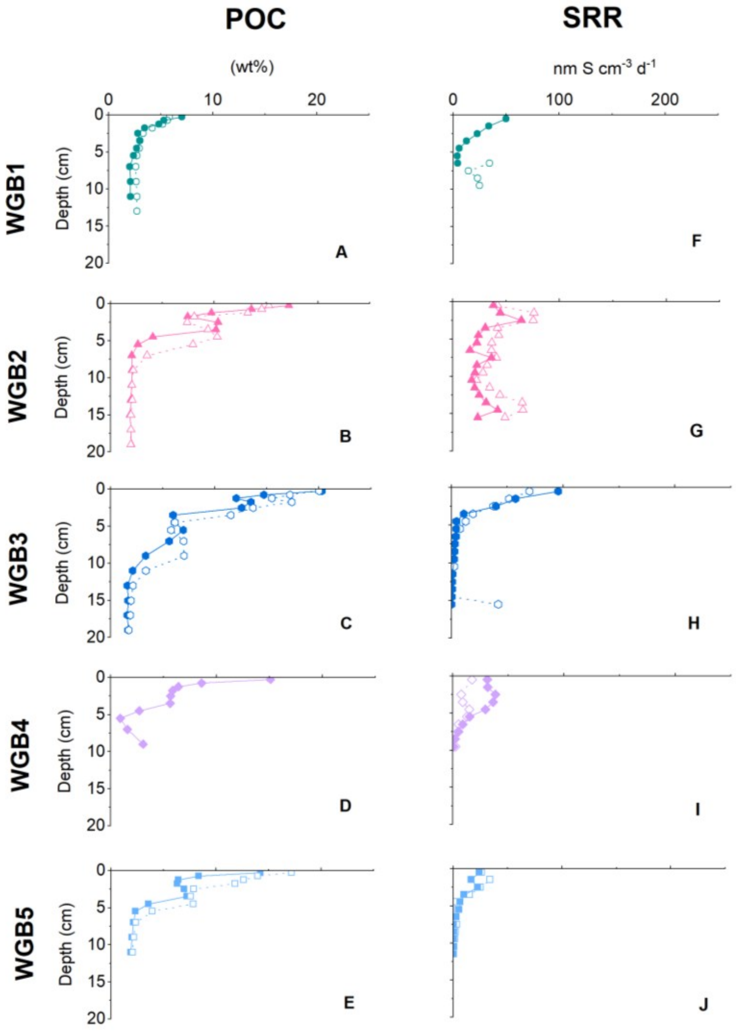

**Figure 2: Particulate organic carbon POC (A-E), and sulphate reduction rates (SRR) profiles (F-J) at all locations. Full and empty symbols are duplicate cores.**

Generally, bulk OC reactivity (approximated by the bulk first-order decay constant *k*) decreases with OC age as more reactive 175 compounds are mineralized first, leaving behind the less reactive fractions (Middelburg et al., 1997). The *k* values we found in the WGB range from $10^{-1}$ to $10^{-3}$, in line with reported values for sediments, ranging from $10^{0}$ to $10^{-6}$ (Katsev and Crowe, 2015; Middelburg, 1989). These high OC reactivity values corroborate the very low OC burial efficiencies found in the WGB by van de Velde et al. (2023). Katsev and Crowe (2015) demonstrated that the relationship between reactivity and age differs between OC exposed to $O_2$ and OC mineralized anoxically (Figure 3), in line with previous empirical evidence suggesting that 180 the OC mineralization efficiency increases with $O_2$ exposure time (Hartnett et al., 1998; Hulthe et al., 1998). Since large parts of the WGB are long-term anoxic, the calculated *k* values are expected to fall along the reactivity-age relationship derived for anoxic sediments. Intriguingly, when the *k* values are plotted against OC age, they mainly fall along the reactivity-age relationship derived for oxic conditions (Figure 3). Note that since the true age of the OC may be underestimated (section 2.4 OC reactivity *k* and age, the points could lie further to the right, shifting the data even more toward the trendline for oxic conditions.

Importantly, the OC reactivity derived for oxic conditions in the compilation of Katsev and Crowe (2015) predominantly consisted of water column data, whereas their anoxic conditions were taken from sedimentary environments. A large fraction of the particulate organic matter is fragmented into smaller fractions during the sinking to the benthic environment and is exposed to microbes, zooplankton, and nekton that consume the more reactive fractions. Consequently, the remaining particulate organic matter reaching the sediment is comparatively less reactive than its water column counterpart and it is often found sorbed to mineral surfaces or within aggregates with the sediment particles (Arndt et al., 2013; Burdige, 2007). The high OC reactivity estimated in this study, despite anoxic conditions, suggests that the pattern observed by Katsev and Crowe (2015) could be driven by the interaction between OC and sedimentary particles, rather than a direct $O_2$ effect. Indeed, the high OC reactivity in the WGB sediments could be explained by (i) a lack of physical protection through adsorption to sediment particles, and (ii) a lack of protection by interactions with Fe minerals. We explore these factors below.

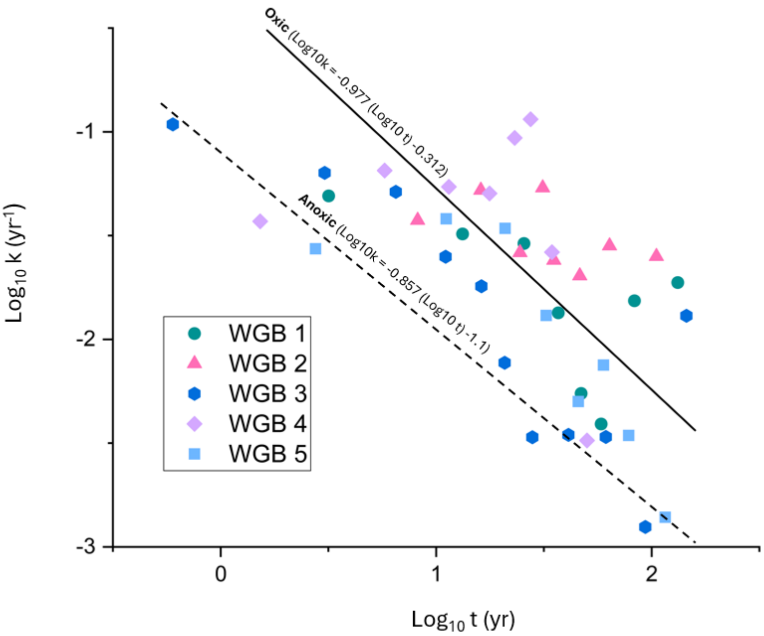

**Figure 3: OC reactivity (*k*) versus sediment age (t) in logarithmic scales. Data are represented per station using different symbols; individual points represent different sediment depths at a given station. The two regression lines are from Katsev & Crowe 2015, where the dashed line is for anoxic conditions (log(k) = -0.857log(t) -1.1), and the solid line is for oxic conditions (log(k) = -0.977log(t)-0.312).**

Because of the often-observed positive correlation between POC content and the sediment SSA, sedimentary POC is assumed to be primarily associated with particle surfaces, which is consistent with the stabilization of OC through sorption to mineral surfaces (Goni et al., 2008; Keil et al., 1994). This physical protection presumably promotes OC burial, making OC loading an important proxy for the OC fate (albeit all OC included in the loading calculations is not necessarily adsorbed to mineral surfaces; (Li et al., 2017; Mayer, 1994b). Local environmental conditions determine the OC loading (Bianchi et al., 2018; Blair and Aller, 2012). Low OC loadings (<0.4 mg OC $m^{-2}$) are indicative of frequently resuspended sediments that possibly undergo disaggregation and are exposed to $O_2$ for prolonged periods, leading to efficient OC mineralization. OC loadings between 0.4 and 1 mg OC $m^{-2}$ are typical for river-suspended sediments and those found downcore in shelf sediments. High OC loadings (> 1 mg OC $m^{-2}$) are commonly observed in sediments from high-productivity regions such as upwelling zones or areas experiencing eutrophication, which have a high OC delivery relative to the detrital sediment input.

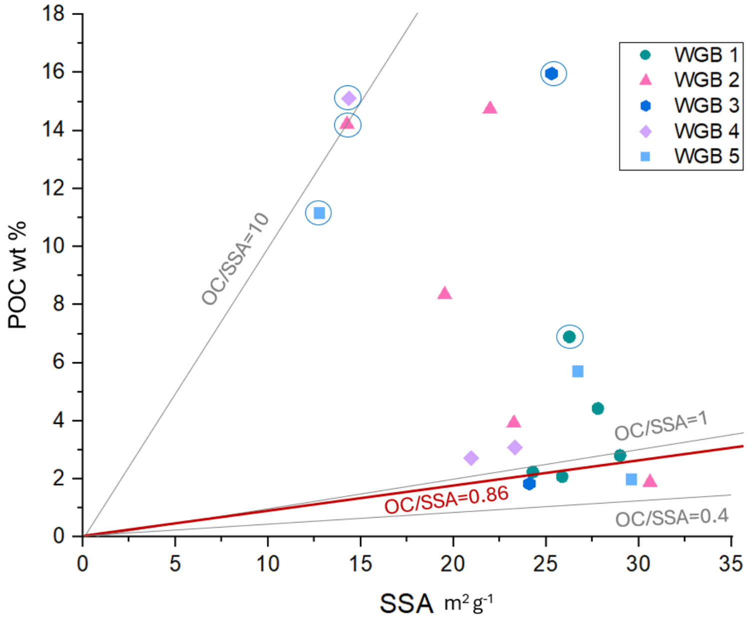

**Figure 4: Particulate organic carbon (POC) content versus specific surface area (SSA). Data are represented per station using different symbols; individual points represent different sediment depths at a given stations with circled data points representing the surface sediments at each station. Lines correspond to specific OC loadings (OC/SSA): 0.4, 1 and 10 mg OC $m^{-2}$. The bold red line corresponds to the monolayer equivalent adsorption (0.86 mg OC $m^{-2}$).**

In the WGB, all surface sediments (see Dataset in Supplementary information for depths) exhibit very high OC loadings, ranging from approximatively 2 mg OC $m^{-2}$ in the hypoxic WGB1 to over 6 mg OC $m^{-2}$ recorded at the other stations, peaking at around 10 mg C $m^{-2}$ in WGB4 (Figure 4). These OC loadings are similar to those found in upwelling regions or areas with high productivity such as the Peruvian slope or Black Sea surface sediments (Mayer, 1994a). All stations also display a consistent decrease in OC loading with sediment depth, reflecting intense sedimentary OC mineralization (in agreement with the relatively high sulphate reduction rates at the sediment surface), with values dropping below 1 mg OC $m^{-2}$ below 10 cm sediment depth. At 15 cm depth, OC loading values fall below the threshold of 0.86 mg OC $m^{-2}$ that denotes the monolayer equivalent adsorption, representing a hypothetical OC monolayer covering all particle surfaces (Mayer, 1994b). While direct observations of the OC distribution on particle surfaces in the sediment are lacking in this study, it has been demonstrated that OC does not form uniform coatings or infillings on sediment particles; rather, it likely exists as discrete blebs on the mineral surface or as non-associated organic debris (Ransom et al., 1997). The latter were shown to disproportionately contribute to OC loading (Bianchi et al., 2018) and we hypothesize that they form a large portion of the OC present in our profiles. The patterns in OC reactivity and the rapid decrease of OC loadings with depth observed here suggest that the exceedingly high OC loading allows for intense OC mineralization. This shows that physical protection plays a limited role in WGB sediments, and/or that particle surfaces are largely saturated by OC.

### 3.3 The rusty carbon sink

The limited role of physical protection of OC in the WGB is further supported by the low %OC-$Fe_R$ measured. On average, $Fe_R$ binds only 1.25 % of total OC (ranging from 0 to ~7 %OC-$Fe_R$) at WGB1 and 0.28 %OC-$Fe_R$ (ranging from 0 to 2.8 %OC-$Fe_R$) at WGB2 (Figure 5, B), compared to a global average for marine sediments of 15-20% (Lalonde et al., 2012; Longman et al., 2022; Zhao et al., 2018). OC-Fe associations were only found within the top 4 cm of sediment, with a maximum value of 7 %OC-$Fe_R$ at WGB1. The decrease of OC-Fe associations with sediment depth suggests decomposition over time, contrary to observations in the Barents Sea where OC-Fe associations persist over millennia (Faust et al., 2021). Although the down-core variability in our measurements indicates that depth trends should be interpreted with caution, a speculative interpretation of this down-core trend could be that the build-up of $H_2S$ can reduce $Fe_R$ thus destabilizing the OC-Fe associations (Chen et al., 2014), which might ultimately precipitate as OC-Fe-sulphide associations. However, this so called ''black carbon sink'' has so far only been reported in laboratory studies (Ma et al., 2022; Picard et al., 2019). The %OC-$Fe_R$ values in the WGB are very low even compared to regions presenting similar environmental conditions, such as the $O_2$-depleted and eutrophic Black Sea, where $Fe_R$ binds ~15% of the OC (Lalonde et al., 2012) despite similar concentrations of $Fe_R$ of ~25 µmol $g^{-1}$ (3 to ~76 µmol $g^{-1}$ in our study, Figure 5, A).

Differences in the %OC-Fe could also be due to mineralogical variations in the $Fe_R$ pool at depth, as the CBD extraction reduces a wide array of $Fe_R$, such as ferrihydrite, goethite, and lepidocrocite, all characterized by small particle size, amorphous crystal structures, and high SSA, which however exhibit differences from mineral to mineral (Ghaisas et al., 2021). These characteristics determine the sorption efficiency, and therefore the extent of the OC-Fe associations. For instance, OC associations with more crystalline $Fe_R$ minerals are believed to be less efficient in preserving organic matter from mineralization, creating mono or multi-layer sorption that are probably more accessible to microbial mineralization (Faust et al., 2021).

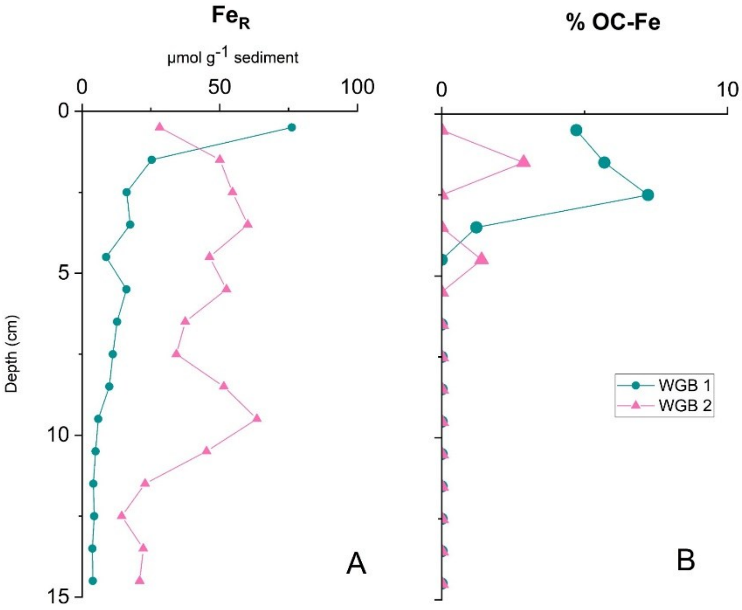

**Figure 5: Downcore profiles of reactive iron (Fe$_R$; A) and fraction of organic carbon associated to Fe$_R$ (%OC-Fe; B) at stations WGB1 and WGB2.**

Higher sedimentary contents of POC and Fe$_R$ in the deeper, anoxic WGB2 compared to the hypoxic WGB1 are likely a consequence of the shuttling of particles toward deeper parts of the basins (Hylén et al., 2021; Nilsson et al., 2021) but are not reflected in an increase in %OC-Fe. In fact, the highest %OC-Fe$_R$ are found in the hypoxic WGB1, despite presenting lower concentrations of both POC (average of 3.5±1.3% in WGB1, and 6.4±4.7% in WGB2) and Fe$_R$ (average of 14.7 µmol g$^{-1}$, ranging from ~3 to ~76 µmol g$^{-1}$ in WGB 1 and average 40.3 µmol g$^{-1}$, ranging from ~14 to ~63 µmol g$^{-1}$ µmol g$^{-1}$ in WGB2). Consistent with previous studies (Faust et al., 2021; Longman et al., 2021; Peter and Sobek, 2018; Sirois et al., 2018), this suggests that the presence of OC-Fe associations is not driven by the availability of POC or Fe$_R$. A previous study on OC-Fe association in fjord sediments in western Sweden also found no trends between the %OC-Fe and Fe$_R$ or POC concentrations, which suggested that these associations were likely formed on land and transported by rivers into the sea to ultimately settle in marine sediments (Placitu et al., 2024). The lack of major rivers in this part of the Baltic Sea could explain the limited amount of OC-Fe found across the WGB sediments, supporting the hypothesis that Fe$_R$ preferentially binds terrestrial organic matter (Dicen et al., 2019; Linkhorst et al., 2017; Riedel et al., 2013; Salvadó et al., 2015; Shields et al., 2016; Sirois et al., 2018; Wang et al., 2019; Zhao et al., 2018, 2023).

## 4 Conclusion

Sediments in the WGB underly hypoxic and anoxic bottom waters, yet the reactivity of sedimentary OC is in line with previous estimates from oxic settings. We find that there is limited potential for physical protection of OC by adsorption on clays and association with Fe oxides in these sediments, demonstrated by high OC loadings and low amounts of OC-Fe associations. Hence, our results suggest that limited physical protection reduces the importance of $O_2$ for OC mineralization, as OC remains easily accessible for microbes, in this case, sulphate reducers. Instead, the presence of reactive surfaces, such as those of clays and Fe oxides, might therefore be one of the primary drivers of OC burial in the ocean.

## Authors contribution

Conceptualization: SP, SJV, SB; Field sampling: SP, SJV, AH, POJH; Formal analysis: SP; Writing – original draft: SP; Writing – review & editing: SP, SJV, AH, ME, POJH, SB; Funding acquisition: POJH, SB, SJV.

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