EGUsphere-2025-3020 Manuscript Review: Limited physical protection leads to high organic carbon reactivity in anoxic Baltic Sea sediments

Summary

To investigate the importance of mineral protection on OC reactivity in anoxic conditions, sediment cores were collected from the anoxic Baltic Sea. Their OC%, C/N ratio, $\delta^{13}C$, sulfate reduction rate, ^{210}Pb age, OC loading, and OC-Fe_R were determined. The downcore increase in OC% and SRR suggested intensive sulfate reduction and OC remineralization, suggesting high OC reactivity despite the anoxic conditions. High OC loading, with downcore decrease in OC/SAA, suggests inadequate mineral surface area for OC stabilization. Low abundance of OC-Fe_R indicated limited protection of OC by Fe_R minerals. In summary, the current study demonstrates that when mineral protection of OC is nearly absent, oxygen depletion alone could not decrease OC mineralization rate.

Major comments

Overall, this manuscript is well-written. The data set presented in the current study is small and simple, yet it addresses an important research question in the chemical oceanography field. Therefore, I believe that the current manuscript contains a global significance that could be beneficial for further scientists who aim to investigate the drivers of OC preservation. Most of the methods and discussions are logical. I'd suggest this manuscript a minor revision, following my comments below.

Specific comments

Line 23-24: " 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"

This statement is true for OC/SAA; however, it might not be right for OC-FeR since the authors discussed that FeR availability is not the major factor controlling OC-FeR association (Line 267-273). Alternatively, I think the lack of OC-FeR in Baltic Sea is likely due to the separate input of FeR (from land) and OC (from freshwater/marine water column). See my comments in line 276-278.

Line 74: Add "," after "(Andrén et al., 2000)".

Line 82: In my opinion, "particulate organic carbon (POC)" is not an appropriate terminology here. Many literatures defined POC as suspended OC particles within water column, which has not deposited and has not been incorporated into sedimentary storage yet (see reviews in Bianchi (2007)). Another set of literature defined POC as a subset of bulk sedimentary OC that is made of fragmented plant litter with low density and large particle size (e.g., Cotrufo et al., 2019). To my understanding, the current study measured OC content in bulk sediment samples. Therefore, to avoid confusion, I'd suggest the authors to change the term "particulate organic carbon (POC)" to "sedimentary organic carbon (SOC)".

Bianchi, T. S. (2007). Biogeochemistry of estuaries. Oxford University Press.

Cotrufo, M. F., Ranalli, M. G., Haddix, M. L., Six, J., & Lugato, E. (2019). Soil carbon storage informed by particulate and mineral-associated organic matter. Nature Geoscience, 12(12), 989-994.

Line 150: What's about OC mineralization by reduction of NO_3^- to NH_4^+, or reduction of Fe^{3+} to Fe^{2+}?

Line 164-165: "...inputs, reflected in the $\delta^{13}C$ signature and C/N ratios of these sediments, highlighting the presence of ‘fresh’ material"

$\delta^{13}C$ and C/N ratios are proxies of OC sources, not their freshness. I do agree with the authors that the principal sources of OC in WGB cores are freshwater and marine planktons. However, these proxies do not reflect whether these OC are made of 'fresh' plankton-derived OC, or 'degraded' plankton-derived OC. To determine whether these OC are fresh or degraded, the authors need additional proxies such as $\Delta^{14}C$ (age of OC) or biomarkers such as stanol/sterol ratios (higher stanol reflected more degraded OC).

Line 182-183: To my understanding, Katsev and Crowe (2015) calculated k-values from changes in concentration of C with depth and time, using the equation $k = -\frac{U}{c}\frac{dC}{dx}$. In contrast, the current study calculated k-values from SRR, through the measurement of ^{35}S radiotracer during laboratory incubation (Van de Velde et al., 2023). Is it possible that the difference between these two methodologies resulted in the shift of data points away from the $\log_{10}k$-$\log_{10}t$ anoxic trendline?

- Was there any possible process that could interfere with the measurement of ^{35}S post-incubation (e.g., partitioning of consumed $^{35}SO_4^{2-}$ to H_2S (g) and FeS_2 (solid))?

- Was there any possible mechanism that can reduce or recycle $^{35}SO_4^{2-}$ without the need to consume OC?

- Was there any new production of OC due to sulfate respiration (e.g., production of new microbial biomass) so that changes in sedimentary OC content does not directly followed 2:1 stoichiometry (Equation 4)?

- Have the authors tried calculating k-values from changes in OC concentration with depth and time (using Katsev and Crowe (2015) method), without using SRR? Did they yield the same or different k-values?

Line 206: add ")" to "...Mayer, 1994b))".

Line 225 (Figure 2): Since the paragraph below discussed changes in OC loading with depth, I'd suggest the authors to improve this figure by showing the depth information on the plot. The authors may adjust the color of data point to represent depth (e.g., lighter color = surficial, darker color = deep), or they may just simply label the depths above every data point.

Line 240: Apart from intense OC mineralization, is there any alternative mechanism that potentially resulted in downcore decrease in OC loading? For example, was there any temporal change in mineral input to the Baltic sea? Was there any historical record of increasing light availability or increasing nutrient input to the Baltic sea which could accelerate the production of autochthonous OC in recent years? Increasing OC production rate could result in higher OC:SSA in younger surficial sediment layers, compared to the older deeper sediments.

Line 276-278: "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"

It's not that Fe_R preferentially binds with terrestrial or marine OC. The literature in this list observed that Fe_R is preferrentially associated with terrestrial "vascular plant" OC, due to the abundance of reactive functional groups (such as phenols and carboxylic) in vascular plant materials. In the current study, molecular structure of OC is not the main factor controlling whether FeR will preferentially bind with terrestrial or marine OC. Vascular plant-OC is nearly absent in Baltic sea sediments while the majority of OC in is made of marine or freshwater POC (Fig. S1). Hence, the input of Fe_R and OC to the Baltic may occur through separate processes. For example, land-derived Fe_R may enter the Baltic Sea via overland flow while POC may be formed in-situ within water column. In this case, pre-formed Fe_R was unable to react with newly formed OC.

This leads to an important discussion that "while allochthonous land-derived OC-Fe_R can survive anoxic conditions in marine sediments over millennia (Faust et al., 2021), the anoxic conditions inhibit autochthonous formation of new OC-Fe_R, even though the Baltic Sea received excessive input of both Fe_R and OC from separate mechanisms".

Line 283: Replace "clay" with "mineral surface". There is no direct measurement of clay-bound OC in the current study.

Line 285-286: "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"

Linguistically, I think "***limited physical protection reduces the importance of O_2 for OC mineralization"*** is not an appropriate statement. I think O_2 is still an important factor for OC mineralization in the condition of limited physical protection. In other words, unprotected OC will be degraded faster in the aerobic conditions (due to the ease of electron transfer etc.), compared to the anaerobic conditions.

I'd suggest the authors to restructure this sentence to "***the absence of O_2 does not necessarily result in deceleration of OC decomposition, as we observed high SRR in anoxic Baltic Sea sediments. This significant loss of OC in anaerobic condition is likely due to limited physical protection of OC by minerals***".