Response to comments of Reviewer 1

Review Sivan et al.

General comments

Sivan et al. investigate biogeochemical processes, in particular the anaerobic oxidation of methane coupled with Fe and/or Mn reduction (Fe-Mn-AOM), in seasonally hypoxic coastal sediments of the Eastern Arabian Sea. The main finding is that Fe-Mn-AOM is observed throughout the sediment core at several specific depths above and below the sulfate-methane transition zone (SMTZ). It is the first study to report Fe-Mn-AOM under sulfidic conditions. The authors argue that the activity of Fe-Mn-AOM at very specific depths is controlled by the distribution of metal-reducing and methanotrophic microbial communities in the sediment core.

While reading the manuscript, several concerns and questions arose. These could be addressed with major revisions. Overall, the article is of good quality, but the written language and some of the figures could be improved.

Comments 1: First of all, the present study lacks a clear/specific research question or hypothesis. In lines 82-84, the authors only describe which aspects (driving factors fueling Fe-Mn-AOM) were investigated. However, the research gap and the specific research question of the study are not explained at this point.

Reply: Thank you very much for the comment. Your feedback is greatly appreciated. The present study aims to investigate the occurrence and behavior of Fe-Mn-driven anaerobic oxidation of methane (AOM) in seasonally hypoxic coastal sediments of the Western Continental Shelf of India (WCSI; Eastern Arabian Sea), particularly under non-sulfatic and mild to moderate sulfatic conditions. The WCSI experiences distinct seasonal variations, including hypoxia and denitrification over the inner and middle shelf from June to October, driven by upwelling during the southwest monsoon (Naqvi et al., 2000; Schott et al., 2001). For the rest of the year, the region is characterized by oligotrophic conditions and normoxia above sediment-water interface. During the southwest monsoon months, the WCSI receives significant inputs of both terrestrial and marine organic matter due to enhanced land runoff and marine productivity associated with upwelling (June to September). Consequently, the WCSI displays contrasting seasonal biogeochemical conditions including variations in hydrography and depositional features (Naqvi et al., 2006; Mazumdar et al., 2012).
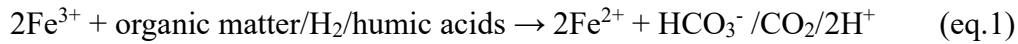
The silt-clay-rich sediments of the study area is characterized by TOC content limited within 1.45 to 31.3 mg/g. Both $(TOC/TN)_{molar}$ ratios (3.47 to 27.32) and $\delta^{13}C_{TOC}$ values (-20.69 to -25.93 ‰) from the present and previous studies (Mazumdar et al., 2012; Fernandes et al., 2020) indicate marked temporal variation in the fluvial and marine organic matter fluxes in WCSI. Moreover, the previous (Mazumdar et al., 2009; Fernandes et al., 2020) and present observations have shown remarkable fluctuations and covariance in methane concentration and $\delta^{13}C_{CH4}$ below the SMTZ in WCSI. This observation could not be explained by variation in the content and nature of organic matter, lithology (data presented in figure 2), or diffusional loss of methane from the sediment core. The research target of the present work is primarily to explain the reason for these fluctuations which has been observed both in the non-sulfatic and moderately sulfatic conditions. So, in order to explain this process, porewater Fe^{2+}, Mn^{2+}, DIC concentrations, $\delta^{13}C_{DIC}$ values, and several other solid phase parameters (Fe speciation, Mn bulk concentrations, FeS_2 concentrations) were investigated. In addition, despite studies on Fe-Mn-AOM in coastal sediments, the feasibility and nature of Fe-Mn-AOM in seasonally hypoxic coastal environments remain underexplored. Moreover, how Fe-Mn-AOM is influenced by past contrasting biogeochemical conditions remains understudied. This study aims to understand this gap by providing new insights into the nature and feasibility of Fe-Mn-AOM in dynamic depositional and redox environments with significant concentrations of both sulfide and sulfate.

Comment 2: The authors state that Fe-Mn-AOM is thermodynamically more favorable than SO_4^{2-}-AOM (lines 52-53). Dissimilatory Fe reduction (DIR) however is thermodynamically more favorable compared to Fe-AOM. How do the authors rule out that the Fe peaks (and Mn peaks) above the SMTZ (where CH_4 concentrations are close to zero) are not due to DIR (or Mn reduction)? The solid-phase data show that high levels of TOC and reactive Fe oxides are present. Furthermore, Mn-AOM is thermodynamically more favorable compared to Fe-AOM (Eq. 1 and however the authors do not distinguish between Fe-AOM and Mn-AOM. Therefore, does it make sense that the Mn and Fe peaks are found at exactly the same depth (especially if the presence of Fe oxides is not the limiting factor)?

Reply: Thanks for the suggestion. There are several subquestions within this. We have answered one by one.

A) Dissimilatory iron reduction (DIR)

Dissimilatory iron reduction (DIR) is assumed to be an important source of dissolved iron (eq.1) in anoxic marine sediments (Lovley & Phillips, 1986; Roden & Wetzel, 2003).

$$2Fe^{3+} + \text{organic matter/H}_2\text{/humic acids} \rightarrow 2Fe^{2+} + HCO_3^- /CO_2/2H^+ \qquad (eq.1)$$

In support of our argument, kindly see Figure 1 given below. The figure 1 shows green shaded zones of porewater Fe^{2+}, Mn^{2+} enrichment coupled with TOC content, $\delta^{13}C_{TOC,}$ and $\delta^{13}C_{DIC}$ values above the SMTZ (marked by pink shaded region). The Fe-Mn-rich zones do not show any unequivocal correlation with TOC content compared to the TOC content in the metal-depleted depths. In addition, the $\delta^{13}C_{DIC}$ within the Fe-Mn-AOM region ranges from -32 to -37 ‰ which is 11 to 15 ‰ more depleted than what is expected via a purely Organoclastic Fe-Mn-reduction pathway. In a purely DIR pathway, the $\delta^{13}C_{DIC}$ value is expected to be slightly enriched or close to bulk $\delta^{13}C_{TOC}$ values (Malinverno and Pohlman, 2011; Fernandes et al., 2018). However, we agree with the reviewer that dissimilatory Fe-Mn reduction may also be taking place above the SMTZ. This process may be happening along with the Fe-Mn-AOM process as suggested by depleted $\delta^{13}C_{DIC}$ values. In agreement with the reviewer, we shall be incorporating the possibility of Dissimilatory Fe and Mn reduction in the revised text.

B) The Fe-Mn covariance in the porewater indicates that both Fe and Mn are responsible for AOM. Distinguishing and quantifying the extent of Fe and Mn in AOM activity have not been attempted in the manuscript because we feel microbiological data may be required to attempt which is currently beyond the scope of the paper. Future expeditions in this region will be in collaboration with microbiologists. In the present work, we have carried out speciation of Fe, however we have not been successful with Mn solid phase speciation. We would sincerely request the reviewer to bear with this shortcoming. Suitable revisions will be made to the text.
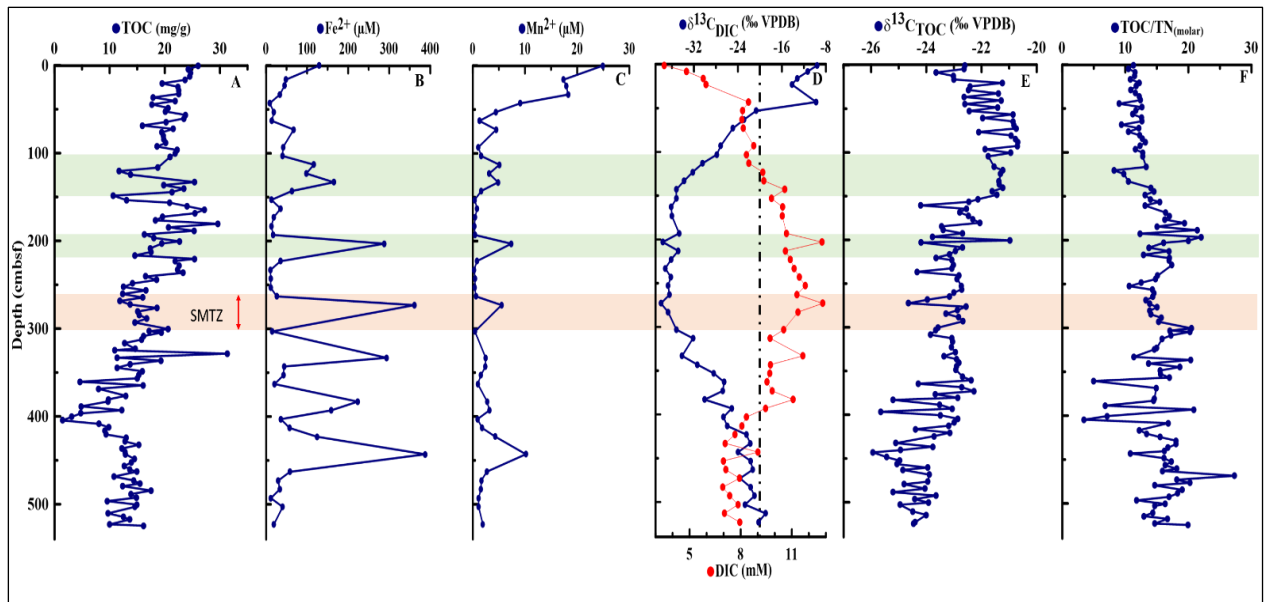
Figure 1: Depth profiles of A) TOC (mg/g), porewater (B) Fe^{2+}, (C) Mn^{2+}, (D) DIC concentration and $\delta^{13}C_{DIC}$, (E) $\delta^{13}C_{TOC}$ and (F) TOC/TN$_{(molar)}$ from the present study. The green shaded zones represent porewater Fe^{2+} and Mn^{2+} enrichment coupled with TOC content, $\delta^{13}C_{TOC,}$ and $\delta^{13}C_{DIC}$ values above the SMTZ (marked by pink shaded region).

Comment 3: My main concern is that no information about the sediment composition/properties (e.g., lithology, grain size, bulk element content, porosity) is given. Only the sedimentation rate is reported (line 227). However, the given range (and hence the resulting sediment age) is also an order of magnitude different. Information on sediment composition is particularly important in an area with changing depositional conditions (as also described by the authors in lines 310-320). How did the depositional conditions change in the past?

Reply: The sedimentation took place in the hypoxic inner shelf off the Eastern Arabian Sea. Based on the previous ^{210}Pb dating from the present coring site, the sedimentation rate ranges from 0.19 cm/yr (below 40 cmbsf) to 1.5 cm/yr (above 40 cmbsf) (Sebastian et al., 2017). The grain size analysis data shows a dominantly clayey silt sediment type where the clay minerals are composed of kaolinite and montmorillonite with very low illite content. The median grain size (D50) data shows a small variability of 6.66 to 17.43 um (Figure 2D). The zones are homogenous in terms of porosity except for some spikes in between. However, those spikes do not correlate with any of the porewater Fe^{2+}-Mn^{2+} spikes. Moreover, the Fe^{2+}/Mn^{2+} enrichment zones do not show any correlation with TOC content and TOC/TN$_{(molar)}$ ratios. The

sedimentological characteristics in the core don't show any obvious correlation with the biogeochemical observations.
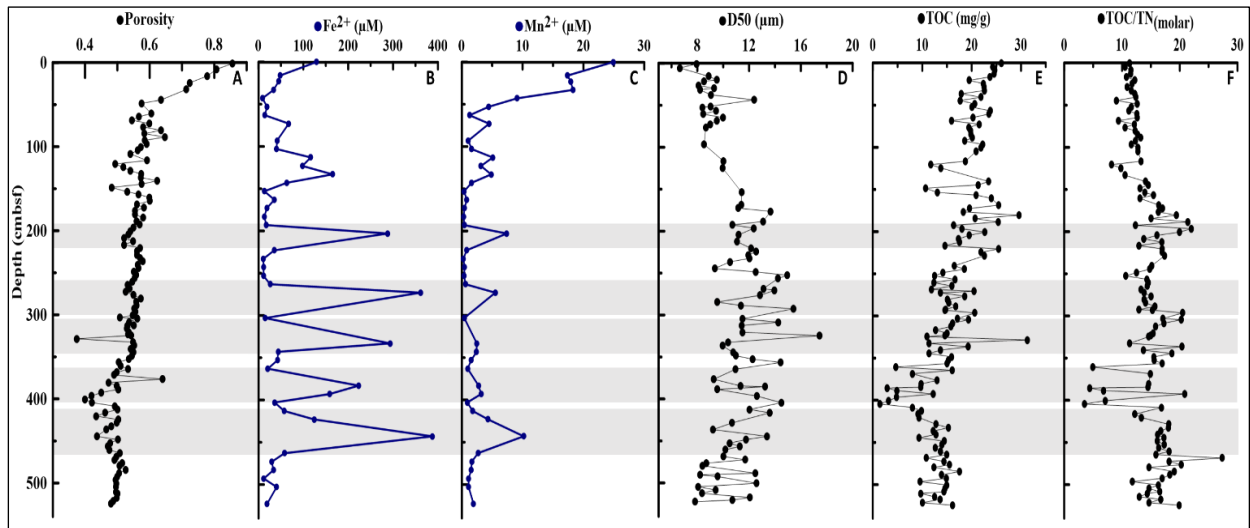

Figure 2: Depth profiles of (A) porosity, porewater (B) Fe^{2+} (C) Mn^{2+} (D) median grain size (D50) (E) TOC (mg/g) (F) TOC/TN(molar) in the present study (SSD070/7/GC6).

Comment 4: Looking at the Table S1 in the Supplemental Material, it is noticeable that the pore-water sample for the trace metal measurement above the Fe and Mn peaks is often missing. Is there a reason for this? Was less pore water extracted at the depths with the Fe and Mn peaks? Could this be related to differences in sediment composition? It is also striking that the Fe and Mn peaks are so regular.

In addition, Zones i to iii were defined only based on the presence or absence of sulfate and the Fe and Mn peaks. For example, are the zones homogeneous in terms of sediment composition?

Reply: The volume of porewater extracted in this core by centrifugation at 8000 rpm was between 6 to 7 ml. This volume was used for all chemical analysis including gravimetry. For the two samples mentioned by the reviewer, the porewater volume was not enough for metal concentration measurements. We have furnished here sediment porosity and sediment grain size data along with the porewater Fe^{2+}-Mn^{2+} data (Figure 2). The sediments of this region are clayey silt with median grain size (D50) showing a small variability of 6.66 to 17.43 um (Figure 2D). The clay mineralogical studies show a uniform mineralogy composed of kaolinite and montmorillonite. The zones are homogenous in terms of porosity except for some spikes in between. Both porosity and grain size data do not show any obvious correlation with porewater Fe^{2+}-Mn^{2+} data. In the previous figure (Figure 2), we have shown that the TOC data also doesn't show any unequivocal correlation with porewater Fe^{2+}-Mn^{2+} data.

The sedimentological characteristics in the core don't show any obvious correlation with the biogeochemical observations.

Comment 5: Is the calculation in lines 247-256 based on the assumption that DIC release is due to Fe-AOM only? There are certainly other degradation processes of the organic material that lead to the release of DIC. Therefore, the value of 11000 µM is probably significantly overestimated. If so much Fe is supposed to have reacted with HS⁻, there should be a high enrichment of Fe sulfides in the corresponding layers. Was the Fe monosulfide, pyrite, or total sulfur content also determined? The solid-phase contents might be essential to support the hypothesis.

Reply: Thank you so much for pointing out the possible iron sulfide enrichment that can occur in Fe-Mn-AOM zones. (A) Fe monosulfide (FeS)

Fe monosulfide could not be detected in this core in spite of using 6N room temperature HCl extraction (Canfield et al., 1986). Previous studies on sulfide speciation from this region also did not report (Fernandes et al., 2020) iron monosulfides which may be attributed to complete pyritization due to high hydrogen sulfide precipitation. In another paper (Sivan et al. in *prep*) the sulfidization pathway in this region will be discussed.

(B) The iron sulfide content (CRS; chromium reducible sulfur)

Regarding your concern about the potential overestimation of Fe-AOM's contribution to DIC, we understand that other processes could contribute to the DIC release, and thus the value may be maximum Fe production via Fe-AOM. However, the observed exact correspondence of DIC concentration and AOM zones (depleted $\delta^{13}C_{DIC}$ and $\delta^{13}C_{CH4}$ values) suggests that DIC production is primarily controlled by AOM. Since these AOM zones are also accompanied by porewater Fe-Mn increase, we attribute the DIC enrichment primarily to Fe-Mn-AOM (Luo et al., 2020). Furthermore, the calculated ferrous productions are 17163.18, 11673.09, 16743.20, 12883.82, 16854.54, 8159.55, 6192.97, 7104.52 µM which is equivalent to CRS contribution of 2.06, 1.4, 2.01, 1.54, 2.02, 0.97, 0.74, 0.85 mg/g. The measured CRS content in those Fe-Mn-AOM peak depths corresponds to 19.66, 47.3, 20.33, 51.3, 57.7, 72.88, 50.98, 73.8 mg/g which is significantly high compared to CRS which might have formed from Fe produced via Fe-AOM. Moreover, the bulk CRS content throughout the sediment core ranges from 3.32 to 102.3 mg/g (mean 35 ± 17 mg/g) (Figure 3D). It's important to note that pyritization in sediments is a cumulative process throughout sediment diagenesis, primarily controlled by the rate of microbial sulfate reduction, sedimentation rate, labile organic flux (Berner, 1985;

Raiswell and Berner, 1985; Wilkin and Barnes, 1997; Werne et al., 2003; Markovic et al., 2015), bottom water oxygenation which supports benthic fauna causing bioturbation and subsequent reoxidation of Fe-sulfide minerals (Chambers et al., 2000; Antler et al., 2019), and the availability of Fe that can react with sulfide (Jørgensen, 1982; Yücel et al., 2010; Zhu et al., 2016; Jørgensen et al., 2019). Additionally, in marine sediments, pyrite formation is influenced by the spatial availability of Fe and S redox reactions (Rickard and Luther, 2007). Both HS^- concentration and isotope profile of HS^- does not match with that of CRS in the present (Figure 3C, E) and previous studies (For eg: Raven et al., 2016; Fernandes et al., 2020) which itself reflects the cumulative effect of sulfidization on speciation and isotope ratios during sediment burial. However, porewater HS^- concentrations and isotope ratios at any depth do not represent a cumulative record and tend to become enriched in ^{34}S with burial (Mazumdar et al., 2012). We do agree with the reviewer that some amount of Fe produced via Fe-AOM is definitely precipitating as iron sulfide. However, given the large range in FeS_2 content, partitioning of H_2S in iron sulfide and organic bound sulfur (OBS) and the complexity involved in the cumulative nature of CRS and OBS makes quantification of Fe-AOM contribution towards additional FeS/CRS precipitation a little challenging especially through gravimetry. **However, we will include this aspect suggested by the reviewer in the revised text.**
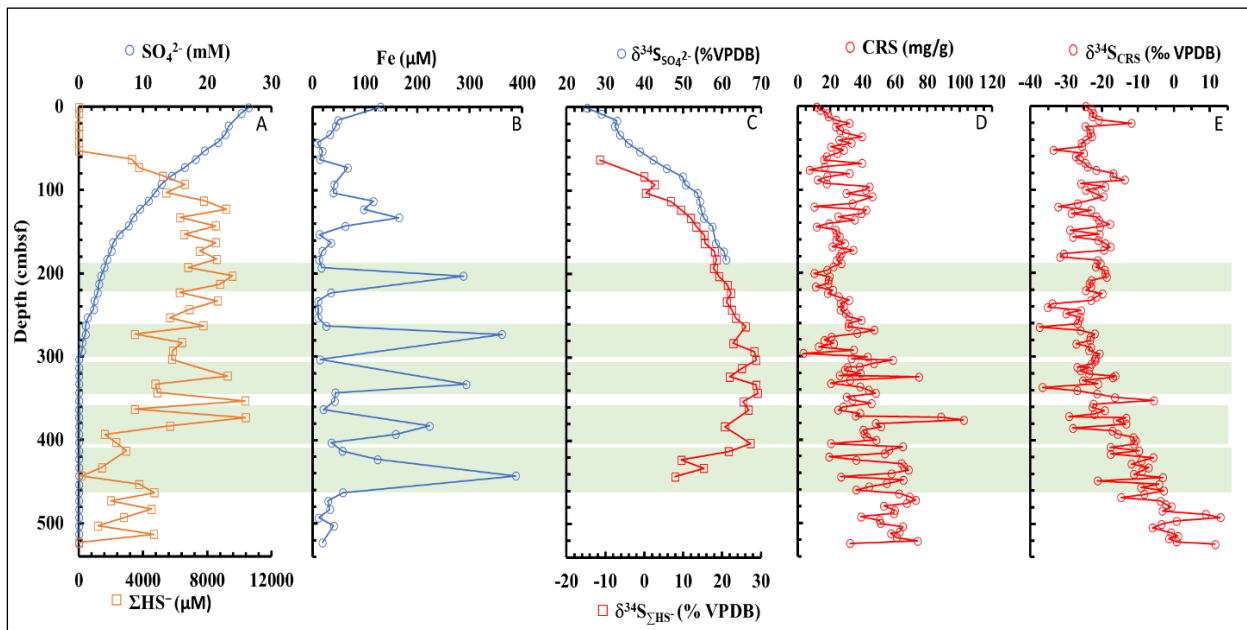

Figure 3: Depth profiles of porewater (A) SO_4^{2-}, ΣHS^-, (B) Fe^{2+}, (C) $\delta^{34}S_{SO_4^{2-}}$, $\delta^{34}S_{\Sigma HS^-}$, (D) CRS and (E) $\delta^{34}S_{CRS}$ in SSD070/7/GC6 (present study).

If I understand correctly, the HS⁻ concentrations in core SSK42/9 (Bhattacharya et al., 2021) are significantly lower than in this study. Are Fe and Mn concentrations also available for this core? Do the profiles also show the Fe and Mn peaks? Are the samples listed in Table S3 from layers with high Fe concentrations? Otherwise, the comparison with the microbial data from core SSK42/9 does not necessarily support the hypothesis that the Fe-Mn AOM activities in the specific zones are solely due to the presence of specific microbial communities.

Reply: We agree that the HS^- concentrations in core SSK42/9 (Fernandes et al., 2020; Bhattacharya et al., 2021) are significantly lower, ranging from 41.2 to 1196 μM. Unfortunately, porewater Fe and Mn concentrations were not measured in SSK42/9. As a result, we cannot confirm whether the samples listed in Table S3 correspond to Fe and Mn peaks. **We have cited Bhattacharya et al. (2021) just to show that Fe-Mn reducing microbial communities are present in these shelf sediments.** Whether these bacteria are concentrated in specific zones can also be proved in microbiological studies in future work. We agree with the reviewer that in the absence of porewater Fe^{2+}-Mn^{2+} data, Bhattacharya et al. (2021) has limitations. We will not be elaborating on the data but instead, limit the discussion to show evidence of the presence of Fe-Mn-reducing microbial communities in these shelf sediments.

Comment 7: The figures in the manuscript are very pixelated and some figures could be improved (please see specific comments).

Reply: Thank you for your feedback regarding the quality of the figures in the manuscript. We apologize for the pixelation and any lack of clarity. During manuscript submission, we uploaded high resolution figures. However, the merged manuscript probably becomes a low resolution. **We will replace the current figures with higher-resolution versions in the revised manuscript.**

Specific comments

Although not required by the journal, it would be useful to separate the Results and Discussion sections for an easier understanding.

Reply: Thank you for your suggestion to separate the Results and Discussion sections. We will carefully consider this revision and reorganize the manuscript to present the Results and Discussion in separate sections to improve the overall understanding for the readers.

Abstract

Line 22: $\delta^{13}C_{CH4}$ and $\delta^{13}C_{DIC}$ were not introduced.

Reply: Thank you for pointing out that $\delta^{13}C_{CH_4}$ and $\delta^{13}C_{DIC}$ were not introduced before line 22. The text will be revised to include both.

Introduction

Line 61: Aromokeye et al. was published in 2020.

Reply: Thank you for the observation. Aromokeye et al. (2019) will be changed to Aromokeye et al. (2020) in line 61 in the revised manuscript.

Line 70: The sentence "The global distribution of Fe-Mn-AOM is plotted in Figure 1a" is a bit lost here. The global occurrence of Fe-AOM should be better integrated and discussed in the introduction.

Reply: The text will be revised accordingly.

Line 82-84: The specific research questions are missing. In addition, this is almost the same sentence as lines 70-71.

Reply: Thank you very much for the comment. Your feedback is greatly appreciated. The present study aims to investigate the occurrence and behavior of Fe-Mn-driven anaerobic oxidation of methane (AOM) in seasonally hypoxic coastal sediments of the Western Continental Shelf of India (WCSI; Eastern Arabian Sea), particularly under non-sulfatic and mild to moderate sulfatic conditions. The WCSI experiences distinct seasonal variations, including hypoxia and denitrification over the inner and middle shelf from June to October, driven by upwelling during the southwest monsoon (Naqvi et al., 2000). For the rest of the year, the region is characterized by oligotrophic conditions and normoxia above sediment-water interface. During the southwest monsoon months, the WCSI receives significant inputs of both terrestrial and marine organic matter due to enhanced land runoff and marine productivity associated with upwelling (June to September). Consequently, the WCSI displays contrasting seasonal biogeochemical conditions, including variations in hydrography and depositional features (Naqvi et al., 2006; Mazumdar et al., 2012).

The silt- clay rich sediments of the study area is characterized by TOC content limited within 1.45 to 31.3 mg/g. Both (TOC/TN)$_{molar}$ ratios (3.47 to 27.32) and $\delta^{13}C_{TOC}$ values (-20.69 to -25.93 ‰) from the present and previous studies (Mazumdar et al., 2012; Fernandes et al., 2020)

indicate marked temporal variation in the fluvial and marine organic matter fluxes in WCSI. The previous and present observations have shown remarkable fluctuations and covariance in methane concentration and $\delta^{13}C_{CH4}$ below the SMTZ. This observation could not be explained by variation in the content and nature of organic matter, lithology (data presented in the revised study) or diffusional loss of methane from the sediment core. The research target of the present work is primarily to explain the reason for these fluctuations which has been observed both in the non sulfatic and moderately sulfatic conditions. So, to explain this process, porewater Fe, Mn, DIC concentrations, $\delta^{13}C_{DIC,}$ and several other solid phase parameters (Fe speciation, Mn bulk concentrations, FeS_2 concentrations) were investigated. In addition, despite studies on Fe-Mn-AOM in coastal sediments, the feasibility and nature of Fe-Mn-AOM in seasonally hypoxic coastal environments remain underexplored. Moreover, how Fe-Mn-AOM is influenced by past contrasting biogeochemical conditions remains understudied. This study aims to understand this gap by providing new insights into the nature and feasibility of Fe-Mn-AOM in dynamic depositional and redox environments with significant concentrations of both sulfide and sulfate.

Methods

Line 108: For headspace methane analysis, the sediment was extracted using 50 ml cut syringes at an interval of 10 cm and transferred into 20 ml headspace vials filled with 3 ml of KOH and 3 ml of NaN_3 to trap CO_2 and [stop instead of arrest] microbial activities respectively.

Reply: Thank you for pointing out the wording issue in Line 108. **The text will be revised accordingly.**

Line 115: Which constituents exactly?

Reply: The porewater was stored at 4°C for measurement of SO_4^{2-} concentration, sulfur isotope ratio of SO_4^{2-} and H_2S, DIC, and stable carbon isotope composition of the DIC ($\delta^{13}C_{DIC}$).

Line 117: In what ratio were the samples acidified? How long after sampling were the trace metal aliquots acidified? Were the trace metal samples all diluted equally (i.e., 1:40)?

Reply: Immediately after sediment core recovery, sediment samples from the cores were centrifuged on board and different aliquots were collected under Argon atmosphere in a box (Figure 4) with a clear PVC strip curtain to extract porewater for chemical analysis. For trace metal analysis, porewater samples were acidified with 100 µl of concentrated supra-pure

HNO$_3$. All glass vials were flushed with argon, sealed, and stored at 4°C until shore-based analysis. All samples were diluted equally at 40 times for trace metal analysis.
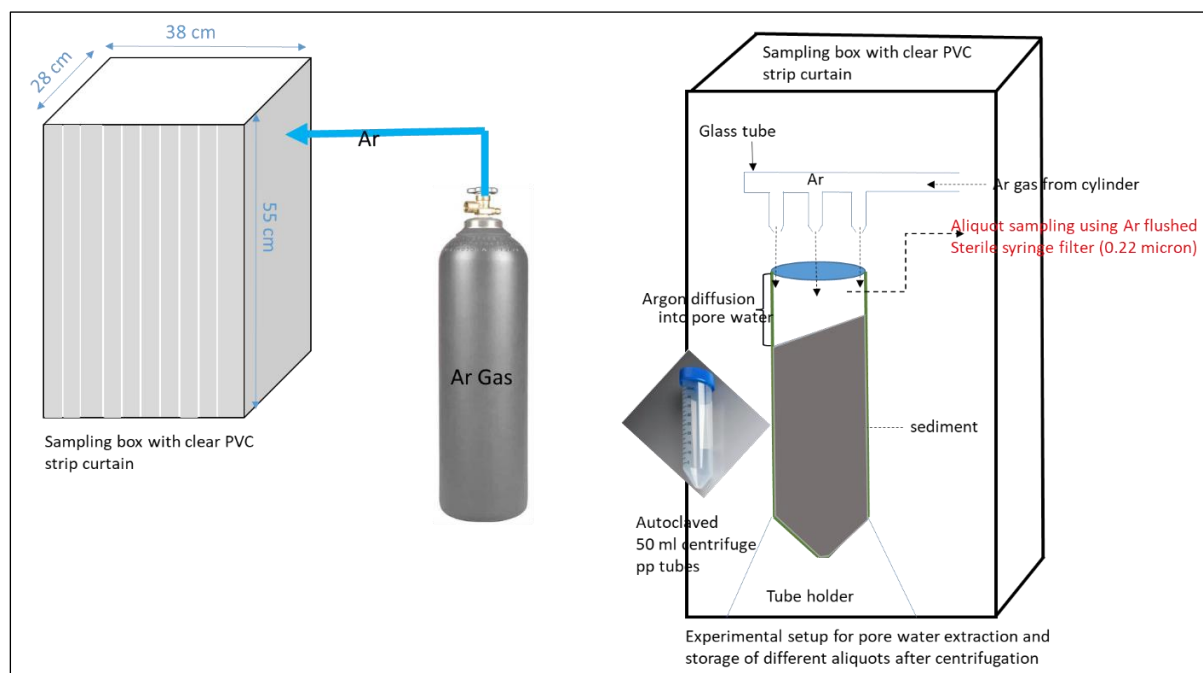

Figure 4: Schematic diagram showing the sampling protocol followed for porewater extraction followed in the present study

Line 124: GC was not introduced.

Reply: Thank you for your observation. The suggested change will be made in the revised manuscript.

Line 161-162: Was the sediment thawed and homogenized before extraction? How much sediment and how much extraction solution were used? Was the water content taken into account when weighing the sediment?

Reply: Yes, the sediment for Fe$_{ASc}$ and Fe$_D$ extraction was thawed and homogenized before extraction following Ferdelman (1988) and Raiswell et al. (2010). All sediments were thawed at room temperature under a nitrogen shower box and extracted for Fe speciation. Sequential extractions were carried out under anoxic conditions. The leaching solutions were nitrogen-flushed before extraction. Around 0.5 to 1 g of sediment sample was treated with 50 g L^{-1} sodium citrate (0.17 M), 50 g L^{-1} sodium bicarbonate (0.6 M), and 10 g L^{-1} of ascorbic acid (0.057 M). The Fe$_{Asc}$-free sediment residue was leached for 2 hrs using sodium dithionite buffer (50 g L^{-1} buffered to pH 4.8 with 0.35 M acetic acid/0.2 M sodium citrate) for determination

of dithionite extractable iron (Fe_D) content following previous works (Mehra and Jackson, 1960; Canfield et al., 1989). The water content in the samples was determined separately and the reactive Fe content was determined on a dry weight basis.

Results and Discussion

Line 211-213: What does the negative correlation mean?

Reply: Thank you for the comment. Normally in any porewater profile, below SMTZ, a decrease in DIC content and an increase in DIC carbon isotope ratio is observed which may be attributed to hydrogenotrophic methanogenesis (Whiticar et al., 1999) that results in a negative correlation. On the other end, the AOM involves DIC production and depletion in the DIC isotope ratio which also results in a negative correlation (Yoshinaga et al., 2014; Egger et al., 2017; Luo et al., 2020). If required, this may be incorporated into the result/discussion.

Line 232-245: "Tell-tale" is not the appropriate word here. I would write "clear" instead.

Reply: Thank you for your suggestion. The term "tell-tale" will be replaced with "clear" in the revised manuscript.

Line 234: In line 230, the authors state that AOM activity is not associated with significant pore water Fe^{2+} and Mn^{2+} peaks in Zone-iii, but in line 234 they state that Fe-Mn AOM occurs in Zone-iii. These two statements are contradictory.

Reply: In line 230, we meant to convey that from the CH_4, DIC concentrations, and carbon isotope ratio of CH_4 and DIC, there is evidence of AOM taking place at those specific depths. AOM activity is identified by simultaneous depletion in CH_4 concentrations (1848.03 to 403.8 µM) and C-isotope ratios of CH_4 ($\delta^{13}C_{CH4}$: -106.39 to -73.63 ‰) and DIC ($\delta^{13}C_{DIC}$: -22.676 to -23.609 ‰) (Riedinger et al., 2014; Yoshinaga et al., 2014; Egger et al., 2016a,b; Luo et al., 2020; Aromokeye et al., 2020; Wegener et al., 2021). Since these AOM zones are also accompanied by porewater Fe^{2+}-Mn^{2+} increase, we attribute AOM to Fe-Mn reduction (Luo et al., 2020). According to Fe-AOM stoichiometry, for every mole of DIC produced via Fe-AOM, 8 moles of Fe^{2+} are produced. The DIC concentration perturbations (along the blue dashed lines) may be converted to equivalent µM of Fe^{2+} produced via Fe^{3+} reduction in the pore waters. The stoichiometrically calculated amount of Fe^{2+} produced ranges from 11673 µM to 17163 µM in zone-i-ii and 6192 to 8259 µM in zone-iii. The measured porewater Fe^{2+} concentrations are approximately 1.65-3% of the calculated Fe^{2+} in zone-i-ii and 0.2-0.6 % in zone-iii. Thus, the measured Fe^{2+} concentration is the residual Fe^{2+} left after sulfidization

(FeS/FeS$_2$: Hensen et al., 2003; Treude et al., 2014; Peketi et al., 2015). Therefore, the lack of significant Fe^{2+} and Mn^{2+} enrichment in zone-iii may indicate complete consumption of Fe^{2+} and Mn^{2+} via sulfidization.

Line 278-279: CH$_4$ concentrations are generally low above the SMTZ (Otherwise there would be no SMTZ) and not only in the layers with Fe and Mn peaks.

Reply: We agree with the reviewer that above the SMTZ, the low CH$_4$ concentrations and an increase in DIC concentration are because of methanotrophy and the absence of methanogenesis. However, we have attributed the Fe-Mn enrichments in this zone to Fe-AOM mainly because of its covariation with DIC concentration and $\delta^{13}C_{DIC}$ values (Riedinger et al., 2014; Egger et al., 2016a,b; Li et al., 2019; Luo et al., 2020) similar to what observed below SMTZ.

Line 357-359: The last sentence is too general. Furthermore, SPOM is not the focus of this study and has only been mentioned once before. In the concluding sentence, the importance of the present study should be emphasized.

Reply: We agree with the reviewer. We will be deleting the SPOM component from the text and only the main conclusion and significance of the study is retained. The comprehensive geochemical investigation of the sediment core (5.25 m) retrieved from the seasonally hypoxic shelf sediment off the eastern Arabian Sea (west coast of India) has unveiled compelling evidence of focused Fe-Mn-AOM occurring at multiple depths beneath the seafloor. The accumulation of porewater Fe^{2+} and Mn^{2+}, despite elevated concentrations of ΣHS^-, suggests the predominant production of Fe^{2+} and Mn^{2+} rather than consumption through metal sulfidization processes. This study demonstrates that Fe-Mn-AOM remains a significant biogeochemical phenomenon even within SO$_4^{2-}$ and ΣHS^--rich sediments. Our findings are also relevant in assessing the consumption of CH$_4$, a greenhouse gas in organic-rich coastal sediments, thus having implications for climate change research. This study presents a novel perspective by documenting the biogeochemical heterogeneity in the occurrence of Fe-Mn-AOM, possibly attributed to deposition-controlled Fe-Mn reducing microbial population distribution in a highly dynamic coastal environment sensitive to climate change. Our results clearly call for the examination of the microbial communities in seasonally hypoxic sediment at high depth/temporal resolution, which may unravel the complex interactions between microbial life and the environment. The findings of the present study may have a far-reaching

influence on coupled CH$_4$-Mn-Fe-S cycling in expanding hypoxic coastal regions of the global ocean.

Figures

Figure 1b: What does the red line at the bottom right mean/indicate?

Reply: The red line in Fig. 1b in manuscript represents the Mandovi estuary

Figure 2: The figure is compressed. Labels a) to e) are not the same size and not at the same height.

Reply: Thank you for pointing that out. We uploaded a properly scaled file, however, the merged file became compressed. The revised figure will be included in the updated manuscript.

Figure 3: Can these two figures be placed side by side?

Reply: Thank you for the suggestion. The adjustment will be included in the revised manuscript.

Figure 4: The figure is also compressed. The TOC profile could also be added here.

Reply: Thank you for the valuable feedback. We will address the compression issue in Figure 4 and add the TOC profile to provide a more comprehensive view of the data. These changes will be incorporated into the revised version of the manuscript.

Figure 5a: The Fe monosulfide and pyrite content is also shown schematically in this figure. Is it assumed to be constant with depth (see also General Comment 4)?

Reply: The arrow does not indicate pyrite content, it only indicates the direction of pyrite burial.

Figure 5c: The CH$_4$ concentrations in the schematic representation reach near-zero values above the SMTZ (which is reasonable). How does Fe-Mn-AOM occur without any CH$_4$ above the SMTZ?

Reply: Above the SMTZ, the CH$_4$ concentrations range from 68.28 to 364.14 μM. Since it is significantly low compared to that below the SMTZ, we are unable to show that in the schematic diagram. We will be including the concentration ranges above the SMTZ in the schematic diagram in the revised manuscript to show that the values are non-zero. Moreover, the low CH$_4$ concentrations above the SMTZ are also associated with high DIC concentration

and low $\delta^{13}C_{DIC}$ values along with dissolved Fe-Mn enrichments which may be attributed to AOM (Riedinger et al., 2014; Egger et al., 2016a, b; Egger et al., 2017; Li et al., 2019; Luo et al., 2020).

References

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