

Reviewer #2 (Prof. Dr. Sabine Kasten)

We appreciate the comments and feedbacks from Prof. Dr. Sabine Kasten, which we find them very helpful. We agree with most of the comments from Dr. Kasten and will gladly revise the manuscript accordingly. Similar to what we responded to reviewer #1, we would like to point out that one of the greatest challenges is to have enough constraints for the model results, especially in the case of pyrite formation. We are aware that our current model has only a simplified reaction pathway. However, this is mostly due to the limited constraints we have; i.e., we have only porewater sulfide and Fe(II) concentrations and CRS abundance to constrain three different processes in the current model. We feel like this is perhaps the optimal setup we can have at the moment. Future improvement is possible with constraints from the isotopic signatures of these porewater species and information from other intermediate sulfur species. Here we reply to the major concerns of the reviewer upfront and provide detailed point-to-point explanations later.

- (1) **The formation pathway of pyrite:** We reply to the same question from reviewer #1 as follow. The assigned reaction pathway in our model is inspired by Rickard and Luther (2007), the same literature as the reviewer #1 suggested. To better justify our choice, we summarize some of the conclusions from the paper. Rickard and Luther (2007) reviewed the processes proposed in the literatures about pyrite formation in section 7.4. The most often mentioned pathway: $\text{FeSm} + \text{S}(0) \rightarrow \text{FeS}_2\text{p}$ (Berner et al.) was concluded by the authors to be "*could not describe a mechanism since S(0) is in the form of S₈, which would make this an impossible multimolecular reaction step*". Rickard and Luther also concluded that "*Certainly, it has been unequivocally demonstrated experimentally and in natural systems that FeSm does not “transform to pyrite” in the sense of a solid-state transformation. FeSm, where it occurs, dissolves, and pyrite forms from the reaction between dissolved iron and sulfur species to which the products of the FeSm dissolution reaction contribute*". This conclusion justifies our choice not to involve the amorphous iron sulfide phase in the reaction network. Rickard and Luther (2007) suggested that the Bunsen reaction (polysulfide controlled) and Berzelius reaction (sulfide controlled) are two more likely pathways, in which these reactions involve an aqueous FeS intermediate (Eq. 45, 46, and 51 in the paper). More importantly, both pathways produce H₂ as a by-product. Rickard and Luther (2007) also pointed out these two pathway can be fast under low-temperature condition with the presence of certain microbes operating sulfur disproportionation. As the formation of this aqueous intermediate, FeS, is not a rate-limiting step of the overall reaction, it is adequate to use the reaction we assigned in the model.

We also include some newly-obtained d34S data from both CRS and AVS to show that the two sulfur fractions underwent very different history and may use different pools of hydrogen sulfide when forming. We feel that these new data included will also help justify our choice of pyrite formation pathways.

- (2) **The contribution from organic matter:** We entirely agree with the reviewer's opinion that the deposition of organic matter will also have large impact on the Fe cycle. In the original manuscript, we discussed briefly this affect by comparing two sites with different organic matter degradation pathways (Fig. 9). We are aware that this may not be obvious for the readers so we will extend this discussion and focus a bit more on this aspect as the reviewer requested.
- (3) **The application of pyrite abundance as paleo-SMT indicator:** Thanks for the suggestions from Dr. Kasten, we will revise the literatures we cited in the discussion of sulfur record in the Black Sea. We will also soften our criticism about the application of pyrite as paleo-SMT indicator. We agree such application may work in other locations. However, based on the data we presented for some of our sites, we see that pyrite abundance is not necessary applicable for this purpose at least for our study sites.

The contribution by Latour et al. investigates the biogeochemical cycling of Fe, S and C in cold-seep surface sediments around Svalbard and the continental shelf and fjords in northern Norway. A particular emphasis is put on the impact of the dynamic cycling and reaction pathways of these elements on the solute fluxes of Fe²⁺ towards the upper oxic layer of these deposits and across the sediment/water interface. Rates of biogeochemical processes and fluxes of Fe²⁺ towards the uppermost oxic surface sediments and into the bottom water were derived from transport/reaction modelling. Before I prepared my own evaluation report I had a look at the Interactive comment of Referee #1 and agree that several important (bio)geochemical reactions and transport processes (e.g. bioirrigation, mixing induced by bubble ebullition, etc.) that were previously shown to be important at cold seep sites have not been considered. I also encourage the authors to consider these because some of these transport processes and reaction do significantly control the flux to and release of Fe from surface sediments.

My major points are: Throughout the manuscript the authors speak of (direct) precipitation of pyrite. However, numerous studies have shown that pyrite formation, which can occur via several different pathways, does mostly not occur via direct precipitation from pore water but via several intermediate/precursor iron sulfide mineral phases. This should be considered throughout the manuscript and also be implemented into the reaction network/model. As a

consequence what is schematically shown in Fig.2 – i.e. that HS and Fe²⁺ directly react to form pyrite is not correct.

Please see our reply (1) above.

Moreover, in most of the literature dealing with the transformation of precursor Fe sulfide minerals to pyrite it is discussed that the conversion into pyrite is primarily controlled by the availability of hydrogen sulfide. In this manuscript the authors only discuss Fe to be the limiting factor for further transformation to pyrite. I therefore recommend to also add a discussion about the significance of hydrogen sulfide and time (!) to exert a major control on transformation of iron sulfide precursor phases into pyrite and also cite the respective/relevant references.

We agree that sulfide plays an important role in the formation of pyrite and we are willing to discuss this factor (together with time) in the revised manuscript. We also would like to stress that our intension for the current work is to emphasize more the significance of Fe(II) supply in pyrite formation, especially in the topmost 10 cm of sediments. Our solid phase data clearly show a rapid increase in CRS abundance at the base of the iron reduction zone, where porewater Fe(II) is almost undetectable and porewater sulfide concentration starts to rapidly increase. We feel like this is a less discussed aspect when it comes to pyrite formation and we would like to have a bit more emphasis on this process.

The authors have theoretically simulated the impact of changes in methane fluxes and input of Fe oxyhydroxides. What about the role of changes in organic matter fluxes and/or quality/reactivity over time? Changes in the burial flux of organic matter will certainly have a profound impact on the resulting rates of organoclastic iron and sulfate reduction in surface sediments and thus also determine the thickness of the Fe-rich zone and the steepness of the upward-directed dissolved Fe gradient – thus the flux of Fe²⁺ towards the uppermost oxic layer of the sediments and across the sediment/water interface - and the amount of iron sulfides formed (see specific comments below).

We agree that deposition of organic matter will also have a great impact on benthic Fe(II) fluxes. We briefly discussed this factor by having the sensitivity test on sites with different organic matter abundance and sulfate reduction pathways (organoclastic vs. AOM-coupled) as shown in Fig. 9. We agree this may not be that obvious for the readers and we will expand this discussion a bit and/or amended with some more sensitivity test to explicitly discuss the influence of organic matter deposition.

I do not agree with the discussion about the usage of pyrite to trace former depth of the SMT both in the discussion chapter, the abstract and the conclusions. The authors question the use of pyrite – however their discussion and reference to relevant papers is not correct as it stands. Any statements and conclusions in this respect should thus be carefully re-considered and revised.

We appreciate the comments and we will revise the text and references to tone-down a bit in this section. It is not our intension to accuse these earlier works using pyrite abundance as a paleo-indicator of SMT. However, based on the solid phase data from two of our cores and the porewater data from all the other cores, we intend to show that significant pyrite formation can occur at the interface between the iron reduction zone and sulfate reduction zone; such formation of pyrite is not directly linked to methane flux (or the depth of SMT) but is also controlled by iron supply. At least from the one core (1521GC) we have data showing pyrite formation is much more prominent in the surficial sediments than at the depth of SMT.

With respect to the two points raised above and the fact that the title of the manuscript is “dynamic interaction” I did somehow miss a reconstruction of the “real” geochemical and biogeochemical history of the sediments at the study sites - at least for a few sites representative of each of the three groups or for those where solid-phase data are available. The sensitivity tests presented remain a bit “hypothetical” for my taste and I would have liked to see a discussion of how the current geochemical zonation and the positions of reaction fronts fit to the distribution of the different Fe sulfide mineral phases determined at a few selected sites. If these do not fit – can this tell you something about past changes in methane fluxes or in the input flux of Fe oxihydroxides or amount and/or reactivity of organic carbon? Can you speculate on potential drivers, which have most likely caused these past variations at your study sites?

We agree that there was not too much discussion of reaction zones on the solid phase data. We will have a section discussing the reaction zones through the comparison of porewater and solid phase geochemistry (including the new d_{34S} -CRS/AVS we obtained) as the reviewer suggested.

I hope that the points given above and the specific comments listed below will help the authors to revise the manuscript. The English also needs a bit of polishing.

We appreciate all the comments and suggestions from the reviewer. We will polish the language to meet the expectation.

Specific comments:

Page 2 l. 7: In marine sediments . . . l. 16 ff.: . . . along global continental margins . . .; Has to be Niewöhner (please also correct this in the list of references); I suggest to add the following references here: Riedinger et al. (2005) and (2017)

We will include these references.

Page 3 Ls. 21, 30: has to be “Wehrmann”

Thanks for the correction.

Page 4 l. 4: What exactly do you mean with “contrasting fluid seepage behavior”? This is not clear to me. Please specify.

This sentence will be modified to "Seepage of methane in different phases, gaseous vs. dissolved, were observed...."

l. 10: So, what is the sedimentation rate? Would be interesting and of relevance to know.

We have added this information. The sedimentation estimated from one gravity core is 9 cm/kyr for the first meter of sediment and 80 cm/kyr from 1-3 mbsf.

l. 18: . . . high methane concentration”s” – What are high methane concentrations? Please give the range of concentrations.

We have added the range of concentration (20-60 nM).

Page 5 l. 14: What does the abbreviation “GHM3” stand for? Please explain.

We have added the explanation.

ls. 15-17: at the end of this sentence I propose to add: “. . . according to the procedure presented by Seeberg-Elverfeldt et al. (2005)”.

We have amended the sentence.

Page 6 Ls. 1-2: Was bottom water removed before the pore-water was collected by rhizons? Please explain.

We always kept ~5-10 cm of coretop water in the linear while Rhizons were collecting the porewater to prevent oxygen invasion in the sediments.

Pages 6 and 7 In my version of the manuscript the title of the table was missing.

We will check the table.

Page 9 l. 19: I guess you mean “gravity” cores instead of sediment cores (all the other samples you have worked on are also sediment cores)

Only 1521GC is a gravity core; the other two are multi cores.

l. 32: content”s”

We have corrected this.

Page 10 Ls. 26/27: No, I do not agree with this statement. As already outlined above the reaction between Fe²⁺ and hydrogen sulfide does not produce pyrite directly but precursor iron sulfide minerals. Here, the authors state that they have excluded other intermediate sulfide minerals. However, numerous studies have shown that such intermediate iron sulfide sulfides or intermediate sulfur species precipitate at the Fe²⁺- sulfide reaction interface – as can also be seen from the study by Jørgensen et al. (2004) that they cite and other references (e.g., Kasten et al., 1998; Fu et al., 2008; review paper by Roberts in Earth-Science Reviews; Riedinger et al., 2017) and that the further conversion of such precursor phases to pyrite is often controlled by the availability of hydrogen sulfide. This is however not discussed at all in this manuscript.

Please see our reply (1) above.

Page 10 ls. 31/32 and Page 13 l. 1: which kind of “dissolution” process precisely did you use in your model approach? Reductive dissolution?

Such dissolution is only controlled by the concentration of Fe(II) in the porewater; i.e., dissolution occurs when Fe(II) concentration drops to a certain level.

Page 12 How did you determine the amount of iron oxide minerals in the surface sediments? At least the information and data are not given in the manuscript.

This is only obtained by data fitting. We were able to constrain how much Fe is fixed in pyrite minerals and how fast Fe(II) is produced (from porewater Fe(II) profile). The assigned abundance of iron oxide should be sufficient to satisfy these two constraints. We will explain this better in the text.

Page 13 l. 11: To my knowledge there are several papers by Verona Vandieken, Niko Finke and co-authors presenting hydrogen concentrations of marine pore waters.

Thanks for the information. We will add these references to the list.

Page 15 l. 17: There is a contradiction between the number of cores given here (12), in Table 1 (13) and Fig. caption 3.

The different numbers of cores listed in the text and table/figure are correct. We only categorize the 12 multi-cores while 13 cores (including the gravity cores) were reported in the paper. We will try to clarify this statement a bit.

Fig. 3 A, B: What are the black dots in the left graphs (sulfate and HS) of several of the sites? Please explain this in the figure caption.

We will correct this.

Ls. 18 ff. and throughout the manuscript: When referring to the shape of pore water profiles I prefer to speak of “steep” decrease/gradient rather than “rapid”.

We will correct this.

l. 17/18: How do you know that sulfate turnover is “slow” . . . you only have pore water profiles which give you net rates. I would rather speak of a “minor decrease in sulfate concentrations with depth”. The Results chapter already contains some interpretation. Please check this and potentially shift this to the

We will modify the statement. It is our intention to provide some preliminary discussions in the result section when describing the profiles, so that the discussion part can be more dedicated to the other aspects that require more attention.

Page 23 l. 8 and throughout the manuscript: use “uppermost” instead of “first” ls.

We will change this throughout the text.

15, 18, throughout the manuscript and in the references: has to be “März” ls.

We will correct this.

18/19: Below “this” depth, the abundance of CRS “steeply” increases “coinciding” with a sharp decrease . . .

This will be modified.

Page 24 It would be good if the pore water profiles of Fe²⁺ and HS⁻ would also be included/shown next to the graphs depicted in figure 4 because it would then be easier and straightforward to see where reaction fronts are currently located and how the position of these active reaction fronts compare to the depth distribution of the operationally defined iron sulfide minerals AVS and CRS. By the way, the susceptibility profiles of cores 904MC and 938MC look strange to me. Please check the data.

Yes, we will modify this figure and place porewater data alongside the solid phase data and have discussion about the reaction zones. We will check the MagSus data from those two cores.

Page 25 l. 2 end: . . . in these fjord sediments

We have modified this.

Page 31 l. 3: Who says that sulfate is the most abundant electron acceptor in marine environments? Please give the respective references – including key papers by B.B. Jørgensen on sulfate reduction in marine sediments. Perhaps also the paper by Bowles et al. (2014; Science) may be of interest for you in this context.

l. 11: . . . suggests “a” tight coupling . . . ls. 22/23: Which interface precisely are you referring to here? Do you mean the diffusive interface where Fe^{2+} and HS react? Numerous papers – in particular those presented by Jørgensen and coworkers as well as Postma and Jakobsen (1996; GCA vol. 60) have shown that sulfate and iron reduction can cooccur within a broad depth interval or that the depth sequence in which Fe and sulfate reduction occur can even be reversed – depending on the reactivity of the available Fe (oxi)hydroxides.

We will include these references for the statements.

Page 33 l. 2: Which microbial process precisely do you refer to here? Please give the relevant references.

l. 27/28: . . . with very little “net” sulfate reduction . . . As already mentioned above sulfate reduction can occur at considerable gross rates without any distinct decrease in pore-water sulfate concentrations as has been shown by numerous papers of Jørgensen and co-workers.

We will modify the statement in the context of references suggested.

l. 31: The fluxes of “which two compounds” are you referring to here? Please explain.

We will explain this.

Page 34 l.1 : Has to be “Wehrmann”

We will check and correct this throughout the text.

l. 5: Which kind of “dynamics” precisely are you referring to here? This is not clear to me.

We will explain this.

l. 6/7: What is the role/contribution of the precipitation/formation of Fe oxihydroxides at the Fe redox boundary – i.e. at the upper boundary of the Fe²⁺-rich zone?

This was not accounted for in the model. The abundance of Fe oxyhydroxides is assigned as the top boundary condition, which can be from the water column or from the precipitation as the reviewer suggested. We will explain this in the revised manuscript.

l. 10 ff.: As already mentioned above not only the upward flux of hydrogen sulfide from the zone of AOM but also co-occurrence of organoclastic iron and sulfate reduction can control the concentrations of Fe²⁺ and the thickness/extent of the ferruginous zone.

This is true and we have intended to show this in fig. 9. As our reply earlier, we will expand this part and discuss the role of organic matter in the Fe cycle.

l. 11: I do not understand what precisely you mean with “initially” here? . . . and also not in figure 12.

We will explain this better.

l. 30 ff.: Pore-water Fe concentrations as those reported here have also been observed in other coastal marine depositional environments – also in settings not affected by active methane seepage (for example Oni et al. (2015; *Frontiers in Microbiology*).

We will include the reference suggested.

Page 35 ls. 3 ff. until end of paragraph: I do not agree with the statement that “rapid formation of pyrite is generally observed at the SMT” and with the comments concerning the paper by Jørgensen et al. (2004). Formation of pyrite in relation to methane-mediated sulfate reduction occurs close to the SMT if the sulfidic zone is confined to a relatively thin zone around the SMT and if the SMT is fixed at a specific sediment depth for a prolonged period of time. This allows the initial precursor Fe sulfide mineral phases to be successively converted into pyrite by reaction with hydrogen sulfide continued to be produced at the SMT (e.g. Riedinger et al., 2005, 2017; März et al., 2008). Generally the formation of “AVS” (e.g. Fe monosulfides, greigite) occurs at the diffusional interface of Fe²⁺ and hydrogen sulfide – generally also referred to as “sulfidization front” (e.g. Kasten et al., 1998, GCA; Riedinger et al., 2017). This reaction front can also nicely be seen in the data presented by Jørgensen et al. (2004) in Black Sea sediments, where AVS formation occurs at the current depth of the sulfidization front. Above this reaction front – i.e. in shallower sediments - abundant pyrite contents are found, which were formed during the downward migration of the SMT as a result of the deglacial flooding of the Black Sea with seawater and the profound increase in bottom water sulfate concentrations. During the downward migration of the SMT and the sulfidization front

the uppermost sediments were permanently sulfidic and the initially formed AVS was further “matured” and converted into pyrite during ongoing exposure to/availability of hydrogen sulfide. You may also be interested in the paper by Henkel et al. (2012; GCA vol. 88) who modelled the downward migration of the SMT as a result of the deglacial flooding of the Black Sea with Mediterranean-sourced seawater. In this way – and in contrast to what the authors state here, in the abstract and in the conclusions - pyrite contents can thus well trace the past migration of the SMT and the sulfidization front. In addition, pyrite formation resulting from organoclastic sulfate reduction in surface sediments should also be discussed as a potential option to explain the occurrence of pyrite close to the sediment surface. To conclude, I suggest to discuss (and perhaps model) whether the finding of elevated pyrite contents close to the seafloor at sites 904MC and 1521GC may result from a downward migration of the SMT (and a thus a shallower depth position of the SMT and sulfidization front in the past) in response to a temporal decrease in the upward methane flux or from organoclastic sulfate reduction occurring close to the sediment surface.

Please see our reply (3) above.

Ls. 16 ff.: In chapter 5.3 the authors present and discuss the results of two sensitivity tests varying the fluxes of methane and the input of Fe oxides. Although the authors state on page 34 that organic matter is not the key driver of diagenetic/biogeochemical processes in the surface sediments at their study sites I suggest that changes in the input (both amount and quality/reactivity of TOC) may well impact the rates of biogeochemical processes and resulting solute fluxes – in particular of organoclastic sulfate reduction - within the surface sediments. It is not clear to me if and how they have varied organic matter burial fluxes in the two sensitivity tests. Please describe this more precisely. I agree that at the sites under profound impact of methane seepage (in particular the third group of sites) the temporal variation in the flux of TOC to the seafloor is certainly not a key driver. However, at the sites not dominated by upward methane fluxes, changes in the amount and/or reactivity/quality of organic matter will definitely have profound effects on rates of organoclastic Fe and sulfate reduction and resulting diffusive fluxes – as well as the rate of iron sulfide formation (including pyrite) in the surface sediments.

We appreciate the suggestion from the reviewer. We entirely agree that organic matter can have a big impact on Fe cycling, even though it may not be that significant at our sites. We have briefly examined this by comparing the two sites with different organic matter content (as shown in fig9 (a&B) vs. (c&d)). We now realized our intention was not obvious to the reader. We will extend this part and have a more thorough discussion on the effect of organic matter.

L. 29: What do you mean with “disturbance” here?

We meant the different amounts of iron (oxyhydr)oxides from water column. We will modify this.

Page 36 l. 2: Which “two mineral phases” precisely do you refer to here? Please explain.

We meant between (oxyhydr)oxides and other iron-containing minerals such as goethite. We will clarify this.

l. 9: increasing

corrected.

l. 14: does the word/term “scatterness” really exist?

It has been changed to scattering.

Page 37 l. 2 – end of sentence: either: . . . is not a “variable” or . . . is not “variable” Caption of Fig. 10: . . . with variable methane supply . . .

We have changed the sentence to "seafloor iron (oxyhydr)oxide input is constant".

Page 38 l. 3: “milder” ? sounds odd l. 24: “this” flux? Please, say which flux precisely you mean here. l. 28: chemosynthesis-based

We have corrected these.

Page 39 l. 9: (oxihydr)oxide ls. 10, 12, 15, 16: I think it has to be “Oligobrachia” – please correct this accordingly here and in the caption of Fig. 11 - and check throughout the manuscript

The spelling of (oxyhydr)oxide is correct and the same as in other literatures. We have corrected this throughout the text and caption.

l. 16: What do you mean with “localized” sulfidic bottom water condition?

We meant the local bottom water may be rich in sulfide concentration. We will clarify this.

l. 19: . . . complicated . . . that the bacteria that form these mats . . . l. 20: Please, precisely state which “speculation” you mean here.

We meant the speculation that the bottom water sulfide concentration is higher in the region where Fig 11C was taken. We will clarify this statement.

Page 41 I find the schematic representation relatively hard to follow. You need to refer to or mention the boxes highlighted in red. I do not understand at all what precisely you mean with

“initial increase” and “sequential increase” or “subsquential increase (please check spelling)?

Please, describe this precisely here and in particular in the text.

We will clarify this and find another way to illustrate what we meant in Fig. 12.

Page 47 l. 17: Bohrmann, G. is missing as the last co-author of this paper.

We have corrected this.

Please add. Best regards, Sabine Kasten