

Interactive comment on “Dynamic interactions between iron and sulfur cycles from Arctic methane seeps” by Pauline Latour et al.

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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

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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. 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. 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). 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. With respect to the two

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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? 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.

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)

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

Page 4 l. 4: What exactly do you mean with “contrasting fluid seepage behavior”? This is not clear to me. Please specify. l. 10: So, what is the sedimentation rate? Would be interesting and of relevance to know. l. 18: . . . high methane concentration”s” – What are high methane concentrations? Please give the range of concentrations. Page 5 l. 14: What does the abbreviation “GHM3” stand for? Please explain. Ls. 15-17: at the end of this sentence I propose to add: “. . . according to the procedure presented by Seeberg-Elverfeldt et al. (2005)”. Page 6 Ls. 1-2: Was bottom water removed before the pore-water was collected by rhizons? Please explain.

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

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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) l. 32: content’s”

Page 10 Ls. 26/27: No, I do not agree with this statement. As already outlined above the reaction between Fe^{2+} 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 Fe^{2+} -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. Page 10 l. 31/32 and Page 13 l. 1: which kind of “dissolution” process precisely did you use in your model approach? Reductive dissolution?

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.

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.

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

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”. 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 Discussion chapter.

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Page 23 l. 8 and throughout the manuscript: use “uppermost” instead of “first” l. 15, 18, throughout the manuscript and in the references: has to be “März” l. 18/19: Below “this” depth, the abundance of CRS “steeply” increases “coinciding” with a sharp decrease . . .

Page 24 It would be good if the pore water profiles of Fe^{2+} 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.

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

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 . . . l. 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 co-occur 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.

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. l. 31: The fluxes of “which two compounds” are

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you referring to here? Please explain.

Page 34 l.1 : Has to be “Wehrmann” l. 5: Which kind of “dynamics” precisely are you referring to here? This is not clear to me. 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? 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. l. 11: I do not understand what precisely you mean with “initially” here? ... and also not in figure 12. 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*).

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 bot-

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tom 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.

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

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diffusive fluxes – as well as the rate of iron sulfide formation (including pyrite) in the surface sediments.

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

Page 36 l. 2: Which “two mineral phases” precisely do you refer to here? Please explain. l. 9: increasing l. 14: does the word/term “scatterness” really exist?

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

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

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 l. 16: What do you mean with “localized” sulfidic bottom water condition? l. 19: ... complicated ... that the bacteria that form these mats ... l. 20: Please, precisely state which “speculation” you mean here.

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.

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

Best regards, Sabine Kasten

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