Reviewer #1:

We appreciate the time and effort from this anonymous reviewer. We find the comments insightful and can substantially improve the quality of our work. The major criticisms are that there are a few unaccounted reactions/processes in our model, which may change the conclusions of this paper. We agree with most of these criticisms and will improve our model accordingly. However, we also want to keep the solution of our modeling unique, especially when it comes to the very complicated coupling between Fe and S. A certain degree of sacrifice and compromise is therefore necessary. For example, we are aware that aerobic processes are very important overall; however, due to the lack of any oxygen concentration measurements at our sites, modeling of these processes will be no more than educated speculation. Nonetheless, we are still willing to implement these reactions to have an assessment on how critical these processes are. We reply to the major criticisms raised by the reviewer upfront and provide detailed point-to-point explanations later:

(1) **Solute transport:** The first criticism being that we consider only diffusion but not other solute transport mechanisms, such as bioturbation and/or water movement. We have ruled out the possibility of water movement (both upward and downward) in our earlier paper (Hong et al., 2017) by using one of the cores discussed in this paper (904MC). We will discuss this in more detail in the revised manuscript. As for bioturbation, we argue that, as a result of limited oxygen penetration for the majority of our sites, this is a less likely process to perturb the porewater system. The other support for our argument lies in our flux calculation (as presented in Table 1) where we did include the effect of bioturbation by assigning apparent "diffusion coefficients". These coefficients are two orders of magnitude smaller than the solute diffusion coefficients and therefore result in a very small contribution from bioturbation. We are aware that these "diffusion coefficients" for bioturbation are very crude estimations. Bioturbation may be important for the sites with rather bizarre structures in porewater profiles (e.g., 1029PC and 1123BLC). We will simulate the effect of bioturbation and discuss its importance for elemental cycles at these two sites in the revised manuscript.

(2) **Pyrite formation:** The second criticism that the reviewer has is about the pyrite formation pathway we assigned in the model. The assigned reaction pathway in our model is inspired by Rickard and Luther (2007), the same literature as the reviewer 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: FeSm (the amorphous iron sulfide form) + S(0) → FeS2p (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, which involve an aqueous FeS intermediate (Eq, 45, 46, and 51 in the paper). More importantly, both pathways produce H_2 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. In the revised version of the manuscript, we will also include newly-obtained d34S-CRS/AVS data to show that the two sulfur phases have undergone very different formation histories and may use different porewater sulfide pools.

(3) **Aerobic processes:** As shown by our porewater profiles, we argue that the sedimentary oxic layer is very thin (<1mm) for most of our sites. We will however implement a few aerobic processes, such as sulfide oxidation and nitrification, and assess how essential these reactions are with respect to the elemental cycles, despite the lack of oxygen measurement at any of our site to constrain these processes. We will emphasize that the modeling results can only be used to infer fluxes towards the oxic layer of sediments while the calculation results applying Fick's law are better for inferring fluxes leaving the sediment layer.

We will also amend the revised manuscript with supplementary tables showing the detailed reaction expressions, thermodynamic entries, diffusion coefficients, and initial/boundary conditions. Please see our following point-to-point replies to other comments of the reviewer's.

The cycling of iron and sulfur in methane-rich sediments at various seep locations near Svalbard is investigated. Pore-water profiles are used to calibrate a reaction-transport model that takes into account intermediate organic matter breakdown species, such as acetate and molecular hydrogen (H2). This approach provides potentially interesting insights into the coupling of various reaction pathways. For instance, they argue that pyrite formation may produce H2 and stimulate sulfate reduction, and that the accumulation of dissolved iron inhibits sulfate reduction. The calibrated model is then used to explore the effects of increasing iron oxide loading and methane influx on the turnover of chemical species and the partitioning between various reaction pathways. The data and model are also used to estimate dissolved iron fluxes to the overlying water. Although I find the modeling approach very interesting, a number of important reactions are missing. First of all, sulfidic reduction of iron oxides is not included, which is, as the authors acknowledge, important (page 23, line 14-15). For pyrite formation they use a reaction pathway in which H2 is produced. It may be more likely that most pyrite is formed through the FeS + S0 → FeS2 reaction, where FeS can be formed by sulfidic reduction of iron oxides and the Fe(II) + H2S reaction (see the specific comments).

From the low bottom-water temperature and the abundance of polychaetes (see paragraph 5.4) one may expect a high influx of oxygen into the sediment, but the model does not include oxygen and re-oxidation reactions.

See our reply (3) above.

This is likely to have a large impact on the estimated Fe(II) and H2 fluxes to the overlying water. In Fig. 5 there is a rapid decrease of ammonium in the upper 5 cm, which may be caused by nitrification or rapid transport/mixing.

The reviewer may refer to the profiles from MC21 and MC26, where the ammonium concentration for the first 5 cm of the core is below ~10 microM. We agree that there may be unaccounted nitrification in the shallow sediments of these sites. We will implement this in the revised model.

The data does not provide direct constraints on the transport in the model. The authors briefly mention methane seepage, gas bubble irrigation, and bioturbation as potential drivers of transport for the cores in Fig. 3C. In a cold seep one may expect up- or downward water flow (Tryon and Brown, 2004 and references therein), and the high number of large polychaetes makes it likely that also bioirrigation is important. All these flow processes could affect the profiles in Fig. 3A,B as well. The transport may have a large impact on the interpretation of pore profiles, so the authors may want to discuss these processes in more detail.

Please see our (1) reply for this point. We will include the bioturbation simulation for cores 1029PC and 1123BLC.

The results and discussion in the paper could also be better embedded within the context of other studies. Here are some examples that the authors may find interesting to consider: there are papers about reaction-transport models in cold seeps (e.g. Luff and Wallmann, 2003; Luff et al., 2004). There is a paper on carbon, iron, sulfide cycling in methane-rich sediments (Rooze et al., 2016), which may provide information about the importance of re-oxidation reactions and iron solids that are not included in the model. Rather critical I think are papers that discuss dissolved Fe fluxes to the overlying water (see paragraph 4.5 in Raiswell and Canfield, 2012; Dale et al. 2015). These papers stress the importance of aerobic iron re-oxidation and bioirrigation - factors that are ignored in the model.

We appreciate the information from the reviewer. We will discuss our results in the context of these publications.

In summary my main concerns are that a few important reactions are not included in the model and that the transport is not well constrained. Both factors could have a major influence on estimates of the dissolved iron fluxes. The reactions could be added to the model, and the authors may want to explore and describe the sensitivity of the model towards different transport regimes.

Specific comments:

Page 2: Line 8: “Redox reactions. . . carbon oxidized.” To which ‘order’ does this sentence refer? If they refer to the stratification it is important to note that it is not always the case; for instance, bioirrigation, bubble irrigation, and transient diagenesis can mix the sequence up.

Yes, we refer to the classical redox stratification. We will explain this in more details in the context of other processes as the reviewer pointed out.

Line 18: “a quantitative. . . still lacking.” This does not do justice to the body of literature that already exists and deals with cold seep biogeochemistry.

We will change this statement.

Line 20: “Previous studies. . .” Which studies exactly? The reduction of iron oxides also depends on other factors, such as the crystal structure and pH.

We will revise this statement and explain the other factors.

Line 24: Pyrite formation The authors focus on one mechanism of pyrite formation, which involves the production of H2. They do not include the FeS + S0 → FeS2 reaction, where the FeS can be formed by Fe + H2S + 2 HCO3 → FeS + 2 CO2 + 2 H2O and 2 FeOOH + 3 H2S

$\rightarrow$ 2 FeS + $S0$ + 4 $H2O$. How likely is it that the reaction pathway in which $H2$ is produced occurs in Arctic sediments? Rickard and Luther (2007) briefly discuss this reaction (see reaction 29 in the article) and indicate that this reaction may only occur at higher temperatures. Can the authors make a case for the use of this particular reaction pathway and leaving out other pathways with FeS as an intermediate? Rickard (2012) provides a good overview of the various mechanisms that can produce pyrite in sediments.
See our reply (2) for this comment.

Line 30-32: “It is therefore expected. . . oxic layer in the sediment.” Is this based on literature? Since dissolved Fe and sulfide react rapidly, would it not be more common that either all sulfide or all dissolved Fe is titrated out of the pore water?
No, such statement is based on the consideration of the iron reduction and pyrite formation together. In situations of very high or low sulfide production rates, indeed either Fe(II) or sulfide will be completely titrated out of the porewater. However, as shown by most of our porewater profiles, we usually observed the transient condition of those two extreme cases. To some extent, we are interested in such transient condition and intent to investigate how the Fe and S cycles would be in such situation. We will modify this statement to better reflect our thoughts.

Page 3: Line 7: “bioavailable” The authors make somewhat broad statements that should be backed up with references. Since Fe(III) can actually be taken up by microbes it is also bioavailable (Raiswell and Canfield, 2012).
We will better define the term throughout the text.

Line 8: “Soluble Fe(II) . . . can only be produced from anoxic environments” This is imprecise. Fe(II) can be produced in the water column, but most of it will be rapidly reoxidized.
We will modify this statement.

Page 5: Fig 1: The font size is too small.
We will modify this.

Page 10: Line 16: Perhaps it is better nomenclature to call these processes hydrogenotrophic and acetoclastic sulfate reduction.
We will change the way we call these reaction.

Line 30-31: “it is mathematically best to assume only the overall reaction” It is not clear to me how this can be proven mathematically. The explanation of the model is very terse. It is rather difficult to find all the information since the governing equations are not provided, there are no tables that sum up all the state variables, reaction stochiometries, and rate constants, and the information can only be found in other articles. The authors mention Hong et al. (2016) for which there is no entry in the bibliography. The other reference is to a supplementary file from a Nature Communications paper, but it seems only to give information about the reactions, not the transport.

What we meant for that statement is, as we only have the concentrations of Fe(II) and hydrogen sulfide to constrain the production/consumption of both ions (which are already five reactions in our current model), we find it the best to minimize the set of reactions and only focus on the overall process. Unless there are additional data, such as isotopic signatures, it is likely that we have more variables than what can be constrained. We are sorry for such difficulties to the readers. We will provide supplementary tables with detailed rate expressions, stoichiometry information, and equilibrium constant calculations.

Page 11: Fig 2: In the figure Co3 should be CO3. Sulfate is negatively charged. It takes effort to find all the labels in the figure, especially since so many different colors are used. For people with poor sight or bad printers it would be nice to have an overview of all the reactions in a table. It is not clear whether the reactions are reversible.

We appreciate the suggestion. The figure will be amended and tables will be provided to explicitly state all reactions in the revised manuscript.

Line 5-10: “For the reactions involving minerals (R1, R3, R9. . ..” The paragraph starting here is a bit terse. Why did the authors choose this approach? The way this rate law is written implies that it is reversible, since (1 – Q/K) can be positive and negative. To describe POC hydrolysis as a reversible equilibrium reaction appears troublesome to me.

We apologize for the unclear statement about the reaction network. We will amend the paper with tables explicitly showing the reaction, boundary conditions, initial condition and other important factors used in the model. As for organic matter hydrolysis, this specific reaction is not reversible.

Page 12: Line 4-5: “the equilibrium constants for other reactions were calculated. . . assuming 25 C” The actual temperature is ~1 degree Celsius (table 1) and thus significantly lower than the 25 degree Celsius the authors use. It is a large difference. Why can the equilibrium constants not be corrected for the in-situ temperature?

We will correct this.

Line 9-10: “For reactions . . . Monod-type reaction with the basic form of” Why do the authors choose to use this rate expression? It’s not clear whether the term (1-Q/Keq) act as an on/off switch or that the reaction is reversible.

See our reply above. We will provide more detail information about the model setup. We can make the reactions irreversible in the model, such as for the case of POC hydrolysis.

Line 19: “we set an imaginary mineral to produce methane. . .” Why do the authors choose this approach?

This is to overcome the limitation from the software package we used, which does not allow us to define boundary conditions differently for different ions. In order to use “no-flux” lower boundary condition for most ions and “constant flux” lower boundary condition for methane, we figured the best way is to have an imaginary source of methane at the bottom of model regime.

Line 23: “We used. . . as the initial condition” What are the initial conditions of the solids?

See our reply above. We will provide detail information about this in the amended manuscript. All minerals, except for Fe(OH)3, were included in the initial condition. Fe(OH)3 is supplied from the top of sediment column by deposition.

Line 27: “We then assigned the amount of iron hydroxide in the surface sediments (i.e. the upper boundary condition)” I guess that ‘iron hydroxide’ should be ‘iron oxide’. It is not clear to me what is used as boundary condition for the solids. A table with all boundary conditions would be helpful.

See our previous reply. This will be provided in the amended manuscript.

Page 13: Lines 14-18: “For a. . . balance requirement” I am wondering how sensitive these fluxes are to computational errors. Would it not be better to calculate the fluxes across the top boundary directly?

The fluxes across the top boundary condition (i.e., seafloor) have been estimated through the application of Fick’s law. Such mass balance presented was meant for the consumption/production of materials within the model domain. We will present an additional sensitivity test to evaluate the influence of computational error.

Line 26: There should be a minus sign in eq. 3.

We have corrected this.

Line 29-line 8(page 14): How did the authors calculate the specific values for the diffusion coefficients?

These were calculated based on the temperature-dependent equations listed in Boudreau (1998). Seafloor temperatures at each site were used. The diffusion coefficients will be included in the new supplementary table.

Line 29 suggests they were somehow corrected for different temperatures, but in line 32 it is stated that only one value was used. Why is the effect of bioturbation included for dissolved iron but not for sulfate? Middelburg's relationship for Db is a function of water depth, and is an average from different sites. However, given the rich seep biota it is likely that seeps form outliers with much higher Db values. The organization could perhaps be improved by making separate subsections about the reaction network, boundary conditions, and initial conditions. Information on the input of methane and other boundary conditions seems to be missing, and I also cannot find the parameterizations for the different fits. I don't recall reading anything about the advection of dissolved species.
See our reply (1) for bioturbation. We will also consider bioturbation for sulfate in our flux calculation.

Page 14: Equations 5 and 6: It is somewhat inconsistent that here the authors account for the re-oxidation of reduced iron, but not in the reaction-transport model.
Similar to our reply (3) on aerobic processes, we see our modeling results only provide flux estimation to the oxic layer in the sediments (which is likely only < 1mm thick). On the other hand, the calculation from porewater profiles can be used to infer the bulk flux leaving the sediment layer (i.e., even considering the aerobic processes). We see the two estimations complimentary to each other. We will explain this in more details.

Page 15: Line 15-16: "Such profiles may indicate a non-steady-state fluid system." I think the authors should elaborate on this in the discussion.
We will elaborate on this and investigate these two sites with modeling including bioturbation.

Page 16: Lines 4-8: "The porewater profile have complicated structures which can potentially be explained by. . ." The authors may want to consider adding a description of the complicated structures here and moving the interpretation to the discussion.
Yes, we will have a new section elaborating on these two sites. See reply (1) above.

Page 17: Fig.3: - NO4 should be NO3. - Consider adding DIC to the d13C label. - What are the black dots in the left lower panel? - Consider rescaling the NH4 axis. At present ammonium appears to be zero throughout the domain, while from Fig. 5 it’s clear that it is not the case.

We will modify the figure accordingly.

Page 23: Line 14-15: “minerals, such as magnetitie, have been shown to dissolve when exposed to high concentration of sulfide in porewater for considerable time.” This provides a strong argument to include sulfidic reduction of iron oxides in the model.

We agree that sulfidic reduction of iron oxide is important in the deeper sediments where sulfate is absent. However, as our main focus of the paper is on the processes in the iron and sulfate reduction zones, we decided not to implement this into our reaction network.

Page 26: Fig. 5. Most fits look good. However, there appears to be a mismatch for the ammonium and phosphate profiles. This may indicate that the model does not resolve the remineralization of organic matter well. The authors should fix it or explain the problems in the text. Also there seems to be an issue with the Mg(2+) profiles.

We will modify the organic matter degradation to hopefully resolve the unsatisfactory fitting of ammonium and phosphate. As for Mg, we suspect some of the scattering of the data is due to analytical issues. We will double check this and explain it in the revised manuscript.

Page 35: Line 22-23: “We examined the entire reaction network. . . Fe(II) fluxes towards the oxic sediment layer” I find it slightly confusing that occasionally the authors seem to treat Fe(II) fluxes out of the model domain as fluxes towards the bottom-water and at other places as fluxes towards an oxic sediment layer not included in the model.

As we stated earlier in the reply, we meant to use the model results to infer fluxes to the sedimentary oxic layer and the calculation with Fick's law to infer the overall fluxes leaving the sediment layer. We will clarify this throughout the text.

References: Dale, A. W., Nickelsen, L., Scholz, F., Hensen, C., Oschlies, A., & Wallmann, K. (2015). A revised global estimate of dissolved iron fluxes from marine sediments. Global Biogeochemical Cycles, 29(5), 691-707. Luff, R., & Wallmann, K. (2003). Fluid flow, methane fluxes, carbonate precipitation and biogeochemical turnover in gas hydrate-bearing sediments at Hydrate Ridge, Cascadia Margin: numerical modeling and mass balances. Geochimica et Cosmochimica Acta, 67(18), 3403-3421. Luff, R., Wallmann, K., & Aloisi, G. (2004). Numerical modeling of carbonate crust formation at cold vent sites: significance for fluid and methane budgets and chemosynthetic biological communities. Earth and Planetary Science Letters, 221(1-4), 337-353. Rickard, D. (2012). Sulfidic sediments and sedimentary rocks (Vol. 65). Newnes. Rooze, J., Egger, M., Tsandev, I., & Slomp, C. P. (2016). Irondependent anaerobic oxidation of methane in coastal surface sediments: Potential controls and impact. Limnology and Oceanography, 61(S1). Tryon, M. D., & Brown, K. M. (2004). Fluid and chemical cycling at Bush Hill: Implications for gas and hydrate rich environments. Geochemistry, Geophysics, Geosystems, 5(12). Other references can be found in the manuscript.