

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

Anonymous Referee #1

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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 reac-

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tions 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 $\text{FeS} + \text{S}^0 \rightarrow \text{FeS}_2$ reaction, where FeS can be formed by sulfidic reduction of iron oxides and the $\text{Fe(II)} + \text{H}_2\text{S}$ 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. 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 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.

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

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are ignored in the model.

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.

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.

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

Line 24: Pyrite formation The authors focus on one mechanism of pyrite formation, which involves the production of H₂. They do not include the $\text{FeS} + \text{S}_0 \rightarrow \text{FeS}_2$ reaction, where the FeS can be formed by $\text{Fe} + \text{H}_2\text{S} + 2 \text{HCO}_3 \rightarrow \text{FeS} + 2 \text{CO}_2 + 2 \text{H}_2\text{O}$ and $2 \text{FeOOH} + 3 \text{H}_2\text{S} \rightarrow 2 \text{FeS} + \text{S}_0 + 4 \text{H}_2\text{O}$. 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.

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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?

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).

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.

Page 5:

Fig 1: The font size is too small.

Page 10:

Line 16: Perhaps it is better nomenclature to call these processes hydrogenotrophic and acetoclastic sulfate reduction.

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 stoichiometries, 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.

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Fig 2: In the figure Co_3 should be CO_3 . 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.

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.

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?

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 $(1-Q/K_{eq})$ act as an on/off switch or that the reaction is reversible.

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

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

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.

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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?

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

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

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.

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.

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 compli-

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cated structures here and moving the interpretation to the discussion.

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.

Page 23:

Line 14-15: "minerals, such as magnetite, 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.

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.

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.

References:

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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.

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Other references can be found in the manuscript.

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