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

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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

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Discussion paper

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 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. 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 point-to-point replies to other comments of the reviewer’s from the attached file.

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2018-223/bg-2018-223-AC1-supplement.pdf

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