

July 1, 2019

Stockholm

Dear Dr. Kei Ogata

It is our pleasure to re-submit a revised manuscript No. SE-2019-50, entitled “*Can anaerobic oxidation of methane prevent seafloor gas escape in a warming climate?*” In accordance with the reviewers’ comments, our revisions focused on clarifying, to the reviewers and in the manuscript, the novelty of the numerical modelling approach we present and to discuss some of the challenges involved.

We have gone through the text in great detail and have corrected and clarified formulations pointed out by the reviewers. Most noticeably, we have added a new figure where the evolution of the hydrate dissociation and gas formation are shown. This was called for by reviewer #1, and when reading the comments of reviewer #2 it became clear to us that the absence of this figure made the basic concept of our experiments somewhat difficult to grasp.

Reviewer #2 had some misconceptions regarding the basic experimental set-up, and we have put a lot of effort into responding thoroughly to each and every point raised by the reviewer. The response to the reviewers’ comments is therefore quite lengthy (more than 12 pages) but as you will notice, the actual revision of the paper is minor.

We feel that these revisions have significantly improved the manuscript, and we are grateful to the reviewers for their constructive comments.

Yours sincerely



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Reviewer #1

1) As the authors have pointed out, the thickness and rate of AOM zone is one of the biggest assumptions in this model, which may depend upon many factors, e.g., biodiversity, nutrient supply, sulfate concentration, etc. Some previous studies (Borowski et al., 1996; Bhatnagar et al., 2011) tried to relate the sulfate reduction depth to the underlying methane flux. Thus, the thickness of AOM zone is variable with the underlying methane gas. This makes me wonder if the authors have thought of trying different boundary conditions for the model (i.e., the sulfate concentration is fixed at the seafloor)?

The reviewer is correct in that the thickness of the AOM zone is dynamic and a function of a number of known (and possibly unknown) parameters such as biodiversity, nutrient supply and sulfate concentration. These parameters are not considered in TOUGH+Hydrate, and in order to implement a dynamic SRZ we need to be able to reduce the problem to something we can actually model. As the reviewer points out, one approach is to define SRZ depth as a function of the vertical CH₄ flux from below. We have considered this possibility, but are hesitant to implement it because:

1) The implementation is not straightforward since vertical CH₄ flux is a function of depth below seafloor (especially when there is AOM) and it is not trivial to define the interface over which the flux (which would then control the SRZ depth) should be calculated. Furthermore, in order to keep the model stable (from a numerical point of view) we would need to define other unknown parameters, such as a maximum speed the SRZ depth will be allowed to move within the sediment column.

2) Research into AOM dynamics is rapidly evolving, and it might be better to wait until more is known. The model is not well constrained at present (something we emphasize in both the abstract and in the discussion) and our concern is that such additional complexity would not improve this aspect nor the conclusions of the paper.

2) The current modeling results make a lot of sense to me, given the above assumption. Only in the fracture-dominated flow with base-case AOM rate, the dissociated methane can bypass the AOM zone to escape to the seawater column.

Yes, this is essentially correct - in the base-case the gas escape from the seafloor is at least a factor of four larger in low permeability sediments (fracture-dominated flow) compared to higher permeability sediments (porous flow).

3) This study has some other assumptions and its conclusions are only applicable to the shallow gas hydrate within the featheredge on the slope, where 1) gas hydrate is most susceptible to seafloor warming and 2) pressure buildup due to hydrate dissociation in such shallow sediment can easily generate and propagate fractures to the seafloor. Hugh Daigle presented a talk at AGU 2018 entitled "can gas associated with hydrate fracture shallow marine sediment?" - his study suggested that gas-driving fracturing is only likely in the shallowest 10 meter and porous flow of gas is the preferred flow model below this depth. This is somehow different from your work.

The talk (and poster) presented by Hugh Daigle at AGU 2018 was very intriguing and interesting! Our fracture module is based on previous work by Hugh Daigle and his group. Although the fracture criterion he presented at AGU is more sophisticated than ours, there might be additional reasons for the apparent discrepancy. In our simulations the dissociation is quite rapid due to the admittedly pessimistic scenario of a 3 °C

seafloor temperature increase over 100 years. This can lead to high over-pressures, also at depth. In the Stranne et al. (2017) paper we show that without geomechanical coupling, the over-pressure in low permeability (10^{-17} m^2) sediments approaches 0.8 MPa at 16 mbsf (corresponding to a normalized over pressure of around 8). This can be seen in Figure 2f in Stranne et al. (2017). These high overpressures can only develop when permeability is so low that the gas is essentially immobile. For permeabilities of 10^{-15} m^2 and higher, any fracturing is restricted to the top ~5 m (referred to as the permanently fractured zone in the Stranne et al. 2017 paper). From Hugh Daigle's AGU abstract it is not clear what range of sediment permeabilities he was investigating, but apart from that, he did not perhaps consider the high over-pressures created during rapid warming-induced dissociation of a thin hydrate deposit within the featheredge of stability. To sum up – Hugh Daigle is developing a more elaborate fracture criterion, it is not clear if he is assuming larger gas mobility within the sediments, and he might not force the system as hard as we do (we have quite high dissociation rates in our experiments).

Figure 4 is a bit difficult to understand, if the readers are not familiar with Stranne et al., (2016, 2017). I would recommend to show a few 1D models coupled with AOM before showing Fig. 4

We have added a new Figure 4 showing two base case model simulations. The figure illustrates the development of: hydrate saturation, GHSZ, gas saturation and aqueous saturation. We hope that the inclusion of this figure will make it easier for the reader to follow the text.

5) After I zoom in the Figure 4g (AOM rate=0), there is a small component of “cumulative dissolved gas (orange color). This is slightly different from Figures 4a and 4d. Please elaborate on what drives this small difference between fracture vs. matrix flow regimes with AOM rate=0.

While the difference in terms of seafloor release of dissolved CH_4 between high and low permeability is an interesting phenomenon, it is not trivial to explain. The aqueous flow is described by Darcy's law but is complicated by the formulation of relative permeability in the TOUGH+Hydrate code (based on Stone et al. 1970, and described in detail in the TOUGH+Hydrate manual). The actual transport of dissolved CH_4 is a function of not only the relative permeability and of the pore pressure development within the sediments (which is a complicated story in itself), but ultimately also of the concentration of dissolved CH_4 (which, if saturated, is a function of pressure and temperature, and of AOM if present). The situation becomes even more complex when considering the effect of hydraulic fracturing – what is the difference between having short periods of very high permeability (corresponding to opening and closing of hydraulic fractures) in low permeability sediments vs long periods of low flow rates in higher permeability sediments? The variations in the in-situ pore pressure with time is certainly very different, which in turn effects both flow (gaseous and aqueous) and CH_4 solubility.

In summary, we do not understand these dynamics well enough to provide the reviewer with a more complete answer to his/her question. We hope to be able to dig deeper into such intricate effects of the coupled T+H-GeoMech code in future studies.

Very important in this context, however, is the fact that the overall contribution of dissolved CH_4 flux to the total CH_4 flux is negligible. In the original ms (P8L22-23) we state: “Note that we use the terms CH_4 escape and CH_4 gas escape interchangeably

throughout the text, as the dissolved fraction of the seafloor CH₄ escape is negligible (Fig. 4, 5c)".

6) Technical corrections:

Page 1 Line 34-35: awkward sentence "the temperature-sensitive part of the marine hydrate reservoir"

Fixed

Page 2 Line 8 – what's IPCC AR5?

Fixed

Page 2 Line 9: double parentheses

Fixed

Page 5 Line 5 – (Boswell and Collett. 2011)

Fixed

Page 5 Line 6: "As pointed out"

Fixed

Page 6 Line 7: Rodrigues et al. (2017) measured

Fixed

Page 11 Line 16: awkward sentence "the efficiency of microbial filter becomes a questions of permeability"

Changed "question" to "function"

Page 15 Line 31: double parentheses

Fixed

Page 15 Line 27: AOM_{max}<1e-8 mol cm⁻³ day⁻¹)

We failed to see the problem here

Reviewer #2

Methane gas transport within the hydrate stability zone has been long recognized since the extensive work done at Hydrate Ridge (ODP Leg204) (Torres et al., 2004, Milkov et al., 2004, Liu and Flemings, 2006, Torres et al., 2011). Researchers are also puzzled by the appearance of methane gas in hydrate stability zone due to the obvious violation of thermodynamic prediction that only dissolved phase and gas hydrate are allowed. Hydraulic-fracturing as a result of gas over-pressure and geochemical inhibition have been proposed as two competing explanations (see Torres et al., 2011 for review). To advance our current knowledge on such issue and provide a holistic view of how methane gas migrates within gas hydrate stability zone, numerical modeling that adequately considers the transport of multi-phase fluids, geomechanics of the sediments, and thermodynamics (and kinetics) of gas hydrate is one of the important way forward.

In this work, the authors performed model sensitivity tests with a numerical model that couples geomechanical with AOM to understand the relationship between gas production (through hydrate dissociation), gas migration (through hydraulic fracturing or permeable layers) and gas release from the sediments. The authors primarily focus on the migration of methane gas within sediments of different permeability and investigate how methane consumption through AOM is controlled by gas transport. The modeling approach adopted by the authors is indeed novel and adequate to the research question at hand.

However, I found the work premature with a few assumptions require more careful assessment. There are a few recent papers also discuss the transport of methane gas in hydrate stability zone (Liu et al., 2019, Fu et al., 2018, Meyer et al., 2018). Though AOM is not considered in these papers, the transport mechanism should be similar. The authors should discuss and compare with these recent works.

We recognize that a significant amount of work has been invested in modelling hydrate dynamics and gas transport through marine sediments. We have been heavily involved in this area of research over the past 4 years (Stranne et al., 2017; Stranne et al., 2016a; Stranne et al., 2016b; Stranne & O'Regan, 2016). The novelty of the current study lies in trying to integrate a fully coupled AOM module into a state-of-the-art multi-phase flow hydrate model.

The reviewer seems to acknowledge this, but suggests that we may have overlooked some key new work on methane transport in sediments that could alter our results or interpretation. In revisiting the three suggested papers, we do not see how they can help address our main research questions. Here we provide our perspective on these papers in regard to our submitted work.

***Liu et al., 2019* use a close to identical fracture model to the one we have implemented in this paper. This model was first implemented in TOUGH+Hydrate by our research group in 2017 (Stranne et al., 2017). However, our implementation is more advanced than the Liu et al 2019 version, since it considers both the opening and closing of fractures. Moreover, the questions we seek to answer are fundamentally different than those addressed by Liu et al. They are investigating how methane gas can migrate through the GHSZ, something that is commonly observed in various geological settings. They force the system with a constant methane gas source below the GHSZ that creates over-pressure and eventual hydraulic fracturing. In our paper, we look at hydrate dynamics related to thermal forcing at the seafloor (as a result of projected future ocean warming). There is no gas migrating thorough a stable GHSZ in our experiments, as fracturing occurs at the upper dissociation front (see Figure 7) where conditions are either at the three-phase thermodynamic equilibrium or unstable. When a shallow hydrate deposit at the feather edge of hydrate stability is heated from above, the deposit will start to dissociate and gas forms. A wide number of modelling studies have attempted to constrain the possible rates of methane escape from the seafloor when this occurs (Biastoch et al., 2011; Darnell & Flemings, 2015; Hunter et al., 2013;**

Kretschmer et al., 2015; Reagan et al., 2011; Reagan & Moridis, 2008; Stranne et al., 2016a; Thatcher et al., 2013). Hydrates are never forming in these types of experiments, and gas is never assumed to be transported through the GHSZ. We have added a sentence in the Abstract where we explain the basic model experiment set-up in order to make this clearer to the reader. We have also added a new Figure 2 in the revised version of the ms, where the seafloor temperature forcing is shown in panel a of that figure.

Fu et al., 2018 – This paper is about nonequilibrium thermodynamics of hydrate growth on a gas–liquid interface. The paper is quite technical and deals with gas–liquid–hydrate systems far from thermodynamic equilibrium. They conclude that persistent gas conduits in some hydrate bearing sediments can occur during hydrate formation, as a result of hydrate growth being a two-staged process. In our paper there is no hydrate formation. In this respect we struggle to see the relevance of Fu et al.’s work to the present ms.

Meyer et al., 2018 – In this article, the authors study hydrate formation in sand in laboratory experiments. Again, this paper provides important new insights into gas migration through the GHSZ. However, there is no hydrate formation in our model experiments, and again we fail to see how this paper is relevant to our study.

In summary, we believe that the focus of our current paper on the interplay between AOM and gas escape from hydrates is clearly stated in the title and the Introduction. The importance of the research question and approach is acknowledged by Reviewer 2, but we disagree that the suggested additional references highlight critical oversights in our paper and/or approach.

Major comments: (1) The lack of hydrate formation at shallow depth: A brief introduction about how hydrate stability is modeled in the T+H model should be given. I wonder why there is no hydrate formation at the shallower depth (<20 meters) where methane concentration can be over saturation and P-T conditions are suitable?

As explained in the Method section, the hydrate deposit is initially in thermodynamic equilibrium and extends down to the base of the GHSZ. This is a common starting condition for modelling studies that investigate how seafloor warming will influence methane escape from sediments (Biastoch et al., 2011; Darnell & Flemings, 2015; Hunter et al., 2013; Kretschmer et al., 2015; Reagan et al., 2011; Reagan & Moridis, 2008; Stranne et al., 2016a; Thatcher et al., 2013). In the actual model simulations, the temperature at the seafloor is linearly increased by 0.03 °C per year over 100 years (see Table 1). We perform this experiment for different kinds of sediments (with different permeabilities). As can be seen in Figs. 4 and 6 in the original ms, gas starts to form from hydrate dissociation after about 15 years, regardless of sediment permeability. At this point, the whole hydrate deposit is at the three-phase thermodynamic equilibrium (see panel b of the new Figure 4 and the new Figure S3 in the Supplementary Information). During the rest of the simulation, the hydrate deposit thins and eventually disappears while gas is forming at the GHSZ boundaries (predominantly at the upper boundary but also to a lesser extent at the lower boundary). This can be seen in Fig 6. Hence, there is no (nor should there be) hydrate formation at shallow depths.

The authors should present the phase diagram for methane within the model frame so that it will be clear to see where and when gas hydrate can form/dissociate in the model.

We have added a new figure to the Supplementary Information (Figure S3) showing the phase transition boundary at different times throughout the baseline (A4) model

simulation. Note that hydrate does not form when temperature at the seafloor increases because the system goes from stable to unstable conditions.

The lack of hydrate formation in the shallow depth can significantly impact the model outcome as a) hydrate formation as a result of gas seepage can take up the pore space and greatly reduce permeability

Again, hydrate does not form in our simulations where a hydrate deposit in thermodynamic equilibrium is heated from above (through seafloor temperature increase). The clogging of pore space due to hydrate formation close to the seafloor (as seen in the Liu et al, 2019 paper) occurs only when there are stable conditions at the seafloor - this is not the case in our experiments.

b) the gas flux towards seafloor may be greatly reduced as the result of hydrate formation

Due to the way the modeling experiment is designed, no hydrate is forming in our experiments (see previous comments)

c) the amount of methane consumed by AOM may also increase as the retention time of methane in the sediments increased.

Due to the way the modeling experiment is designed, no hydrate is forming in our experiments (see previous comments)

(2) Constant thickness for SRZ: the authors spent a bit of effort try to justify the assigned constant SRZ (5 meters) in their model by saying this represents a “typical” value of SRZ.

This is not entirely accurate – we never state that 5 m is a typical value of the SRZ, but rather: “Our constant SRZ depth of 5 mbsf represents a typical value in many modelling exercises applied to marine gas hydrates”. This is an important difference. A SRZ depth of 5-7 m is indeed a common assumption in the field of hydrate modeling, see for instance (Blastoch et al., 2011; Kretschmer et al., 2015; Reagan & Moridis, 2008; Stranne et al., 2017; Stranne et al., 2016a; Stranne et al., 2016b; Thatcher et al., 2013; Wallmann et al., 2012). We also note that this assumption seems to agree with observations from the Atlantic Ocean (P6L7-8): “Rodrigues et al. (2017) measured SRZ depths between 3-4 mbsf in areas with high gas flow and ca. 7 mbsf in background areas”.

However, we also state in the original ms (P6L1-3): “The base of the SRZ may be found at decimeters to tens of meters below the seafloor, depending on the burial rate of reactive organic matter, the depth of the methane production zone, the transport velocity of methane and sulfate and their consumption rates (Egger et al., 2018; Knittel and Boetius, 2009)”.

We explicitly discuss possible limitations with assuming a constant SRZ depth in the original version of the ms P17L1-6:

“In reality the SRZ depth is dynamic, with a tendency to increase with decreasing methane flux from below (Borowski et al., 1996; Sivan et al., 2007). As the capacity of the microbial filter to oxidize CH₄ that passes through the SRZ depends on the SRZ depth (Fig. S1b), this tendency could decrease the filter efficiency during rapid dissociation of marine hydrates. Overall, the limitations of our modeling approach (including the lack of kinetics and of a dynamic SRZ depth) suggests that the AOM efficiency reported here can be regarded as an upper limit“.

Important in this context is that a dynamic SRZ depth has not been implemented in any other numerical multiphase hydrate models to date, and there may be several reasons for that. When we integrated the AOM module with the T+H-GeoMech code, we decided against trying to implement a dynamic SRZ depth for the following reasons:

- (1) It is a very complex task from a technical point of view**
- (2) some of the important mechanisms such as availability of sulfate are not modelled which means that we could end up with several additional unconstrained parameters.**

It should be noted, however, that we tested the sensitivity to the choice of SRZ depth (see experiments B1 and B2). As we discuss in the text, this is one area of the modeling where there is room for improvement, but such additions would probably entail a separate publication.

I am not sure what is typical for SRZ thickness as it is a function of organic matter degradation rate plus the flux of methane in the sediments and should vary with water depths and organic matter supply to the ocean (e.g., see the global compilation by Bowles et al., 2014).

We are aware of these relations and already discuss this in the ms P6L1-3: “The base of the SRZ may be found at decimeters to tens of meters below the seafloor, depending on the burial rate of reactive organic matter, the depth of the methane production zone, the transport velocity of methane and sulfate and their consumption rates (Egger et al., 2018; Knittel and Boetius, 2009).”

Also, the observed thickness of SRZ can be greatly biased by the type of sampling tool with meter-scale SRZ to be the most often recovered through gravity coring at locations with mostly diffusion-dominated fluid regime. In cold seeps where methane gas bubbles escape from the sediments (which resembles more closely to the case here), cm-thick SRZ can be recovered only through precise push-coring with underwater robots (e.g., ROVs). In the current model, the authors decoupled the AOM rates and the thickness of SRZ and used AOM rate as high as 1 micromole/cm³/day which correspond to cm-thick SRZ in cold seeps.

We apply a fixed SRZ depth in our simulations. We acknowledge the limitations and uncertainties that this results in the ms, and perform a sensitivity study to highlight them. We provide a thorough discussion (almost a full page) regarding the apparent discrepancy between our results and observations at cold seeps in the Discussion section of the original ms (P15L30 – P16L15).

I find the assigned 5 meter of SRZ too much off from a realistic scenario.

The reviewer makes this claim without suggesting what depth would be more appropriate and does not provide any references to articles where such information can be found. The compilation by Bowles et al. (2014) provides no clue as to what the typical depth of the SRZ would be during wide-spread warming-induced hydrate dissociation along the world’s continental margins. Although no one is doubting the fact that this will happen if the world oceans continue to warm, there are actually no observational data describing this phenomenon at present (as we point out in the original ms P17L34-35). This is the reason why modeling studies such as Biastoch et al. (2011), Hunter et al. (2013), Kretschmer et al. (2015), Stranne et al. (2016a) and many others (including this study) have to rely on assumptions. This problem is not unique for the hydrate modelling community, but is common to more or less all model-based research related to climate change.

(3) Besides AOM, the authors should also consider AeOM (aerobic oxidation of methane) which is likely more important than AOM in seeps with high flux of methane (e.g., Boetius and Wenzhöfer, 2013). AeOM operates in the first few cm of sediments and serves as the last line of defense with respect to methane leakage.

The reviewer is correct in that we do not explicitly discuss AeOM in the present ms. This type of oxidation can, however, be seen as integrated in the AOM module – the code does not discriminate between different types of oxidation but acts merely as a sink on the dissolved fraction of the CH₄ in pore space. Implementing aerobic methane oxidation explicitly into the model requires knowledge on the availability of oxygen for methane oxidation which cannot be modelled in a straightforward way, because of the many competing sinks for oxygen in marine sediments. As explained in Boetius & Wenzhöfer (2013), these are complex processes that extends far beyond the scope of the present study: “Whether anaerobic or aerobic processes govern the oxidation of methane at the seafloor–water interface depends on the supply of oxygen from bottom waters, in turn dependent on bottom-water currents, the irrigation of the sea floor by animals and the speed of upward fluid flow”.

In accordance to the reviewer’s comment we have added the following text to the Discussion section:

“Because the largest proportion of the sediment column is anoxic, the most important CH₄ sink in marine sediments globally is AOM (Knittel & Boetius, 2009). As a general rule, AOM dominates the CH₄ consumption within the sediments while aerobic oxidation of CH₄ (AeOM) dominates the CH₄ consumption within the water column (Reeburgh, 2007; Valentine, 2011). AeOM in the benthic layer can, however, also be an important CH₄ sink – it has been shown that at some contemporary cold seeps, AeOM dominates over AOM (Boetius & Wenzhöfer, 2013). In this study we focus on AOM, but as the AOM module does not discriminate between different types of oxidation, the modeled bulk CH₄ oxidation within the SRZ can in a sense be regarded as including all methane oxidation in the presence of sulfate, which thereby extends methane oxidation up to the seafloor where in reality other electron acceptors such as oxygen may oxidize methane.”

(4) I feel like the title is misleading as the impact of ocean warming on gas hydrate stability is not modeled in this work. The scenario considered is applicable to any situation with a great supply of methane from greater depths and not necessarily related to gas hydrate dissociation. The connection to gas hydrate dissociation can be strengthened by relating the methane production rate assigned in the model with realistic numbers, such as dissociation of certain % of gas hydrate for a given time. Discussion about under what circumstance such hydrate dissociation rate could occur will help to connect the modeled scenario with real world situations.

As we have tried to point out after the introductory comments, our study (and experimental set-up) is focused on how AOM can influence gas escape from a thawing hydrate deposit in response to ocean warming. We understand that AOM is also an important control on methane escape from seep systems where methane is supplied from depth. However, this requires a different experimental design to address.

In this regard, the reviewer seems to confuse this study with the recent Liu et al 2019 paper. The Liu et al. is similar to this study in that they use a next to identical approach in terms of implementation of fracture dynamics (originally presented in Stranne et al., 2017). However, beyond this there are few similarities. Most importantly, we do not have a “great supply of methane from greater depths” – that is the experimental set-up in the Liu et al paper.

The reviewer writes “the impact of ocean warming on gas hydrate stability is not modeled in this work”, but this is in fact exactly what we do. In the introduction section

of the original ms P3L35-P4L3 it is stated: “As in Stranne et al. (2017) we focus on the feather edge of hydrate stability - the part of the marine hydrate reservoir most sensitive to ocean warming (Ruppel, 2011). We address the hypothesis of Buffett & Archer (2004) by investigating how the efficiency of the microbial filter varies as a function of the intrinsic permeability of the sediment (which in turn controls the vertical migration of CH₄) during seafloor warming-induced hydrate dissociation”.

As we do not assign a methane production rate in this study, it is difficult to respond to the comments related to production. We realize that that we may have failed to communicate the basic experimental set-up in the original version of the ms and in the revised ms, we have tried to make this clearer - see Abstract and Introduction sections in the tracked changes version of the revised ms. We have also added a new Figure 2 where the top panel is showing the seafloor temperature forcing, in order to emphasize the basic experimental set-up.

Minor comments:

P2L1-4: at several places in the paper, the authors intend to link anthropogenic ocean warming with hydrate destabilization. Such connection is hypothesized mostly from numerical modeling without any confirmation from field observations. On the other hand, recent works on the cold seeps around Svalbard, have shown that the gas emission cannot be attributed to gas hydrate dissociation as a result of contemporary ocean warming (Berndt et al., 2014, Wallmann et al., 2018, Hong et al., 2017). I would advise the authors to modify these statements according to these recent findings.

In the original version of the ms (P17L34-36) we tried to make the same point as the reviewer makes above: “However, because evidences of on-going anthropogenic warming-induced hydrate dissociation are inconclusive (Ruppel & Kessler, 2017) and observational data are still scarce, we have to at least partly rely on numerical hydrate models for the time being”. We have not, however, seen any publications disagreeing with the prediction of widespread hydrate dissociation, should ocean warming continue (which is the assumption in the present ms). This may not be the case for the seeps found off Svalbard, but globally, it remains a concern.

P2L17: I don't think AOM is an overlooked process. Extensive work has done for the past three decades at least.

The reviewer is correct in that there is a wealth of literature on AOM associated with contemporary seeps and with marine sediments in general. However, as the reviewer has pointed out previously, these studies are not related to climate warming-induced hydrate dissociation (see e.g. the Berndt et al. 2014 paper or the Wallmann et al. 2018 paper). How AOM will modify seafloor CH₄ escape in a warming climate is an open question, as pointed out by Ruppel & Kessler (2017), and the present study is taking a first step towards answering that question.

The sentence in the original version of the ms the reviewer is referring to reads: “A mechanism that has been largely overlooked in this context, however, is anaerobic oxidation of methane (AOM) in marine sediments (Ruppel & Kessler, 2017)”. The context we are referring to is the text in the previous paragraph which is about hydrate dissociation in relation to climate change. As far as we know, the dynamics of how AOM modifies the amount of gas escaping the seafloor in an ocean warming scenario has not been investigated previously.

P3L10-11: See my major comment (3). Aerobic oxidation of methane is also a very important process stopping methane from escape (Boetius and Wenzhofer, 2013). It is probably more important in places with high methane flux, such as the condition focused in this work.

See the answer to major comment 3 above.

P3L13: More precisely, AOM only controls the flux from sediment to the ocean

As far as we can tell, the formulation should be accurate (see the cited papers in the same sentence). The AOM is most efficient within marine sediments, and even though there are separate sinks and sources in the water column, the AOM in marine sediments still exerts an important control on the CH₄ transport over the ocean-atmosphere interface (as it represents a very large overall sink in sediment-ocean-atmosphere system).

However, we agree with the reviewer that it might be easier for the reader if we present seabed AOM as having a direct effect on the sediment-ocean transport, as this is the focus of the present ms. We have changed the sentence accordingly:

“Although AOM efficiently controls the methane flux from the world’s seafloors in general ...”

P3L18-19: again, no need to emphasize anthropogenic. Regardless of the trigger, warming of ocean will result in hydrate destabilization.

We agree with the reviewer and we have deleted the word anthropogenic from the sentence.

P4L8: Should be Moridis et al. There are three authors contributing to this manual.

We have corrected this.

P4L9-10: Goes back to my major comment (1). it seems like that there is no formation of gas hydrate assigned for depth shallower than 20 meters despite it is still within gas hydrate stability zone.

We are not sure what the reviewer means by this. Hydrate formation is never assigned but controlled internally in the TOUGH+Hydrate code. See previous comments regarding the GHSZ, and note the new additional Figure S3.

P4L10-11: though such condition with feather edge hydrate stability is vulnerable to climate change, the contribution to global methane emission as a result of gas hydrate dissociation is probably small due to such thin hydrate stability zone and lower quantity of overall hydrate comparing to locations where hydrate stability zone could extend to hundreds of meters.

It is not entirely clear how much of the global GHSZ that would be affected by an increase of the seafloor temperature on a centennial time scale. Stranne et al. (2016b) showed that the contribution from GHSZ’s thicker than 100 m would be small. However, if integrating the total GHSZ volume in the world oceans that are affected by a seafloor temperature increase on a centennial time scale, this would become a large volume (see e.g. Biastoch et al. 2011 and Kretschmer et al. 2015). As the reviewer points out, the initial hydrate saturation becomes a very important question in this context. This is unfortunately a poorly constrained parameter, as pointed out by e.g. Ruppel and Kessler (2017). In this study we investigate the sensitivity to the initial hydrate saturation in experiments C1-C2.

P5L14-15: See my major comments (2). The constant thickness of SRZ is a potential problem despite the authors have tried to convince the readers otherwise.

We do not try to convince the readers that the SRZ depth is trivial. In fact, we explicitly discuss the possible consequences and limitations of assuming a stationary SRZ in the Discussion section P17L1-6. See previous comments on this for a more detailed description of why a dynamic SRZ was not implemented in this study. Also note that no other model study employing a numerical multiphase hydrate model has implemented such dynamics.

P6L4: Again, see my major comments (2). The so call “typical SRZ thickness” requires more justification.

Again, in the hydrate modeling community a SRZ depth of around 5 m is a common assumption. A few examples are: (Biastrach et al., 2011; Kretschmer et al., 2015; Reagan & Moridis, 2008; Stranne et al., 2017; Stranne et al., 2016a; Stranne et al., 2016b; Thatcher et al., 2013; Wallmann et al., 2012).

See replies to previous comments for more details regarding possible problems with an implementation of a dynamic SRZ in TOUGH+Hydrate.

P8L12: I assume it is also methane gas in the matrix flow?

The reviewer is referring to the following statement: “In the matrix flow regime, which is predicted in higher permeability substrate ($k > 10^{-15} \text{ m}^2$), CH_4 is percolating through the porous media in a continuous, regular fashion through intergranular pore spaces”. By CH_4 we mean both gaseous and dissolved CH_4 . On P8L22-23 we state: “Note that we use the terms CH_4 escape and CH_4 gas escape interchangeably throughout the text, as the dissolved fraction of the seafloor CH_4 escape is negligible (Fig. 4, 5c)”.

The reviewer is correct – while the flow is smaller than that in the low permeability fracture flow case, it is still significantly different from zero (compare e.g. panels b and f in Figure 6).

P11L28: See my major comment (4). What is the rate for CH_4 production? Is it of a realistic rate?

The CH_4 production rate is essentially controlled by the forcing (seafloor warming) and should be realistic, given the assumptions made regarding e.g. initial hydrate saturation, seafloor warming rate etc.

P12L3: correct CH_4 (subscript 4) throughout the text and figures.

We have corrected this

P12L5: ocean warming is not modeled. Delete this statement.

The reviewer is correct in that ocean warming is not modelled. It is, however, the prescribed forcing in our model simulations. In this study, we model the effect of seafloor warming, which is also what we state in this sentence.

P14L26: The AOM efficiency should be defined in the method.

We have moved the definition of AOM efficiency to the methods section, as suggested by the reviewer.

P15L5: this is a weird sentence. AOM is important for consuming the methane release from hydrate dissociation due to climate change

We agree with the reviewer and we have rewritten the sentence. In the revised version of the ms it now reads: “While AOM is important for understanding the potential impact of hydrate dissociation on climate across different time scales ...”

P15L31: check parentheses

Fixed

Water depth controls the phase boundary of methane, and therefore how much methane is in the dissolved phase that is available for AOM. The water depth of sites reported from Boetius and Wenzhofer range from 560 to 4000 meters with widely different methane saturation. This water depth factor is also something that require considered.

The reviewer is correct in that the CH₄ solubility changes as a function of depth (pressure). When investigating the feather edge of stability, these differences are relatively small (seafloor depths ranging ~400-600 m, see e.g. Stranne et al. 2016b). Note that the solubility is adjusted internally in the TOUGH+Hydrate code as a function of pressure and temperature (Henry’s law).

P15L37: check parentheses

Fixed

P16L1: lower than what? and how does the lower bulk average AOM rate reconcile the discrepancy?

The reviewer is referring to the following statement in the Discussion section (P15L30-P16L1) where we discuss two plausible explanations for why the combination of high AOM rates and low AOM efficiency, as observed at some cold seeps, is not entirely consistent with our modeling results.

In the sentence the reviewer asks about, we mean “lower than what is observed in the top few decimeters”. A lower bulk AOM rate would be more in line with our results, see the previous lines in the same paragraph.

P16L4: I don’t think PKF can be called a deep sea cold seep since the seeps are located at water depths shallower than 350 meters.

We agree with the reviewer and we have deleted the “deep sea” in the revised version of the ms.

P16L5-7: Isn't it the same for your simulated case with high permeability that the high permeability remains high regardless of the in situ pore space?

No, there is a fundamental difference between the two cases. When hydraulic fractures form as a result of increased pore pressure, the mobility of the gas increases and the gas is transported away from the high pressure region in the sediment column. After migration, pore pressure is decreased and the hydraulic fracture closes. The opening and closing of a fracture often happens over a period on the order of 1 day. This is illustrated in Figure 7d, and discussed at length in Stranne et al. (2017).

P16L10: doesn't need to emphasize anthropogenic warming as your model results cannot differentiate the different triggers of warming.

As stated in the Abstract and in the Introduction sections, the present ms is investigating how AOM is modifying seafloor gas release in a future ocean warming scenario, as a result of anthropogenic forcing. Even though it is strictly true that the system reacts the same regardless of what is causing the seafloor warming, it is difficult to envision such rapid warming as assumed in this study, without an anthropogenic influence.

P16L12-13: Please check this sentence again. I don't quite follow.

We have rewritten this sentence in the revised version of the ms and we hope that it is now easier to follow:

“We speculate, therefore, that the resulting flow would not resemble present day cold seeps where gas is transported through sub-surface gas chimneys or faults, but that it would be more similar to that simulated in the present study, with the CH₄ gas being transported either through elastic and highly dynamic (opening and closing) fractures in low-permeability sediments, or percolating through the porous media in higher permeability sediments”

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Can anaerobic oxidation of methane prevent seafloor gas escape in a warming climate?

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Abstract

Assessments of future climate warming-induced seafloor methane (CH₄) release rarely include anaerobic oxidation of methane (AOM) within the sediments. Considering that more than 90% of the CH₄ produced in ocean sediments today is consumed by AOM, this may result in substantial overestimations of future seafloor CH₄ release. Here we integrate a fully coupled AOM module with a numerical hydrate model to investigate under what conditions rapid release of CH₄ can bypass AOM and result in significant fluxes to the ocean and atmosphere. [We run a number of different model simulations for different permeabilities and maximum AOM rates. In all simulations, a future climate warming scenario is simulated by imposing a linear seafloor temperature increase of 3 °C over the first 100 years.](#) The results presented in this study should be seen as a first step towards understanding AOM dynamics in relation to climate change and hydrate dissociation. Although the model is somewhat poorly constrained, our results indicate that vertical CH₄ migration through hydraulic fractures can result in low AOM efficiencies. Fracture flow is the predicted mode of methane transport under warming-induced dissociation of hydrates on upper continental slopes. Therefore, in a future climate-warming scenario, AOM might not significantly reduce methane release from marine sediments.

1. Introduction

The atmospheric concentration of CH₄ increased 2.5x since the preindustrial era, and anthropogenic emissions now account for 50-65% of annual global CH₄ emissions (Stocker et al., 2013). CH₄ is an important greenhouse gas accounting for 20% of the observed postindustrial climate warming (Kirschke et al., 2013). Marine sediments along continental margins contain large reservoirs of CH₄ stored as solid gas hydrate (Milkov, 2004; Wallmann et al., 2012). The stability of submarine CH₄ hydrate is primarily a function of temperature and pressure at and beneath the seafloor. Natural hydrate deposits are therefore susceptible to destabilization via ocean warming (Archer et al., 2009; Kretschmer et al., 2015; Dickens et al., 1995). The observed increase in atmospheric CH₄ content is presently attributed mostly to anthropogenic land use. However, a warming climate can lead to destabilization of the [temperature](#)

~~sensitive~~ part of the marine hydrate reservoir [sensitive to temperature perturbations](#), potentially leading to CH₄ transport from sediments to the oceans and atmosphere, where the CH₄ becomes a positive feedback on climate warming. As a result, anthropogenic induced destabilization of natural marine CH₄ hydrate has been proposed as a climate warming mechanism that could exhibit threshold behavior, implying that if climate warming continues this feedback could cause an abrupt and irreversible transition into a warmer climate state (Stocker et al., 2013).

Although estimates of future CH₄ gas release to the atmosphere from hydrate destabilization on regional and global scales vary by orders of magnitude (Biastoch et al., 2011; Hunter et al., 2013; Kretschmer et al., 2015) and are likely overestimated (Stranne et al., 2016b), ~~IPCC AR5~~ [the fifth assessment report of the intergovernmental panel on climate change](#) evaluated the risk of a catastrophic CH₄ release during the 21st century as very unlikely (Stocker et al., 2013). In part, this is because much of the CH₄ escaping from the seafloor will be consumed in the water column before reaching the atmosphere (Mau et al., 2007; McGinnis et al., 2006). On longer time scales, however, the effect of widespread hydrate dissociation on our climate may be irreversible. This is due to the difference between time scales for release (discharge) and accumulation (recharge) - the recovery time scale from the perturbed state is significantly longer than the time it takes for the system to reach this perturbed state (Dickens, 2001; Kennett et al., 2003).

A mechanism that has been largely overlooked in this context, however, is anaerobic oxidation of methane (AOM) in marine sediments (Ruppel & Kessler, 2017). About 85% of the annual global CH₄ production and 60% of its consumption are based on microbial processes and in marine sediments AOM is the dominant biogeochemical CH₄ sink (Egger et al., 2018; Knittel and Boetius, 2009; Martens and Berner, 1977; Reeburgh, 2007). AOM is carried out by microbes within the sulfate reduction zone (SRZ), a feature found in all anoxic marine sediments where the transport of methane from below and sulfate from above provides a source of energy through AOM (Barnes and Goldberg, 1976; Knittel and Boetius, 2009; Malinverno and Pohlman, 2011). It is estimated that, on a global scale, more than 90% of the CH₄ produced in ocean sediments is consumed by AOM (Hinrichs and Boetius, 2002; Reeburgh, 2007). AOM is therefore a critical process that needs to be considered when modelling future climate warming-induced CH₄ release from marine sediments.

Numerical methods for predicting future ocean warming-induced methane release from the marine hydrate reservoir span a wide range of complexities, from the simplest approaches where gas escape from the seafloor is estimated as a function of temperature change (Biastoch et al., 2011; Hunter et al., 2013; Kretschmer et al., 2015) to more sophisticated models that include coupled hydraulic-thermodynamic behavior of multiphase fluid flow in hydrate-bearing porous media (Darnell and Flemings, 2015; Reagan et al., 2011; Reagan and Moridis et al., 2008; Stranne et al., 2016a; Thatcher et

al., 2013). One example of the latter is the TOUGH+Hydrate (T+H) model which predicts the evolution of pressure, temperature, salinity, and the phase saturation distributions in hydrate-bearing systems (Moridis [et al.](#), 2014). Stranne et al. (2017) integrated a geomechanical coupling into the T+H model (referred to as T+H-GeoMech in the text) and showed that such coupling is critical since dissociation of methane increases pore pressure and leads to hydraulic fracturing. Hydraulic fractures increase the permeability of sediments, and dramatically affect rates of dissociation and seafloor gas release. As the majority of the global marine methane hydrate reservoir is dominated by low permeability, fine-grained (silt and clay) sediments (Boswell and Collett, 2011), hydraulic fracturing is an important mechanism controlling potential rates of methane release induced by climate warming. However, as ~~was~~ pointed out by Ruppel & Kessler (2017), AOM in marine sediments is yet another important process that is missing in current numerical hydrate models.

In a warming world, AOM is the main mechanism that can potentially prevent the transfer of huge quantities of methane from sediments to the oceans. The efficiency of AOM under climate warming is still, however, a poorly constrained issue (Knittel and Boetius, 2009; Ruppel and Kessler, 2017). Although AOM efficiently controls the ~~atmospheric~~ methane flux from the world's ~~oceans-seafloors~~ in general (Egger et al., 2018; Knittel and Boetius, 2009; Martens and Berner, 1977; Reeburgh, 2007), there are observational and model-based studies (Luff and Wallmann, 2003; Martens and Val Klump, 1980) suggesting that the rate of vertical CH₄ migration controls the efficiency of AOM (also referred to as the microbial filter). Buffett & Archer (2004) speculate that slow diffusive transport of CH₄ likely results in AOM within the sediments with negligible effect on climate, while a more rapid liberation of CH₄ (in response to ~~anthropogenic~~ climate warming) can lead to fractured pathways within the sediment that bypass the microbial filter and allow for a larger proportion of the CH₄ to reach the ocean and atmosphere. This idea is supported by Stranne et al. (2017), who showed that warming-induced hydrate dissociation in moderate to low permeability sediments (clays and silty-clays) leads to formation of hydraulic fractures and rapid release of CH₄ from the seafloor.

In a review paper by Knittel & Boetius (2009) they list the following as one of the key future issues: “How will global climate change, with regard to the expected increase in temperature and sea level, affect the stability of gas hydrate reservoirs and the efficiency of microbial methane consumption?”. In a more recent review paper on the interaction between climate change and CH₄ hydrates (Ruppel & Kessler, 2017), the authors identify the quantification of the AOM sink in marine sediment as one of the key directions for future research. While Ruppel & Kessler (2017) recommend the use of numerical hydrate models for improved predictions of future warming-induced seafloor CH₄ release, they explicitly stress the need for better handling of AOM in such modeling efforts.

The present study aims at taking a step in this direction, through the addition of a simplistic but novel and fully coupled AOM module to the T+H-GeoMech code. As in Stranne et al. (2017) we focus on the feather-edge of hydrate stability - the part of the marine hydrate reservoir most sensitive to ocean warming (Ruppel, 2011). We address the hypothesis of Buffett & Archer (2004) by investigating how the efficiency of the microbial filter varies as a function of the intrinsic permeability of the sediment (which in turn controls the vertical migration of CH₄) during seafloor warming-induced hydrate dissociation. In other words - to what extent can vigorous CH₄ flow through dynamic hydraulic fractures bypass the microbial filter? [In all model simulations, a future climate warming scenario is simulated by imposing a linear seafloor temperature increase of 3 °C over the first 100 years \(Table 1\).](#)

2. Method

2.1 Model setup

The T+H-GeoMech (Moridis, 2014; Stranne et al., 2017) is set up for mid-latitude conditions with an initial bottom water temperature of 5°C and a ~~methane-gas~~ hydrate stability zone (~~MHSZ~~GHSZ) extending down to 20 m below seafloor (mbsf). This represents the most sensitive “feather-edge” of hydrate stability on the upper continental slope. The initial hydrate deposit is homogeneously distributed within the ~~M~~GHSZ and is in thermodynamic equilibrium with the initial seafloor temperature, geothermal heat flow and the sediment bulk thermal conductivity profile. The model domain extends to 200 mbsf and consists of 160 grid cells with a size of 0.17 m between 0 and 25 mbsf and 19 m between 25 and 200 mbsf. We assume that the upper 5 m of the sediment column is within the SRZ and is initially depleted of CH₄ (Bhatnagar et al., 2011). See Table 1 for a list of parameter values used in the model simulations.

Table 1. Physical Properties and T+H-GeoMech Simulation Parameters (for additional information, see Stranne et al., 2017)

Parameter	Value
Sediment grain density [kg/m ³]	2700
Permeability, k [m ²]	10 ⁻¹⁷ to 10 ⁻¹⁴
Wet conductivity [W/mK]	1.21*
Dry conductivity [W/mK]	0.34*
Heat flow [W/m ²]	0.04**
Porosity	0.6*
Initial seafloor temperature [°C]	5
Seafloor depth [m]	520
Initial hydrate saturation, S_h [%]	5*
Initial/boundary pore water salinity [%]	3.5*
Gas composition	100% CH ₄
Seafloor temperature increase [°C year ⁻¹]	0.03 (over first 100 years), Figure 4a *
Fracture Permeability [m ²]	10 ^{-10**}
Normalized overpressure threshold	1.0**

*From (Thatcher et al., 2013)

**From (Stranne et al., 2017)

2.2 AOM module

The total vertically integrated CH_4 mass within the model domain is distributed between three pools (Fig. 1a): the hydrate pool ($M_{\text{Hyd}}(t)$), the gas pool ($M_{\text{Gas}}(t)$) and the dissolved pool ($M_{\text{Dis}}(t)$). CH_4 can move between these pools over time (t) and leave the system either through AOM within the SRZ ($F_{\text{AOM}}(t,z)$), where z is depth below seafloor, or through gas/dissolved CH_4 flux at the seafloor-ocean interface ($F_{\text{Gas}}(t)/F_{\text{Dis}}(t)$). The $F_{\text{AOM}}(t,z)$ is described as a sink on $M_{\text{Dis}}(t)$ which means that gaseous CH_4 is not directly available for AOM. However, because pore water tends to be fully saturated in the presence of gas, AOM does act as a sink on $M_{\text{Gas}}(t)$, as the constant reduction in CH_4 pore water saturation draws CH_4 from $M_{\text{Gas}}(t)$ to $M_{\text{Dis}}(t)$.

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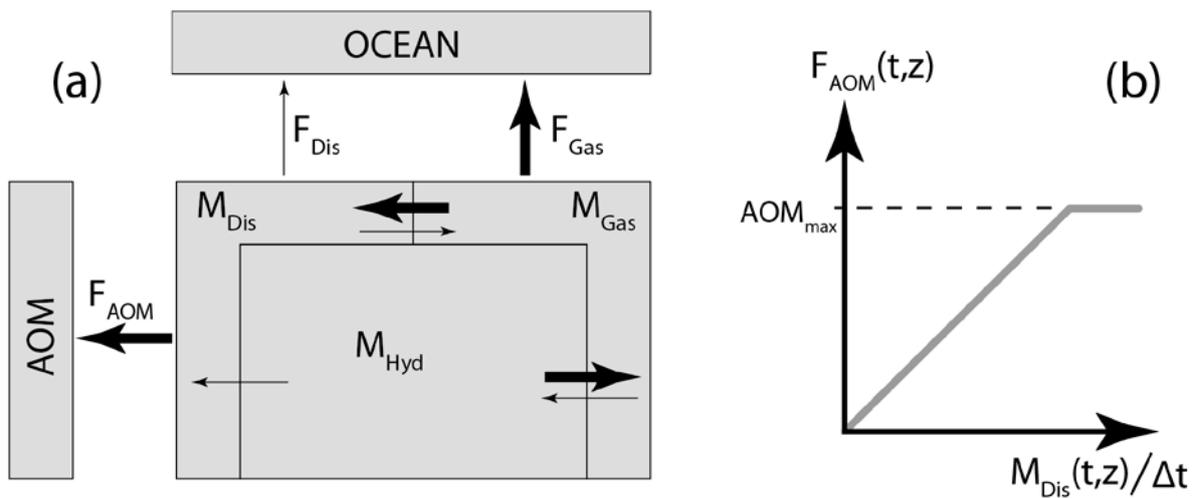


Figure 1. a) A schematic overview of the three CH_4 mass pools within the sediments, and the general direction of the CH_4 mass transport during hydrate dissociation, within and out of the system (illustrated by the thick arrows). b) Modelled $F_{\text{AOM}}(t,z)$ as a function of the dissolved CH_4 saturation (where Δt is the time step) and predefined AOM_{max} .

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Observed AOM rates span from $\sim 10^{-6} \mu\text{mol cm}^{-3} \text{ day}^{-1}$ in subsurface SRZs of deep margins, to a few $\mu\text{mol cm}^{-3} \text{ day}^{-1}$ in surface sediments above gas hydrates (Knittel & Boetius 2009). In this study we cover the range of maximum bulk oxidation rates within the SRZ (AOM_{max}) from zero to $1 \mu\text{mol cm}^{-3} \text{ day}^{-1}$ in Cases A1-7 (Table 2, Figure 2), within a predefined and constant depth of the SRZ extending, in the base case, to 5 mbsf. In each time step, the maximum amount of AOM is calculated (AOM_{max} multiplied by the time step and grid cell volume) in all grid cells within the SRZ. If the dissolved CH_4 content within a grid cell is smaller than or equal to the maximum amount of AOM, the dissolved CH_4 content is set to zero. The AOM within that particular grid cell is then limited by the dissolved CH_4 saturation. If the dissolved CH_4 content within a grid cell is larger than the maximum AOM, then the dissolved CH_4 content is reduced by this amount. The AOM within that grid cell is then limited by the predefined maximum AOM capacity of the system. This means that the modelled AOM rate is a linear

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function of dissolved CH₄ content (which is ultimately controlled by the CH₄ supply from below) up to a point where the predefined AOM_{max} takes over (Fig. 1b). In each grid cell where AOM occurs, an equal mass of water is added in order to keep mass balance within the system (i.e. CH₄ and NaCl are the only two dissolved species in the model and therefore, the end products from AOM is added to the water fraction of the pore space).

The base of the SRZ may be found at decimeters to tens of meters below the seafloor, depending on the burial rate of reactive organic matter, the depth of the methane production zone, the ~~transport velocity flux~~ of methane and sulfate and their consumption rates (Egger et al., 2018; Knittel and Boetius, 2009). Our constant SRZ depth of 5 mbsf represents a ~~typical value in many modelling commonly used in exercises numerical modeling~~ applied to marine gas hydrates (Kretschmer et al., 2015; Reagan & Moridis, 2008; Stranne, O'Regan, & Jakobsson, 2016; Wallmann et al., 2012). ~~This depth is also within the range of measured SRZ depths in e.g. the South Atlantic and measured in high CH₄ flux areas at the feathered edge~~ (Miller et al., 2015; Rodrigues et al., 2017). Rodrigues et al. (2017) measured SRZ depths between 3-4 mbsf in areas with high gas flow and ca. 7 mbsf in background areas. We perform a sensitivity test on SRZ depth by running two additional suites of simulations with SRZ depth equal to 2.5 m and 7.5 m in the Cases B1-2 respectively (Fig. S1). The initial hydrate saturation (expressed as the percentage of pore space, S_h) in the baseline simulations is 5%, homogeneously distributed within the MGH_{SHZ} (except for the SRZ which is initially depleted of hydrate). We perform a sensitivity test on the hydrate saturation by running two suites of simulations with S_h equal to 2.5% and 7.5% in Cases C1-2 respectively (Fig. S2).

~~If we define t~~ The efficiency of the microbial filter is defined as

$$AOM\ efficiency = \left(1 - \frac{(F_{Gas}(t) + F_{Dis}(t))_{Case\ Ax}}{(F_{Gas}(t) + F_{Dis}(t))_{Case\ A1}} \right) \cdot 100\%$$

where Case Ax is one of the cases listed in Table 2. In other words, AOM efficiency is the percentage of CH₄ escape in the 'zero AOM' case (Case A1) that is instead oxidized within the SRZ.

Table 2. Summary of the simulation cases performed in the present study. Each Case involves thirteen 200 year simulations for permeabilities ranging between 10^{-17} and 10^{-14} m² (in total 143 simulations).

Simulation Case	Description
A1-7	AOM _{max} : 0, 10^{-9} , $10^{-8.5}$, 10^{-8} , $10^{-7.5}$, 10^{-7} , 10^{-6} [mol cm ⁻³ day ⁻¹]
B1-2	SRZ depth: 2.5, 7.5 [m], AOM _{max} : 10^{-8} [mol cm ⁻³ day ⁻¹]

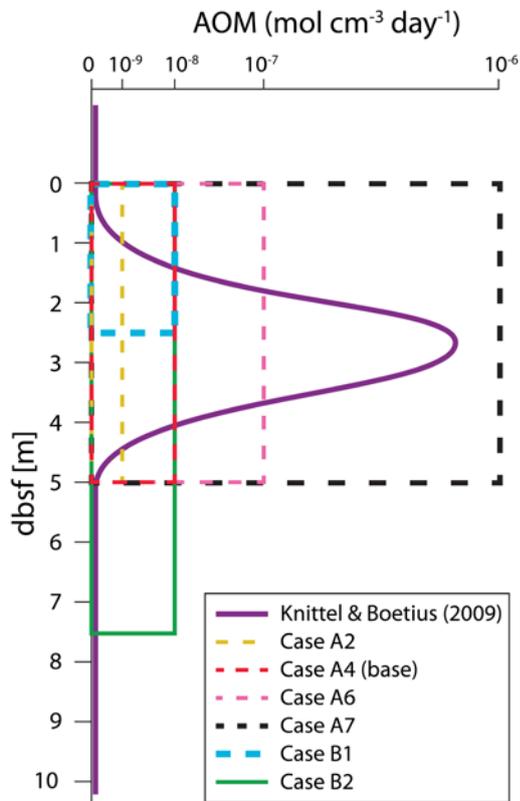


Figure 2. Conceptual AOM rate as a function of depth below seafloor (dbsf, solid purple) based on Knittel & Boetius (2009), and a visual representation of some of the model simulation cases performed in the present study. In Cases A1-7, the base of the SRZ is prescribed at 5 mbsf. We simulate two Cases B1-2 with the SRZ extending down to 2.5 and 7.5 mbsf respectively, both with an AOM_{max} of $10^{-8} \text{ mol cm}^{-3} \text{ day}^{-1}$. Note that the x-axis is nonlinear and that all boxes (each representing a simulation case) have their upper left corner situated at the origin.

10 3. Results

As shown in Stranne et al. (2017), the upward transport of CH_4 within destabilized hydrate-bearing sediments can be divided into three flow regimes. These flow regimes depend on the sediment permeability, and encompass the expected range of permeabilities for hemipelagic sediments composed predominantly of terrigenous silts and clays (Fig. 3).

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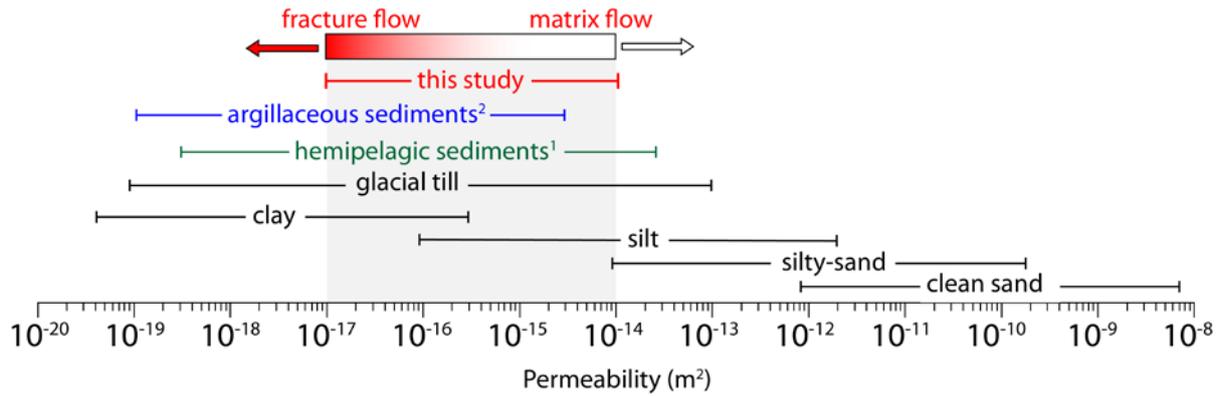


Figure 3. Typical range of permeability for unconsolidated sediments and marine sediments. Data sources are: black - (Freeze and Cherry, 1979); green – (Spinelli et al., 2004), porosity-permeability marine data compilation for porosities between 40-85%; blue – (Neuzil, 1994). Data from Neuzil (1994) are a compilation of laboratory permeability data for natural clay, silt sand mixtures from marine and terrestrial sources with porosities of 40-90%.

The low-permeability *fracture flow* regime ($k < 10^{-15.5} \text{ m}^2$) is dominated by highly nonlinear flow with irregular bursts of gas occurring at the seafloor through the opening and closing of hydraulic fractures (see Stranne et al., 2017 for details). When considering a centennial time scale, *fracture flow* results in the largest vertical transport of CH_4 gas towards the seafloor. In the *matrix flow* regime, which is predicted in higher permeability substrate ($k > 10^{-15} \text{ m}^2$), CH_4 is percolating through the porous media in a continuous, regular fashion through intergranular pore spaces. This slower flow regime will continue long after the hydrate deposit has been depleted because over-pressure persists within the sediments and continues to drive vertical flow. This is distinct from fracture flow that ends the moment hydrate dissociation stops, because excess pore pressure no longer builds up within the sediments to create hydraulic fractures. These two regimes are separated by a mid-permeability *low flow* regime ($10^{-15.5} \leq k \leq 10^{-15} \text{ m}^2$) where the permeability is high enough to allow gas transport away from the dissociation front (limiting the build-up of excess pore pressure and the formation of hydraulic fractures), while at the same time being low enough so that only small amounts of CH_4 reach the near seafloor sediments on a centennial time scale. The development of the sediment column in terms of hydrate saturation, GHSZ, aqueous saturation and gas saturation for two model simulations with different permeabilities (Case A4) are shown in Fig. 4b-g. Seafloor CH_4 release as a function of time for the three fluid flow regimes is shown in (Fig. 4a5a,d,g). Note that we use the terms *CH₄ escape* and *CH₄ gas escape* interchangeably throughout the text, as the dissolved fraction of the seafloor CH_4 escape is negligible (Fig. 54, 5e6c).

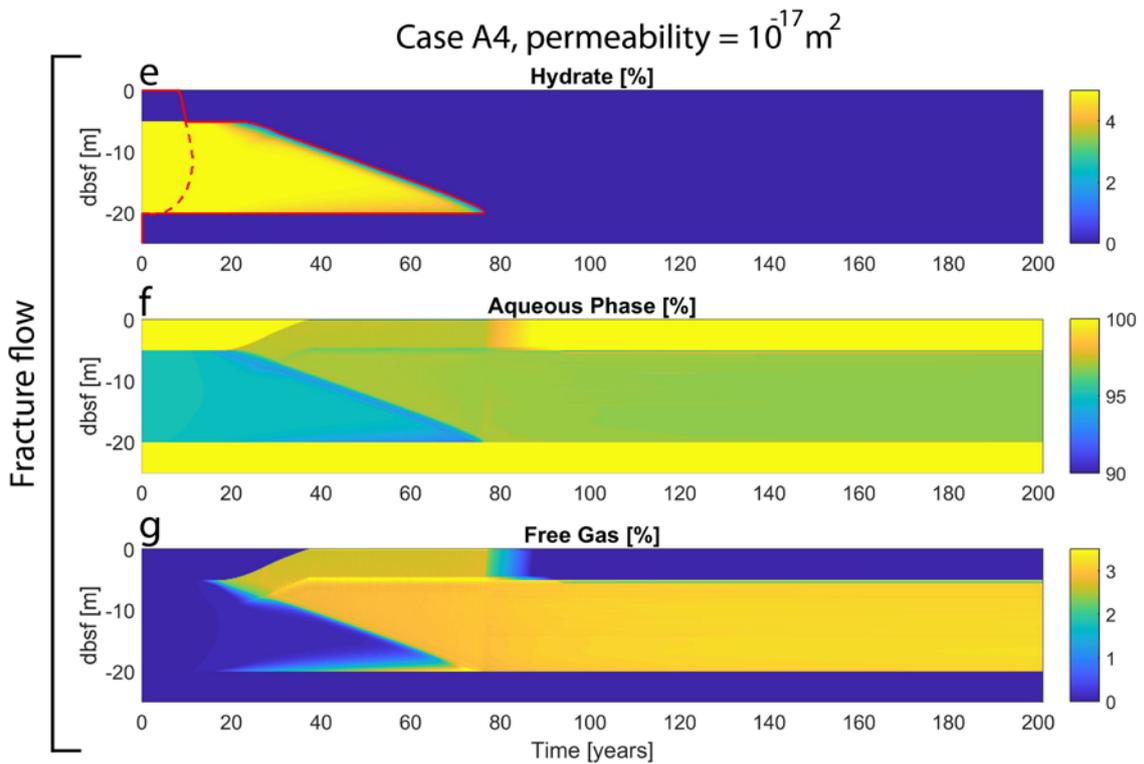
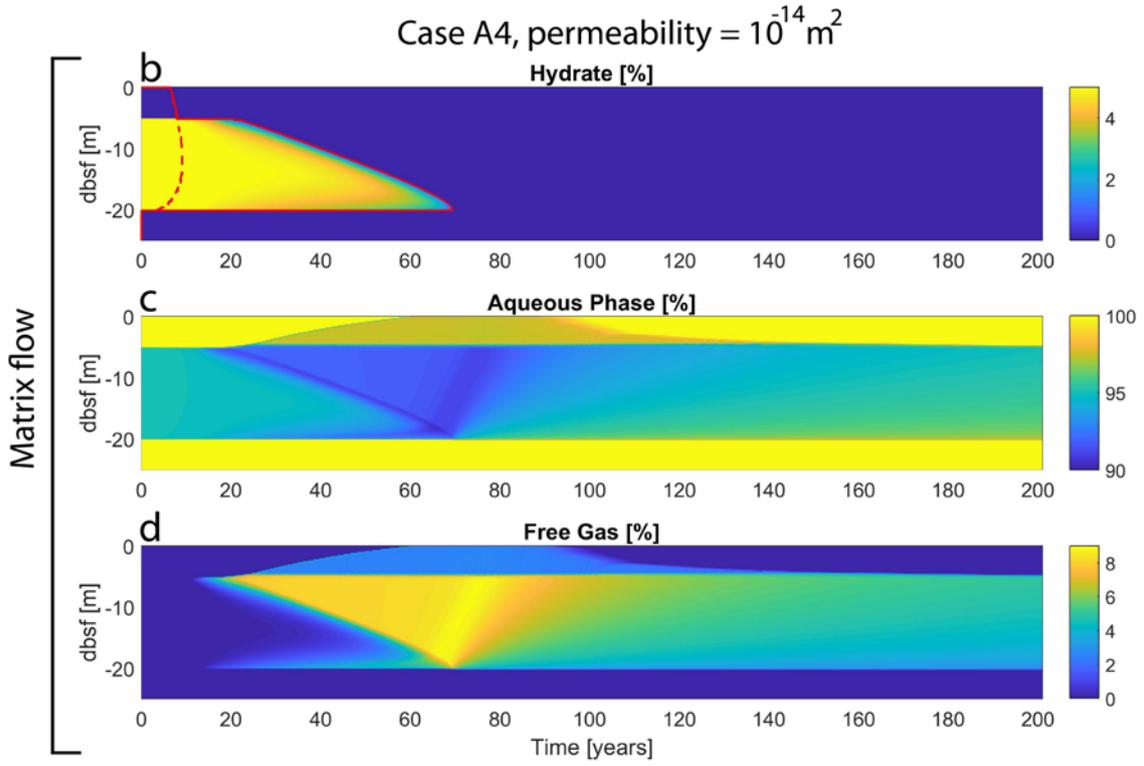
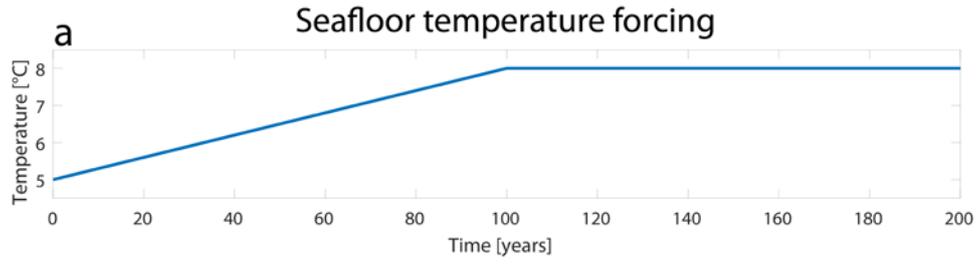
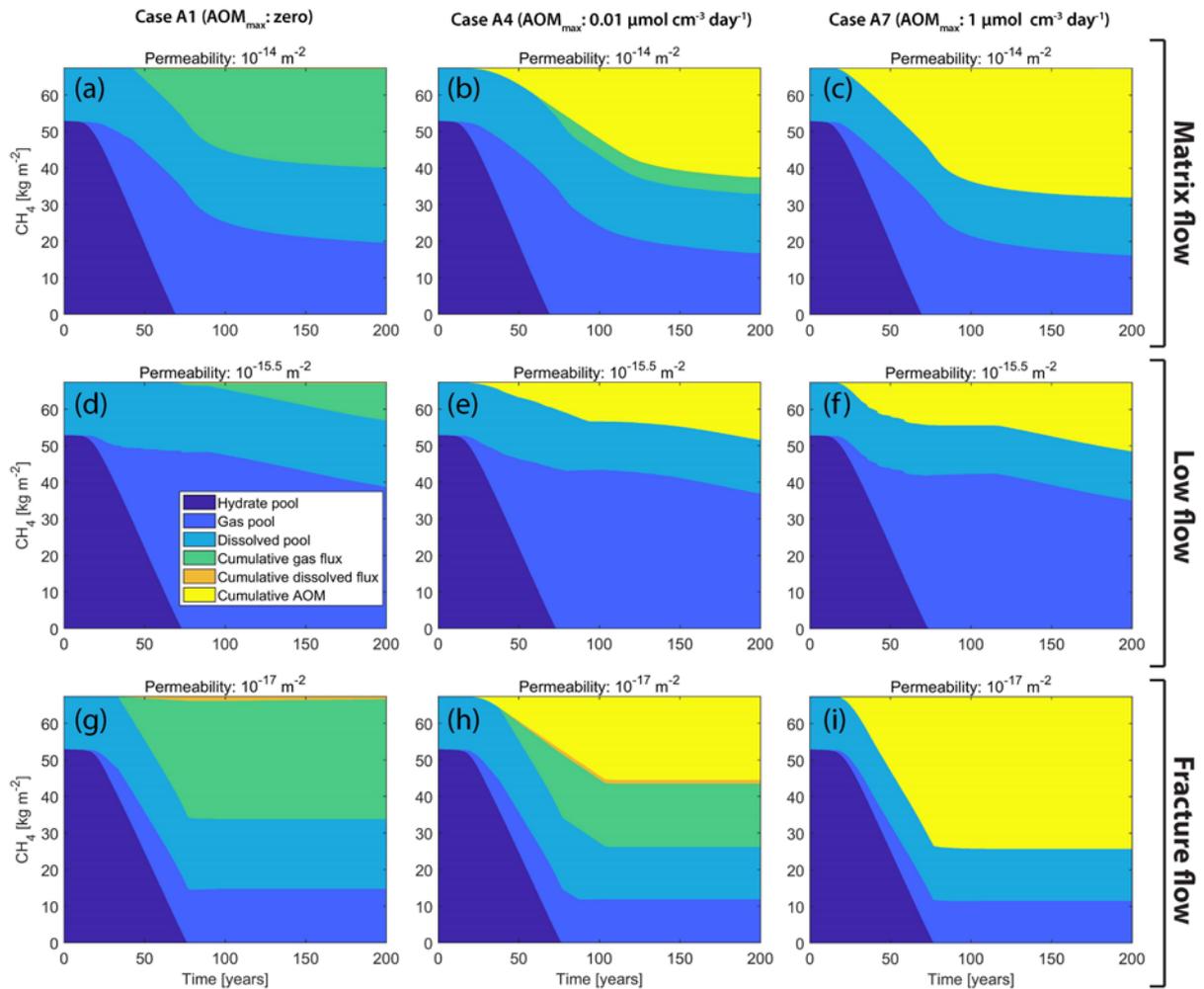


Figure 4. **a** Model simulations are all forced by a linear seafloor temperature increase of 3 °C over the first 100 years. Modeled hydrate saturation (**b,e**), aqueous saturation (**c,f**) and gas saturation (**d,g**) as a function of time and dbfsf for two simulations (Case A4) with permeability of 10^{-14} m^2 (**b-d**) and 10^{-17} m^2 (**e-g**) respectively. Also shown in panels **b** and **e** is the GHSZ where the solid red line indicates the boundary for unstable conditions and the dashed red line indicates the boundary for stable conditions (area in between is at the melting point). The pressure development and the phase transition boundary at different times are shown in Fig. S3.



10 Figure 4₅. CH₄ mass budget over time showing the five components of Fig. 1 with the dissolved and gaseous fluxes separated. Displayed are three examples (high, mid and low permeability, rows) for three different cases (Cases A1, A4 and A7, columns). Note that difference in cumulative CH₄ gas escape (green area) between high and low permeability is significantly larger in Case A4 (panels **b** and **h**) compared to Case A1 (panels **a** and **g**).

15

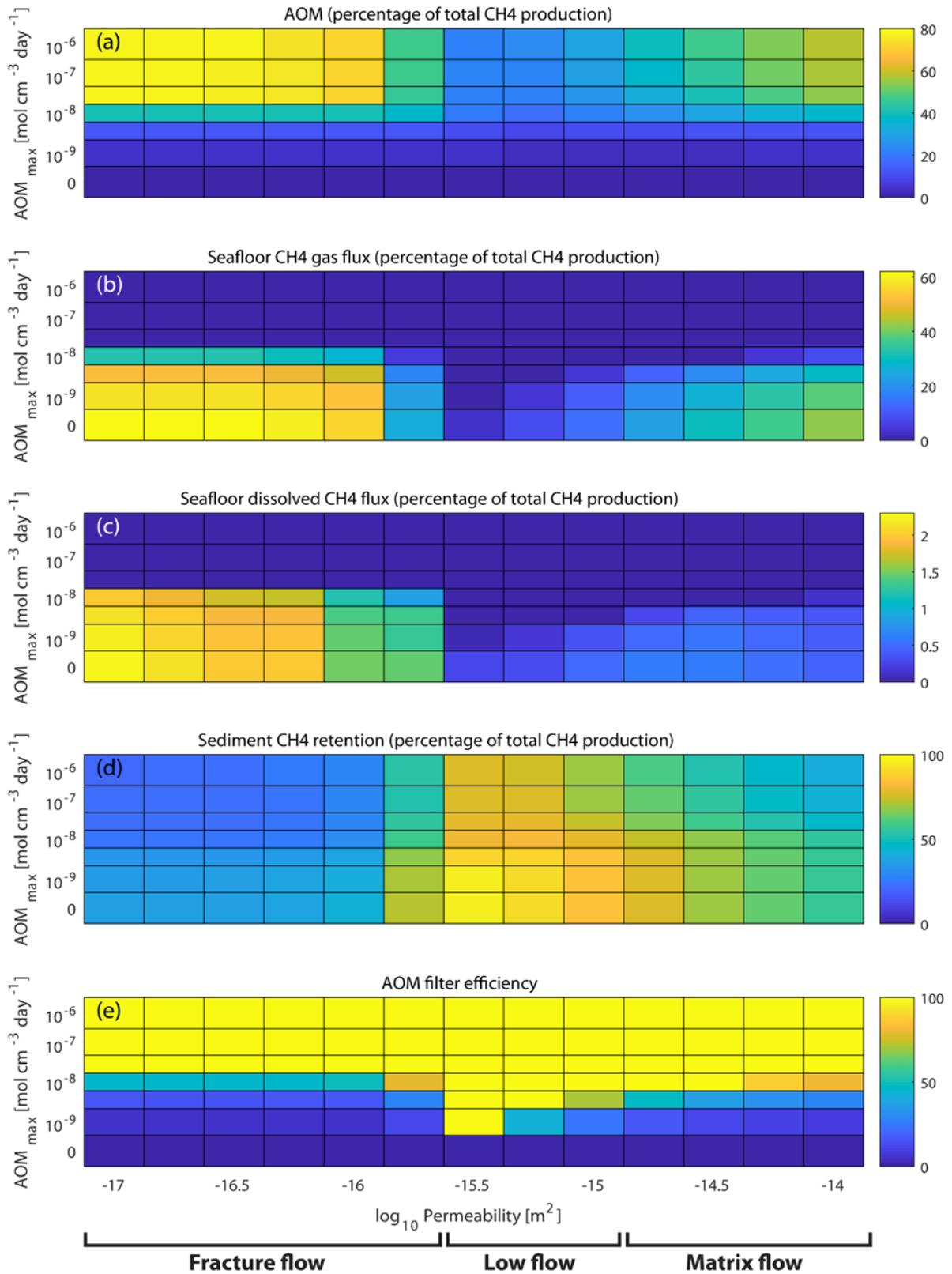


Figure 56. Case A1-7 simulation results after 100 years (each tile represents one model simulation). Panels **a-d** show percentages of the total CH₄ production from hydrate dissociation after 100 years which is identical in all cases and equal to 53 kg m⁻² (the sum of panels **a-d** equals 100%). **a** – the total cumulative AOM increases with increased AOM_{max} rates but is also a function of the vertical CH₄ flow

rate within the sediments (highest values for the fractured flow regime, lowest values for the low flow regime, and intermediate values for the matrix flow regime). **b** and **c** – the cumulative CH₄ release (**b** gaseous and **c** dissolved) decreases with increased AOM_{max}, and also reflects vertical CH₄ flow rates within the sediments (as discussed above). **d** – sediment CH₄ retention is weakly dependent on AOM_{max} (some of the CH₄ that would reside within the SRZ in the zero AOM case would instead be consumed by AOM), but generally reflects the vertical CH₄ flow rates. **e** – the AOM filter efficiency is defined as the fraction of CH₄ escape reduction compared to the corresponding zero AOM case (Case A1). For cases with AOM_{max} larger than 10⁻⁸ cm³ day⁻¹ the model predicts that the microbial filter is 100% effective, regardless of permeability, meaning that no CH₄ can escape from the seafloor. For lower AOM_{max} rates the picture is more complex.

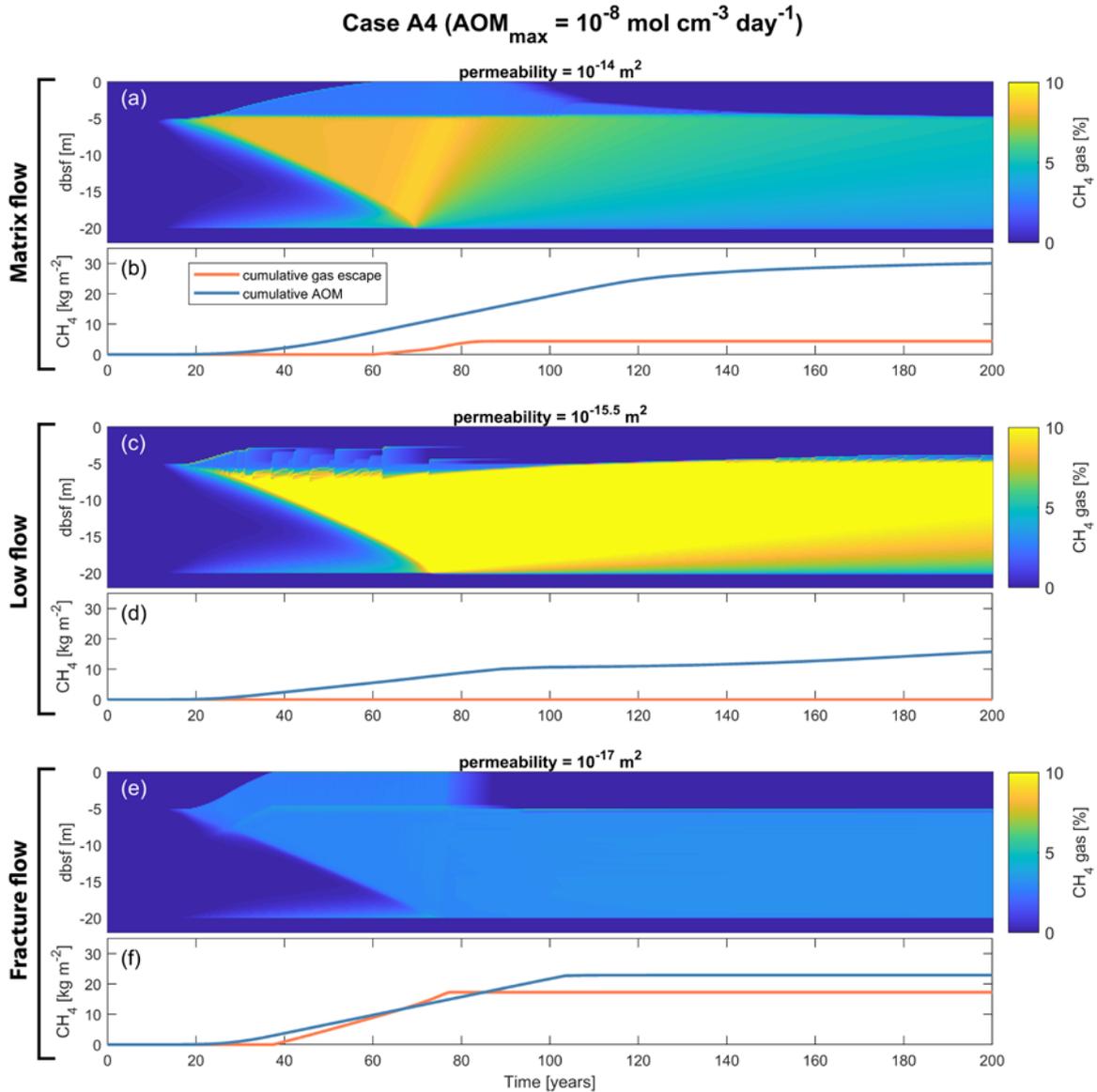
While permeability and fracture dynamics control the supply of CH₄ to the SRZ, the fate of CH₄ that reaches the SRZ is determined by the AOM_{max} rate. A high AOM_{max} rate leads to complete oxidation of the CH₄ before it can escape from the seafloor, while a low AOM_{max} leads to a large fraction of the CH₄ bypassing the microbial filter and escaping into the ocean. However, for intermediate AOM_{max} rates (around 10⁻⁸ cm³ day⁻¹, Case A4) the efficiency of the microbial filter becomes a [question-function](#) of permeability (or flow regime). For the low-permeability *fracture flow* regime, with large vertical transport of CH₄, AOM is limited by the prescribed AOM_{max} rate - thus an increase in CH₄ supply to the SRZ does not result in increased AOM, but larger CH₄ escape from the seafloor. For the *low flow* regime, the opposite is true - all the supplied CH₄ to the SRZ is oxidized and none escapes, meaning that AOM becomes a sole function of the CH₄ supply. The *matrix flow* regime is somewhere in-between these two extremes, and thus AOM and gas release are both strong functions of the CH₄ supply into the SRZ from below.

Case A4 (Base Case)

The fate of CH₄ produced from hydrate dissociation in Case A4 is visualized in Fig. 45b,e and h (where CH₄ production equals the hydrate reduction, shown as the dark blue area) and in Fig. 76a, c and e. It should be noted that the total CH₄ production is identical in all cases, and equal to the amount of CH₄ initially stored in the hydrate deposit.

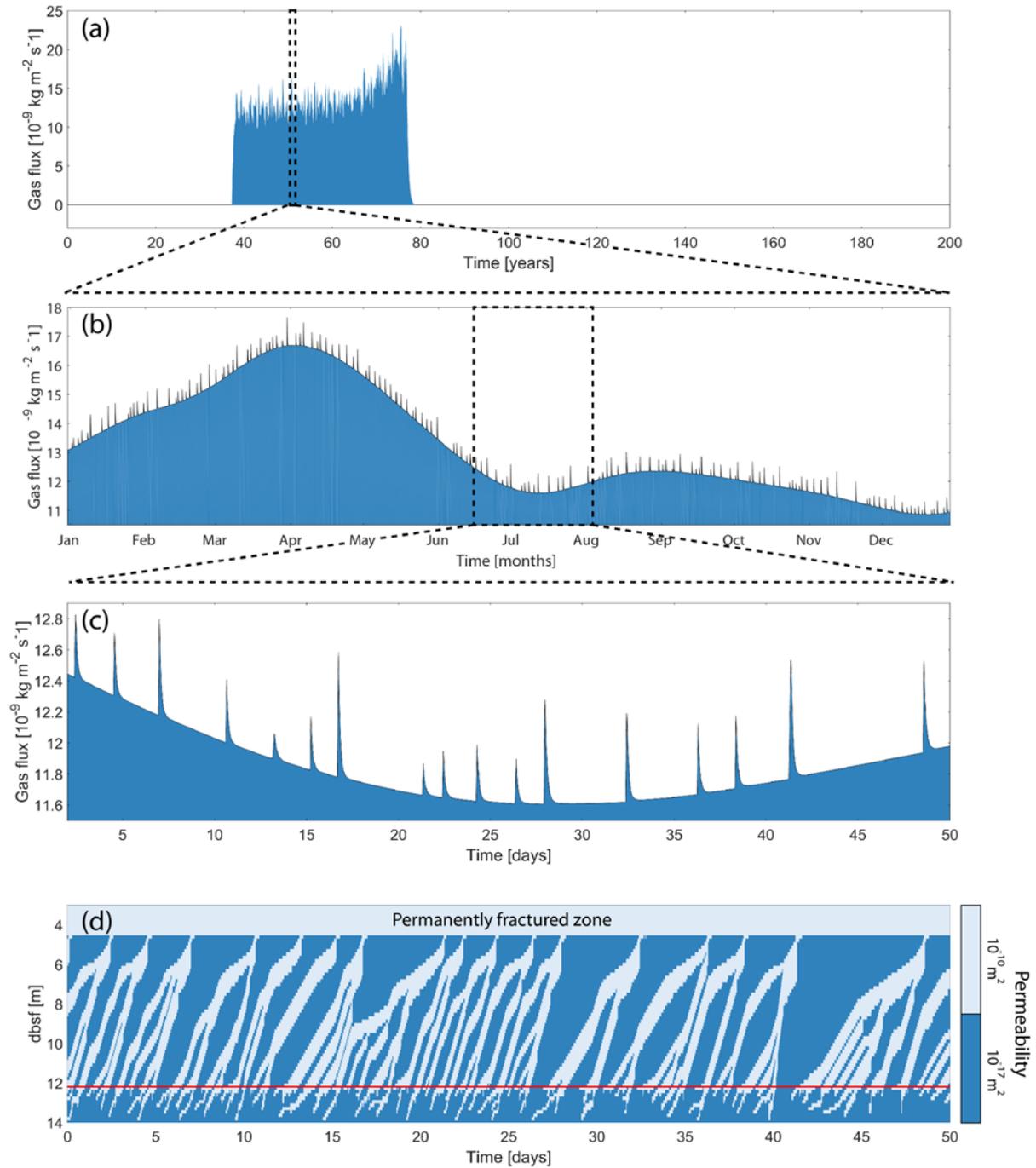
Fig. 76 illustrates the radically different transport capacities of sediments with different permeability. In low-permeability sediments (Fig. 67e) fractures start to appear soon after the onset of hydrate dissociation (around 20 years into the simulation) effectively transporting most of the CH₄ gas away from the dissociation front and up towards the SRZ. The AOM capacity (as controlled by AOM_{max}) is smaller than the CH₄ supply, resulting in gas being released from the seafloor between 40 and 75 years into the simulation. Once the hydrate deposit is completely dissociated, fractures can no longer be created and the seafloor gas escape is immediately shut down. The remaining CH₄ within the SRZ is

then consumed by AOM over the next 30 years (75 to 105 years into the simulation, Fig. 76f). The amount of CH₄ still residing within the sediment after 100 (200) years is about 24% (22%) of the produced CH₄ from hydrate dissociation (Fig. 65d). The transport of CH₄ in low permeability sediments is mainly through fractures which gives rise to variability of seafloor gas release on different time scales (Fig. 87a-c). This highly non-linear response to a constant seafloor warming is related to the opening and closing of fractures within the sediments, which occurs on time scales down to the order of hours (Fig. 87d).



10 *Figure 67. Example of simulation outputs from Case A4, highlighting the different dynamics of the three gas flow regimes within the sediments. Shown are sediment CH₄ gas saturation (percentage of pore space) with time and depth below seafloor, and cumulative CH₄ gas escape and cumulative AOM with time, for three different permeabilities, representing higher permeability matrix flow (panels a and b), mid-permeability low flow (panels c and d), and lower permeability fracture flow (panels e and f). Note*

that the hydrate deposit is initially situated between 5 and 20 mbsf and that gas is forming at the upper and lower edge of the deposit, which is gradually thinning and is completely dissociated after around 75 years into the simulations.



5

Figure 87. Fracture flow in low permeability sediments for the base case simulation (Case A4 with permeability of $10^{-17} m^2$). Seafloor gas flux for the whole simulation (a), over one year (b) and over 50 days (c). d) Fracture propagation within the sediments over the same period as (c). The horizontal red line marks the upper boundary of the hydrate deposit at this particular time, and the permanently

fractured zone is the upper part of the sediments where the presence of gas alone is enough to create fractures (See Stranne et al. 2017 for details).

The CH₄ transport through high-permeability sediments is on average slower than in the low-permeability case, which is reflected by the higher CH₄ gas concentrations developing below the SRZ, and by the gentler slope of the gas front rising up towards the seafloor with time (compare Fig. 76a with Fig. 76e). After about 60 years into the simulation, the vertical CH₄ transport finally overcomes the microbial filter and CH₄ gas is starting to escape from the seafloor (Fig. 76b). The seafloor gas release continues for about 25 years (which is significantly shorter than the low permeability gas release that continues for a period of about 40 years, Fig. 76f). After about 85 years into the simulation the CH₄ supply to the SRZ is smaller than the AOM capacity (imposed by AOM_{max}), leading to a shutdown of seafloor CH₄ gas release and complete oxidation of any CH₄ that is transported into the SRZ. Due to the high permeability, gas continues to flow into the SRZ (although tapering off over time) where it is consumed by AOM. The amount of CH₄ retained within the sediments after 100 years is around 55% (Fig. 65d). Sediments continue to oxidize CH₄ and after 200 years CH₄ retention is only about 35%.

The CH₄ transport rate through mid-permeability sediments is significantly smaller than that through higher and lower permeability sediments, which is illustrated by the high CH₄ gas concentrations building up below the SRZ (Fig. 76c). Much of the CH₄ that ends up in the SRZ is mainly transported there through occasional fracturing. The CH₄ transport through fractures is not fast and large enough for any gaseous or dissolved CH₄ to escape the microbial filter, and the fraction of the produced CH₄ residing within the sediments is about 81% (70%) after 100 (200) years, which is significantly higher than the other cases (Fig. 65d).

The simulations in our base case (Case A4) show that, under some circumstances, sediment permeability and the associated flow dynamics control not only the transport of CH₄ from the dissociation front towards the seafloor (Stranne et al., 2017), but also the amount of CH₄ that escapes AOM within the SRZ. ~~If we define the efficiency of the microbial filter as~~

$$AOM\ efficiency = \left(1 - \frac{(F_{Gas}(t) + F_{Dis}(t))_{Case\ Ax}}{(F_{Gas}(t) + F_{Dis}(t))_{Case\ A1}} \right) \cdot 100\%$$

~~where Case Ax is one of the cases listed in Table 2. In other words, AOM efficiency is the percentage of CH₄ escape in the 'zero AOM' case (Case A1) that is instead oxidized within the SRZ. We see that~~

~~In Case A4, the efficiency of the microbial filter increases from about 45% in low-permeability fracture flow-dominated sediments to 100% in mid-permeability sediments and then decreases towards 80% in high-permeability sediments (Fig. 65e). In absolute terms, this corresponds to a total CH₄ escape after~~

100 years of about 18 kg m^{-2} in sediments with a permeability of 10^{-17} m^2 compared to a total CH_4 escape of around 4 kg m^{-2} in sediments with a permeability of 10^{-14} m^2 - more than a factor of four difference, although part of the difference is associated with fluid flow dynamics within the sediments (Stranne et al., 2017).

5

4. Discussion

While AOM is important for understanding the potential impact of hydrates [dissociation](#) on climate across different time scales (Buffett and Archer, 2004), the strong AOM sink for CH_4 in marine sediments has not been previously assessed with numerical multiphase hydrate models (Ruppel & Kessler, 2017). In this study we have integrated a simplistic but novel and fully coupled AOM module to the T+H-GeoMech code (Stranne et al., 2017) in order to investigate how AOM in marine sediments [affects-modifies](#) seafloor CH_4 release during dissociation of a marine hydrate deposit.

The results presented in Stranne et al. (2017) show that when naturally occurring marine hydrate deposits in low-permeability sediments (clay dominated hemipelagic sediments Fig. 3) are destabilized, transport of CH_4 towards the seafloor is facilitated by the formation of hydraulic fractures. This results in faster flow and ultimately larger fluxes of CH_4 compared to transport through higher permeability sediments (silts and sands). Here we show that, in addition, this type of fracture flow can circumvent the microbial filter more efficiently. The net effect can be substantial. In our base case ($\text{AOM}_{\text{max}} = 10^{-8} \text{ mol cm}^{-3} \text{ day}^{-1}$), the cumulative gas release after 100 years of seafloor warming is around 18 kg m^{-2} in sediments with a permeability of 10^{-17} m^2 , zero in sediments with a permeability of 10^{-15} m^2 and about 4 kg m^{-2} in sediments with a permeability of 10^{-14} m^2 (Fig. [54b](#), e and h). This is in line with previous speculations (Archer et al., 2009; Buffett and Archer, 2004).

With an imposed upper limit of the AOM rate within the SRZ of around $10^{-8} \text{ cm}^{-3} \text{ day}^{-1}$, the model can reproduce the observed relation between AOM efficiency and vertical CH_4 transport (Boetius and Wenzhöfer, 2013; Martens and Val Klump, 1980). For higher AOM capacities ($\text{AOM}_{\text{max}} > 10^{-8} \text{ cm}^{-3} \text{ day}^{-1}$), AOM is sole function of the supply of CH_4 from beneath, and no gas escapes from the sediments. For lower capacities ($\text{AOM}_{\text{max}} < 10^{-8} \text{ cm}^{-3} \text{ day}^{-1}$), on the other hand, the microbial filter efficiency is only marginal.

The efficiency of the microbial filter at some deep-sea cold seeps has been found to be rather limited (down to ~20%, Boetius and Wenzhöfer, 2013). In order to get such low efficiency in our simulations, the maximum bulk AOM rate (AOM_{max}) has to be lower than $10^{-8} \text{ mol cm}^{-3} \text{ day}^{-1}$ (Fig. [65e](#)). This is lower than what is often observed in these geological settings using experimental radiotracer-based methods (Niemann et al., 2006; Treude et al., 2003). There are at least two plausible explanations for this apparent discrepancy (in addition to [slight](#) differences in the definition of AOM efficiency): 1) High

rates of AOM up to $\sim 10^{-3}$ mol cm⁻³ day⁻¹ are observed to be highly localized spanning often no more than a few decimeters in studied sediment cores (e.g. Dale et al., 2010), which means that the average bulk AOM rate integrated over the full SRZ depth might be significantly lower; 2) Deep sea cold seeps might be very different from those forming at the feather-edge of hydrate stability under rapid seafloor warming. [Deep-sea Present day cold](#) seep systems have often been active for longer periods of time, sometimes tens of thousands of years (Berndt et al., 2014; Wallmann et al., 2018) and CH₄ is likely transported through high-permeability channels [known as sub-surface gas chimneys](#) (Giambalvo et al., 2000; Saffer, 2015; Suess, 2010) or faults (Nakajima et al., 2014) through the [MHSZGHSZ](#). Such channeled flow [from the deep geosphere](#) allows for significantly larger CH₄ transport than that through dynamic hydraulic fracturing (as considered in this study) because high permeability channels stay open regardless of the in-situ pore pressure. From the relation between vertical transport of CH₄ and AOM efficiency as found in observations and also presented in this study, a larger CH₄ transport would then also lead to lower AOM efficiencies. During rapid anthropogenic warming-induced hydrate dissociation, however, such high-permeability channels might not exist at the feather-edge of the gas hydrate stability zone. We speculate, therefore, that the resulting flow would [not resemble present day cold seeps where gas is transported through sub-surface gas chimneys or faults, but that it would](#) be more similar to that simulated in the present study, with the CH₄-gas being transported either through elastic and highly dynamic (opening and closing) fractures in low-permeability sediments, or percolating through the porous media in higher permeability sediments.

There are limitations to the modeling approach applied in this study, and the results should be seen as a first step towards understanding AOM dynamics in relation to climate change and hydrate dissociation. One important limitation is that the model code does not consider kinetics i.e. the rate of biogeochemical reactions. This means that the true efficiency of the microbial filter might be lower than reported here. We model AOM as a linear function of the CH₄ supply, with an upper AOM limit imposed by the AOM_{max} parameter. In reality [AOM](#)-microbial communities are dynamic and adapt, not only to the supply of CH₄ from beneath, but also to changes in salinity, temperature and sulfate fluxes (Michaelis et al., 2002; Nauhaus et al., 2007; Treude et al., 2003). Experimental studies show that, for instance, a temperature increase of only 2°C can increase anaerobic organic matter degradation by 40% (Roussel et al., 2015). In diffusive systems, the AOM process has been shown to operate at the thermodynamic limit for cell metabolism (Hoehler and Alperin, 1996), whereas advective systems apparently deliver CH₄ in amounts that allow for abundant cell growth and the development of thick biofilms capable of very high AOM rates (up to 10^{-4} mol cm⁻³ day⁻¹) (Boetius et al., 2000; Nauhaus et al., 2007; Treude et al., 2003). This implies that, while AOM is a highly complex process, the AOM rate within marine sediments is, to a first order, controlled by the CH₄ supply which is consistent with our model assumptions (Fig 1b). We do not know what a realistic value of the maximum bulk AOM capacity could be or what is controlling it, but we note that an AOM_{max} rate of 10^{-8} mol cm⁻³ day⁻¹ reproduces the

observed relation between AOM efficiency and CH₄ transport, at least qualitatively. It is possible that with the inclusion of proper kinetics and additional controls on the AOM process, there would be no need to impose such limitation on the AOM capacity.

5 [Because the largest proportion of the sediment column is anoxic, the most important CH₄ sink in marine sediments globally is AOM \(Knittel & Boetius, 2009\). As a general rule, AOM dominates the CH₄ consumption within the sediments while aerobic oxidation of CH₄ \(AeOM\) dominates the CH₄ consumption within the water column \(Reeburgh, 2007; Valentine, 2011\). AeOM in the benthic layer can, however, also be an important CH₄ sink. It has been shown that at some contemporary cold seeps,](#)
10 [AeOM dominates over AOM \(Boetius & Wenzhöfer, 2013\). In this study we focus on AOM, but as the AOM module does not discriminate between different types of oxidation, the modeled bulk CH₄ oxidation within the SRZ can in a sense be regarded as including all methane oxidation in the presence of sulfate, which thereby extends methane oxidation up to the seafloor where in reality other electron acceptors such as oxygen may oxidize methane.](#)

15 [Another limitation of the present model is the assumption of a static SRZ depth.](#) In reality the SRZ depth is dynamic, with a tendency to increase with decreasing methane flux from below (Borowski et al., 1996; Sivan et al., 2007). As the capacity of the microbial filter to oxidize CH₄ that passes through the SRZ depends on the SRZ depth (Fig. S1b), this tendency could decrease the filter efficiency during rapid
20 dissociation of marine hydrates. Overall, the limitations of our modeling approach (including the lack of kinetics and of a dynamic SRZ depth) suggests that the AOM efficiency reported here can be regarded as an upper limit.

5. Conclusions

25 In general, the modeling results show that the total mass of CH₄ consumed by AOM over time becomes a function of either (1) the supply of CH₄ to the SRZ - when the AOM capacity (imposed by AOM_{max}) is so high that all the CH₄ transported to the SRZ is consumed by AOM or (2) the imposed AOM capacity itself - when the capacity is so low that there is an oversupply of CH₄ to the SRZ, which then also leads to CH₄ escaping the seafloor. In our simulations, the first case is true when AOM_{max} > 10⁻⁸ mol cm⁻³ day⁻¹
30 (efficiency of the microbial filter is 100%) while the second case is true when AOM_{max} < 10⁻⁸ mol cm⁻³ day⁻¹ (AOM is negligible and the CH₄ escape is controlled by the sediment permeability). For values of AOM_{max} in between, on the order of 10⁻⁸ mol cm⁻³ day⁻¹, the AOM efficiency is to a large extent controlled by fluid flow rates (or sediment permeability), which is in line with observations. For example, during low permeability CH₄ flow through fractures, the AOM efficiency (45%) is about half that of
35 high permeability matrix flow (>80%). The combination of larger CH₄ transport and lower AOM efficiency in low permeability sediments (~10⁻¹⁷ m²) results in a seafloor CH₄ release that is more than a factor of four larger than in high permeability sediments (~10⁻¹⁴ m²).

Although AOM in marine sediments is rarely considered when assessing future climate warming-induced seafloor CH₄ release, there is a wealth of articles suggesting that it represents an important component of the marine CH₄ cycle. In this study we can mimic the observed tendency of decreased AOM efficiencies with increased vertical CH₄ transport by imposing a maximum AOM bulk rate within the SRZ of about 10⁻⁸ mol cm⁻³ day⁻¹. We find that the AOM efficiency during fracture dominated flow is less than 50%, and this is likely an overestimate due to limitations in the AOM parameterization. Fracture flow is the predicted mode of methane transport under warming-induced dissociation of hydrates on upper continental slopes and thus, in a scenario with rapidly warming seafloors, more (and possibly significantly more) than half of the CH₄ can escape AOM within the sediments and reach the ocean/atmosphere. These initial results are admittedly poorly constrained and will hopefully be augmented in future studies where kinetics and additional controls on AOM can be implemented. However, because evidences of on-going anthropogenic warming-induced hydrate dissociation are inconclusive (Ruppel & Kessler, 2017) and observational data are still scarce, we have to at least partly rely on numerical hydrate models for the time being.

Code and data availability

All data supporting the figures and text of this manuscript are available upon request from the corresponding author. The model code can be purchased from Berkeley Lab Marketplace (<http://marketplace.lbl.gov>).

Author contributions.

CS conceived the study, developed the model, performed the experiments, made the figures and wrote most of the manuscript. MO, MJ, VB and MK contributed to the text and to the interpretations of the results.

Competing interests.

The authors declare that they have no conflict of interest.

Acknowledgements

Stranne received support from the Swedish Research Council (Vetenskapsrådet, grant numbers: 2014-478 and 2018-04350).

Acknowledgements

Stranne received support from the Swedish Research Council (Vetenskapsrådet, grant numbers: 2014-478 and 2018-04350).

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