

Interactive comment on “A two-dimensional model of the passive coastal margin deep sedimentary carbon and methane cycles” by D. E. Archer et al.

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Dickens comments

Jerry's points 1-7 were largely general comments about the text being too terse, lacking introductory material, too dense, and insufficiently referenced. The only reply we can make to a general comment will also be general, which is that we'll have another go through the manuscript and flesh it out better. He offers many editorial suggestions, which we intend in general to take, as modified or described in our comments here. We also comment here to defend the work or answer any questions that the reviewer posed. We intend to act on editorial suggestions from either reviewer which we pass without comment here.

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The only specifics Dickens offers however in his first section of 7 points have to do with two specific paragraphs, which are indeed dense and can be clarified. He makes allusions to problems with the modeling itself, but no specifics in the first section, so we'll deal with those as they come up later. The substantive geochemical problems he mentions here and expands on later on in this comment and subsequent ones have all been resolved, as we'll get to.

Figure 1 and the geothermal temperature gradient. All of the simulations have been redone with a higher geothermal heat flux, and the model sensitivity to the heat flux has been characterized also as a part of the sensitivity runs.

Figure 3. The model runs have been expanded to 200 Myr duration now, as opposed to 140 Myr in the original manuscript.

Figure 5. A porosity of 200% means that more gas is produced than even the pore volume could hold. In reality this would lead to expansion of the total volume and pore fluid flow driven by the excess pressure. These effects are not included in the model, so the absurdity of a 200% pore volume methane content merely indicates that there is too much methane gas produced, some of it must escape.

Figure 6. The permeable pathways cannot be represented in more detail than the resolution of the model supports. Although some sediment seismic “wipeout zones” are indeed many kilometers wide, other channels could be mere meters wide. The physics are clearly not representable mechanistically or in detail, either in the horizontal scale or in terms of the relative flow volumes or velocities. The scheme as implemented in the code is to represent qualitatively (for that is the best we can do for now) the effect of heterogeneity in flow on the geochemical tracers and processes. Our results show that the impacts on hydrate distributions and tracers like 129-I are indeed significant. A more faithful representation of this phenomenon or mechanism is simply beyond what we are able to do now. At least this model is a step forward from the 1-D models, which neglect or sidestep this effect entirely.

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Figure 7. The downward flow in between the chimneys is due to sedimentation uncompensated for by upward vertical flow. This will be explained more clearly.

Figure 9. The labels will be fixed. The deposition history is intended to represent a reasonable range of natural variability, rather than trying to mimic a particular section exactly. The range of natural variability will be documented more clearly in the text.

Figure 10. The units are moles of methane per meter cubed per time, and they will be labeled (redrafted figures with clearer labels have already been posted to my web server). These are snapshots.

Figure 11. The methane concentration subsurface is indeed different from the source flux distribution, because the CH₄ concentration in the model “fills up” to bubble saturation, then loses CH₄ until the saturation really controls the distribution of concentrations. The geophysics of bubble formation and transport are not mechanistically accurate in the code, however, so the supersaturations evident in some parts of the sediment column are model dependent and not a robust prediction of the model. We could add a snapshot mid-way through the simulation as suggested but the animations also show the evolution of the methane concentration field through time.

Figure 12. It is true that methane hydrate itself is poorly resolved in these simulations. The plot domains can be expanded to show this better.

Figure 13 has been completely redone as shown in my last reply to Dickens. The reviewer and I had a lot of back-and-forth on the question of the DIC concentration in the model and its implication or lack thereof for methane production rates. Figure 13, revised now shows DIC profiles from a suite of sensitivity studies varying the rate constant for DIC uptake by a weathering reaction. I think Dickens is satisfied that the DIC inventory of the pore water doesn't say anything substantive about the methane production rates in the model, only that they are sufficient to explain the DIC concentration. The new figure also adds data from other sites, including as Dickens suggests alkalinity data as a proxy for DIC concentration.

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Figure 14. The model lacks the resolution to reproduce the negative spike in DIC in the near subsurface, but to increase the resolution at this point is beyond the scope of what we can do. The model takes about a week to run as it is, and increasing the vertical resolution just slows it down more. The processes cited by the reviewer are included in the model, including AOM and sulfate respiration (which produces DIC without methane, leaving the DIC isotopically light). I have no doubt that detailed studies and simulations of pore water chemistry such as the one cited by the reviewer, and others by Burdige and Wallmann, can say more than I can with this larger-scale model about the details of reaction rates in the sediment column. However, the large-scale model also brings constraints to bear on the problem, so it is a step forward even at the cost of vertical resolution near the sediment surface, the domain that has already been modeled before at higher resolution than we are able to afford. However, we don't believe there is any “serious mass-balance problem” in the model.

“Basically, the upward fluxes of methane and DIC are considerably off target. Possibilities include that too little methane is accumulating and escaping over time, too much DIC is accumulating and escaping over time, or some combination of both. Alternatively, too much POC is being consumed by sulfate reduction in shallow sediment.”

As has been stated, the concentrations of DIC and CH₄ are uncoupled by CO₂ uptake by the Urey reaction. The production ratio of DIC versus CH₄ is constrained by the $\delta^{13}\text{C}$ of the DIC, but the overall respiration rates are difficult to constrain as closely as would be necessary to be able to predict hydrate inventories a priori. So it would be permissible within the constraints of what we know about deep sedimentary respiration rates (which is not really very much) to increase the source fluxes of both methane and DIC, and the hydrate inventory would then increase markedly. But I don't see any indication that there is a systematic mismatch with data in one direction or the other.

Figure 15. The dissolved iodine concentrations, both stable and radioactive, are indeed being tracked as they flow in the simulation. This will be clarified.

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Figure 16. Moles per meter of coastline. This will be clarified. However, a mole is a mole, so it's both moles of CH₄, and moles of C, whichever you like.

"The systems are open; organic carbon degrades along a geotherm in rapidly accumulating sediment (Burdige, EPSL, 2011; Gu et al., Nat. Geosci., 2011), in striking contrast to way most geochemical studies model early diagenesis (e.g., Middleburg, GCA, 1989); AOM dominates net sulfate consumption in shallow sediment deposited with high organic carbon at low seafloor temperatures (e.g., Chatterjee et al., JGR, 2011). These notions remain heresy in many geochemical circles, although the current manuscript seems to accept them, at least partly, carte blanche with no discussion or reference."

"Is this the classical "Berner" sequence of microbially-mediated reactions in shallow sediment that omits AOM, or a modified sequence with upward transport of methane through open systems with AOM?"

The model does have the process of AOM consuming sulfate. We weren't aware we were being heretical. As stated above the grid resolution is poor enough that the sulfate / methane systematics are not well resolved however, so I wouldn't trust the diffusive gradients to regulate and partition the geochemistry as well as a better-resolved model would.

"Section 3.2 also lacks context with the current Introduction and ensuing text. Basically, why would the manuscript present and discuss changes in gas hydrate across a margin depending on ocean temperature? Of course, there is a very good reason: a series of papers (none referenced) have discussed the issue and its complexities."

On the temperature dependence of the hydrate inventory. As I wrote in the reply to this comment, there was a bug in the code with respect to the deep sea temperature imposed that has now been fixed. Dickens is very interested, both in this review and in the review to the companion paper, in promoting hydrate as the source of the carbon isotopic excursion of the PETM. The bug in the code made it seem more plausible,

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because the POC dependence of the model hydrate inventory seemed to completely overwhelm the temperature dependence, so that a warm POC-rich Paleocene ocean could have had lots of hydrate to melt down. The fixed model result reduces the amount of hydrate the Paleocene ocean would have had according to the model.

This model result doesn't by itself spell doom for hydrate as the culprit for the PETM, because hydrate could have been formed in the Arctic, which was cooler than the global average. However I personally don't believe in hydrates as the source because of the isotopic mass balance, as explained in the Pagani et al paper which Dickens references in his review of the companion paper. Dickens wants to evade that isotopic constraint by saying that the warming (driving oxygen-18) was independent, not due to the greenhouse forcing of the carbon. I don't buy that because of the similarity in recovery trajectory of the carbon and oxygen isotopes.

However, the bottom line is: the question of the source of the isotope excursion of the PETM is simply not what this paper is about. We don't want to expand the discussion of the text into this topic, since the text has enough information it has to convey without taking on this tangential issue.

Page 2928 "So, how do changes in sea level affect sedimentation?" by affecting the deposition or non-deposition of the different sediment grain sizes. The grains only deposit when the "turbulence" (an inverse function of water depth) is low enough for the settling speed (a function of grain size) to power its way through. As to sea level vs. rate of change in sea level, I don't really have the model results to address this question.

Page 2931 "Presumably, the implied link is that times of high sea level are times of greater Earth surface temperature, which affects the solubility of oxygen and leads to enhanced organic carbon burial on the slope. I appreciate the concept, but it is, by no means, widely accepted"

"One means: divorce temperature and sea level; they are good friends but not married."

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The time-independent runs can be used to assess the relative impacts of temperature and POC rain. It never occurred to me to do a sensitivity study for sea level alone, because a constant sea level at a different elevation would just drive the sediment column to accumulate into the higher accommodation space, leaving probably a similar actual distribution of water depths in the evolving simulation regardless of the sea level altitude. Deconvolving sea level and temperature would therefore require an altered time-trajectory simulation, which given the complexity to interpret and the large numbers of simulations already given in the paper, we are reluctant to do.

“how does one suggest that organic carbon reactivity increases down the geotherm when this goes against convention (e.g., Middelberg, GCA, 1989)?”

It is well accepted that biologically-mediated chemical reactions in the environment go faster as temperatures rise from near freezing to 30 or 40 degrees C. This is the effect of temperature with everything else including the reactivity of the carbon held constant. We take this temperature dependence as a multiplier of a calculated rate constant. However, Middelberg shows an even stronger effect, which is a correlation between the rate constant and the age of the carbon. Old stuff decomposes more slowly than young stuff. Presumably warm old stuff would decompose more quickly than cold old stuff. So the reactivity of carbon in the model is calculated from the age, modulated somewhat by the temperature.

“Why does gas need to escape the sediment column rather than forming gas hydrate?”

Gas needs to escape the sediment column below the stability zone boundary. It is indeed helpful to capture some of it in the stability zone, as indicated by the sensitivity studies to the bubble redissolution scale height parameter.

“I would remove the iodine cycle from manuscript because it neither enhances nor detracts from current discussion. It remains a puzzle, and not one solved in the present manuscript.”

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We have shown that heterogeneity in the pore fluid flow is capable of generating very old iodine ages. This is in contrast to the published interpretation that the age of the organic carbon that degrades controls the age of the dissolved iodine. This hypothesis has bearing on interpreting other geochemical signatures of pore fluids retrieved from Blake Ridge and other hydrate-bearing areas. The chemistry of Blake Ridge seems to be better represented by the upward-focused permeable channels of the model. Maybe this result is too boring for the reviewer to bother publishing, but we feel it is one of the major results of the paper.

“– Page 2942 – Lines 1-3: This is not correct as written. Unless I am mistaking things, a problem with the Buffett and Archer (2004) model was that microbial degradation down the geotherm was not considered. I also suspect that AOM was not properly modeled.”

The lines 1-3 must refer to the sentence in the original manuscript “This [increasing the diffusive loss of dissolved methane by making the stability zone thinner by warming the ocean] had the impact of restricting the formation of hydrate to regions of higher POC content, reducing the ocean’s ultimate equilibrium inventory of methane nearly completely with 3 C of warming.” We don’t know what Dickens thinks is incorrect with that sentence; we are describing what that model did, so even if one doesn’t like the model, the sentence is not incorrect. About the model, there was in fact deep biological production of CH₄ and AOM. Achieving nearly linear profiles of SO₄ and CH₄ requires keeping respiration rates near the depth of the methane / sulfate boundary weirdly low, actually, with a surge of methane production down deep, presumably driven by temperature, but it has to be a strong temperature dependence, as Burdidge has found. Bottom line is I can offer rewrite for clarity but we defend the substance of what was written.

Subsequent Dickens comments concerned the question of pore-water DIC concentrations, which I believe are now resolved as described under changes to Figure 13, above.

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Anonymous reviewer #2

However, the authors should clearly show how their model approach differs from existing basin models.

“The model description is incomplete and scattered. Essential key information on model formulation, parametrisation, numerical solution and model performance are not provided.”

Our goal and intent is to provide enough information so that someone else could in principle reproduce our results. I can think of a few examples of things that were not detailed in the paper, such as the mathematics of the sediment deposition scheme. The formulation was described, but the details of the constants etc. were not given. This was because sedimentation is a driver for the model, and all that matters from it is the shape of the sediment column that results, the sedimentation rates, and the grain sizes, all of which were shown. The solubility equation for methane was not given, but the resulting methane concentration field was shown. Enough, in both cases, to assess the significance of the model results. The code is 12,000 lines long; it will be impossible to document everything in a human-readable publication.

We don't think the manuscript is scattered, and are not sure what the reviewer is referring to here. The model is described from sedimentation to the geophysics of fluid flow to geochemistry. Comparisons with data are necessary throughout the description of the model formulation, and often the question arises when describing some poorly-constrained model parameter, what the sensitivity of the model would be to that parameter, so we've included some reference to model sensitivity results in the formulation section.

“I would suggest to restructure the two manuscripts. A first manuscript could provide a comprehensive model description and a critical discussion of the baseline simulations in particular with respect to observational data. More technical journals, such as, for instance, *Geoscientific Model Development* or *Computers Geosciences* provide ideal

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platforms for such a manuscript. The extensive and very interesting sensitivity study for both active and passive margins could be then be outlined in a second manuscript that simply refers to the detailed technical description in the first manuscript.”

We chose to present the material as we did because the science itself is bound up in the formulation of the model. The question is, what does the model formulation require in order to reproduce the observed world we see today? It's not really desirable to bundle off the computational part into a “black box” journal. Comparison with reality is involved for making the decisions that determine the model formulation, so it's not really ideal to break off the discussion of the formulation from a “results” section, let alone break the effort into two papers in that way.

Interactive comment on *Biogeosciences Discuss.*, 9, 2921, 2012.

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