

## ***Interactive comment on “A model of the methane cycle, permafrost, and hydrology of the Siberian continental margin” by D. Archer***

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### Methane hydrate stability in the permafrost zone

One of the strongest and least speculative conclusions of this paper is that methane hydrate is thermodynamically unstable in most of the permafrost zone in the upper sediment column, and will therefore not accumulate or be found there. Shakhova cited soil at temperatures of  $-17^{\circ}\text{C}$ , which is below the freezing temperature for hydrate if salinity is 35 PSU (as assumed by [Romanovskii et al., 2005]), claiming that these sediments are clearly within the hydrate stability zone. I believe this claim is incorrect.

The thermodynamics are illustrated in a phase diagram for ice and hydrate, using salt as a master variable. This figure will be the new Figure 1 in the revised paper. When

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the system consists only of ice and fluid phases, the equilibrium salinity  $\text{Seq}$  increases with decreasing temperature below freezing (Figure 1a, left). Above the melting temperature, ice is unstable, as indicated by the nonzero values of the disequilibrium temperature,  $\Delta\text{Teq}$ ,  $\text{ice} = T - \text{Teq, ice}$ , in contours, even in zero-salinity water (right). For a system consisting of only the hydrate and fluid phases (assuming that ice formation is disallowed, and also assuming gas saturation for methane) (Figure 1b), the behavior is similar but with an added pressure dependence due to the compressibility of the gas phase. When both solid phases are allowed, the overall equilibrium salinity will whichever is higher between  $\text{Seq}$ , ice and  $\text{Seq}$  hydrate. Whichever phase can seize water at its lowest activity (from fluid of the highest salinity) will be the stable phase. The salinity of the brine excluded from that phase will be too high to permit the existence of the other solid phase at that temperature. The contours show  $\Delta\text{Teq}$  for hydrate (solid) and ice (dashed).

Figure 1d shows  $\Delta\text{Teq}$ , hydrate in colors and contours of the excess salinity relative to hydrate equilibrium,  $\text{Smax} - \text{Seq, hydrate}$ . Hydrate is only stable when  $\Delta\text{Teq, hydrate}$  is zero (purple color). Under permafrost conditions of low pressure and low temperature (upper left corner),  $\Delta\text{Teq, hydrate}$  is greater than zero, indicating that hydrate is unstable, coinciding with the salinity forcing from the ice, in overlaid contours. A similar exclusion of ice in part of the hydrate stability zone is seen Figure 1e, but this would only happen in nature in conditions of unlimited methane. The resulting phase diagram for ice and methane hydrate is shown in Figure 1f. Hydrate stability is suppressed in the permafrost zone by this thermodynamic mechanism. I have done a sensitivity study in which pure-H<sub>2</sub>O ice is forbidden to form, which has the effect of allowing the hydrate stability zone to outcrop near the sediment surface, briefly, during the coldest times in the glacial cycle (Figure 2b). This altered-physics simulation, even though indefensible, does not generate a large transient methane emission spike in response to a global warming forcing. This is because the sediment column has already been subjected to the extreme temperature change of inundation by rising sea level. The stability zone boundary quickly retreated downward when that happened. A temperature anomaly

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from global warming has to diffuse hundreds of meters into the sediment column, to catch up to and accelerate that retreating hydrate stability boundary.

#### Sensitivity studies

Many of the reviewers' comments can be addressed by doing model sensitivity studies, which I have now done. I am attaching expanded figures from the manuscript, and a table describing 17 new model sensitivity simulations. A web page server for movies from the model has been updated to include 68 new sensitivity study movies, at <http://geosci.uchicago.edu/archer/spongebob>. Reviewer Nicolsky called for these most directly, but questions about uncertainties in initial salinity, geothermal temperature gradient, rates of hydrological flow, and permafrost impact on gas mobility, can also be addressed by showing the model sensitivity to the parameter in question. Simulations of the glacial cycles and global warming forcings have been done for the parameters summarized below: Biogenic and thermogenic methane production rates. The model brings no real constraint to the rates of methane production, since the sediment accumulation history etc. are not well-constrained. See the discussion on the initial condition to the glacial simulations, next. New sensitivity runs were done scaling the biogenic and thermogenic methane production rates by arbitrary values, to see the impact on the methane cycle in the model. Increasing production increased the release rate to the atmosphere, but in all cases the release was modulated in time through the glacial cycles by inhibition of gas flow by permafrost during low sea-level, and by inundation in the ocean during high sea level. Deposition of high-POC soils on land (Yedoma) increased the methane flux to the atmosphere but had only a small impact on the abundance of methane hydrate.

Permafrost inhibition of gas migration. It turns out that changing the critical ice fraction at which to shut down methane gas mobility has a large impact on the glacial cycles of methane fluxes to the atmosphere, indicating a need for more attention to be paid to this question.

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Geothermal temperature gradient. Changes in the temperature gradient with depth in the sediment column alter the depth of the base of the hydrate stability zone. The top of the zone remains unchanged, because surface sediment temperatures are less affected by the change in heat flux, anchored as they to ocean temperatures. Flow. Runs were done including the vertical permeable channels (at the request of review 1), and excluding horizontal flow. Neither of these changes affects the model behavior or main conclusions in a fundamental or significant way.

#### Glacial cycle simulation initial condition

Tumskoy was offended at the over-simplicity of the spinup simulation used to generate the initial condition for the glacial simulations. The more usual approach in modeling hydrates is to start with an ad-hoc initial condition (for example, [Reagan, 2008; Reagan and Moridis, 2009; Reagan et al., 2011]). For SpongeBOB the model state at any time is the result of the time history of sedimentation, which is driven by the time-evolving depth of the sea floor, and interacting with isostatic adjustment of the crust. The simplest way to generate an initial condition in the model without a startup transient is to spin the model up at low resolution. Because of the over-simplicity of the tectonic, sea level, and sedimentation forcing of the spinup phase, its POC concentrations and methane production rates do not constrain those of the real shelf. The sensitivity of the glacial methane cycles to these uncertain methane production rates is evaluated by scaling the model methanogenesis rates from the spinup result. I would clarify this in the text, and I hope that the sensitivity studies will make this point more concretely as well.

#### Prior literature on hydrology and the fresh / salt water boundary

Reviewer 1 wondered if the ratcheting effect of the fresh-water pump described in my results had been modeled before. I found some hydrological models of the salt / fresh boundary as it changes with sea level change [Kooi et al., 2000; Lu and Werner, 2013; Watson et al., 2010]. These all share the result that freshening is much faster than

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getting saltier, although these were applied to systems of much smaller space ( 10 meters depth) and time ( century) scales than I addressed. These models included mechanisms for salt fingering, which reviewer Nicolsky pointed out is lacking in my code. Since salt fingering is a diffusive mechanism while hydrological flow is advective, salt fingering should get even less important as the size and time scale for the domain increases.

#### cean temperature boundary condition

Tumskoy questioned the validity of the temperature changes in the ocean through the glacial cycles. The model assumed uniform water column temperatures ranging from +1 to  $-2^{\circ}\text{C}$ . For the region of interest, the continental shelf in shallow water, this forcing was incorrect, given that overlying waters are still near freezing today, during an interglacial. All of the new model glacial cycle runs are done with a more realistic thermal boundary condition, with temperature changes at depth in the water column (below about 200 meters) as before, but waters in the top 100 meters pegged at  $-1.5^{\circ}\text{C}$  until the global warming scenario begins.

#### Glacial / interglacial atmospheric methane fluxes.

Shakhova claims that the higher methane concentration in the interglacial atmosphere is proof that emission from the Arctic could not have been greater during glacial time. However, the Arctic is, then as now, a small part of the global atmospheric methane budget, so one cannot constrain Arctic emissions from the global concentrations recorded in ice cores.

#### Sub-grid scale flows

Tumskoy called the response time of the model to a sea level change "absurd", but I don't know of modeling results or measurements on which to base that claim. Permeabilities of the deep sediment column are poorly constrained, and not very important to the major conclusions of the paper. He also claims that I ignore the literature on

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hydrological flow in permafrost. Flow in my model is attenuated by ice, although it was not stated as clearly as it could have been, so perhaps it was missed. It is not completely impeded, so that flow through taliks and faults can still in principle be accounted for as sub-grid scale process, the way clouds are done in climate models. Flow in the model is not well constrained or accurate, but it turns out not to matter to the main conclusions of the paper, according to a new sensitivity study in which horizontal flow is disabled. Although offshore flow carrying methane appears to be an important flux in the methane budget, this sensitivity run only had subtle impacts on the other components of the budget (Figure 3).

#### Application to a large-scale abrupt methane release due to global warming.

The proposal from Shakhova is that methane has been building up as bubbles, sealed by permafrost, which is now unsealing, and perhaps as methane hydrate in shallow sediments, which is now melting, to deliver, on a time scale of a few years, about 50 Gton of methane to the atmosphere. For a transient gas in the atmosphere like methane, it makes a huge difference if it is released in a few years, or a few hundred years. I don't doubt the possibility of mobilizing 50 Gton of methane eventually, only the fast time constant (which is required to get a strong methane-driven climate impact).

Methane hydrate thermodynamic instability in the permafrost zone has already been discussed. Thermodynamics does not control everything, especially at low temperature, but kinetic inhibitions are more often found for nucleation steps rather than decomposition. To find an accumulation of "metastable" hydrate would also require some sort of transport mechanism of hydrate into the region where it's unstable, which does not exist. There is no reason to imagine that hydrate could form in situ when thermodynamic conditions are wrong for it. A kinetic inhibition of water-ice formation would work, but ice doesn't super-cool in a dirty, nucleation-site-rich environment like sediments. Thus hydrates, buried under hundreds of meters of sediment, seem like an unlikely source of an abrupt methane release event.

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The model actually does produce a glacial cycle in bubble inventory, with changes exceeding 50 Gton over a cycle, apparently driven by methane exclusion from ice formation (Figure 4). But the model does not deliver an abrupt release in response to anthropogenic warming for any of its sensitivity studies (Figure 5). One reason why not is that the time scale for a response to anthropogenic forcing is very slow. Permafrost melting has already been going on for thousands of years. In this span of time a temperature anomaly has diffused quite deep into the sediment column. In order for the abrupt temperature anomaly of global warming to further accelerate the ongoing ice or hydrate melting, it will have to diffuse down in the sediment column to where the ice still is. We would get a larger response to global warming if the transition from glacial to global warming sediment surface temperatures hadn't mostly happened thousands of years ago.

Second, a change in the bubble inventory does not necessarily translate to a flux to the atmosphere. Much of the increase in bubble inventory during sea level fall in the model appears driven by methane rejection from forming ice. When the ice melts, much of the methane redissolves.

Shakhova and Tumskoy argue that geological features such as faults and permeable layers dominate the methane cycle in the sediments. A continuum model would predict a smooth methane release response to a warming, growing in on some e-folding time-scale. A world dominated by features that each represent a small fraction of the total methane reservoir will release methane more episodically, but the statistical distribution of the response in time should still show the e-folding time scale of the underlying driving mechanism, the diffusion of heat into the sediment column. The only way I can see to deliver 50 Gton of methane to the atmosphere is for it all to be released from a single geologic feature pent up by ice. Given global traditional natural gas reserves of about 100 Gtons, this seems to me like a large bubble.

## Summary

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A revised manuscript will be significantly improved in response to the reviewers' questions and comments. Most particularly, the new sensitivity studies make it easier to relate the model results to the real world, given the many significant uncertainties involved, and to identify which uncertainties are most problematic, and which have negligible impacts. In addition to the substantive changes described above, there are many editorial suggestions in the reviews which I have already incorporated into a revised manuscript. I have also cleaned up the naming of the movie files in the supplemental material and on my web page server, to correspond more clearly to the figures in the manuscript.

Table 1. Summary of model runs.

SL Sea level changes with constant air and water temperatures

GL SL + glacial cycles in air and water temperature

GW A long-term global warming scenario, a peak and long tail temperature perturbation consistent with CO<sub>2</sub> release and cessation of the glacial sawtooth forcing.

+SLR Adds geologic-timescale sea level rise due to anthropogenic climate change, based on correlation between temperature and sea level in the geologic past (10 meters / °C).

Ctl An extended interglacial with no CO<sub>2</sub> release forcing.

+ LD Land deposition of carbon-rich Yedoma. Base case is 10 m / 100 kyr, with sensitivity runs using 30 and 100 m / 100 kyr accumulation of 30

+ TG Thermogenic methane production rate sensitivity runs, scaling the rate from the spinup result by factors of 10 and 100. Movies in the supplemental material are identified by the tags TGenX10 and TGenX100.

+ Geotherm Sensitivity of ice and hydrate cycles on the geothermal temperature gradient. Temperatures from the Base simulation were adjusted when calculating the

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stability of ice and hydrate, to simulate the impact of geothermal heat fluxes on hydrate stability. Note that other aspects of the sediment column, including the solubility of methane, retained the original temperatures. Heat fluxes simulated include 25 mW/m<sup>2</sup>, 37.5, 50 (Base), 62.5, and 75. Movies of the non-base runs are identified by tags HF050, HF075, HF125, and HF150.

**Ice and Bubble Transport** When the ice fraction exceeds a threshold value methane gas flow is disabled. Base case is 50

**No Ice** The ice phase is disallowed in the thermodynamic calculation. Movies in the supplemental material include salinity. The files are tagged as Nolce

**No Salt from Ice** Ice is allowed to form, but it does not affect the salinity as it determines methane hydrate stability. Movie files are tagged as NoSalFromIce.

**Permeable Channels** Increasing vertical permeability by a factor of 10 every 5th grid cell, to generate heterogeneity in the flow. Tagged as PermChan

**No Horizontal Flow** Horizontal flow is disabled. Tagged as NoHFlow.

Movies comparing altered scenario runs with the Base scenario are given in the supplemental material, and at [http://geosci.uchicago.edu/ archer/spongebob/](http://geosci.uchicago.edu/archer/spongebob/).

Kooi, H., J. Groen, and A. Leijnse, Modes of seawater intrusion during transgressions, *Water Resources Res.*, 36 (12), 3581-3589, 2000. Lu, C., and A.D. Werner, Timescales of seawater intrusion and retreat, *Advances in Water Resources*, 59, 39-51, 2013. Reagan, M.T., Dynamic response of oceanic hydrate deposits to ocean temperature change, *Journal of Geophysical Research-Oceans*, 113 (C12), 2008. Reagan, M.T., and G.J. Moridis, Large-scale simulation of methane hydrate dissociation along the West Spitsbergen Margin, *Geophysical Research Letters*, 36, 2009. Reagan, M.T., G.J. Moridis, S.M. Elliott, and M. Maltrud, Contribution of oceanic gas hydrate dissociation to the formation of Arctic Ocean methane plumes, *Journal of Geophysical Research-Oceans*, 116, 2011. Romanovskii, N.N., H.W. Hubberten, A.V. Gavrilov, A.A. Eliseeva,

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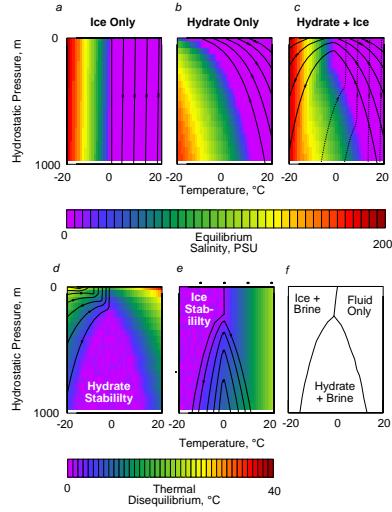
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and G.S. Tipenko, Offshore permafrost and gas hydrate stability zone on the shelf of East Siberian Seas, *Geo-Marine Letters*, 25 (2-3), 167-182, 2005. Watson, T.A., A.D. Werner, and C.T. Simmons, Transience of seawater intrusion in response to sea level rise, *Water Resources Res.*, 40 (W12533), doi:10.1029/2010WR009564, 2010.

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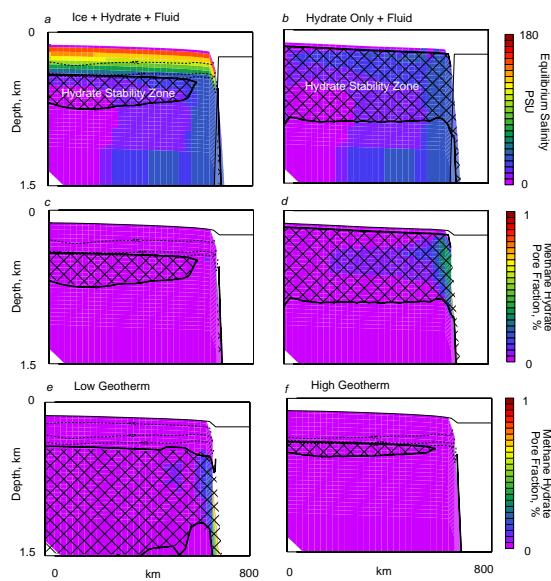
Interactive comment on *Biogeosciences Discuss.*, 11, 7853, 2014.

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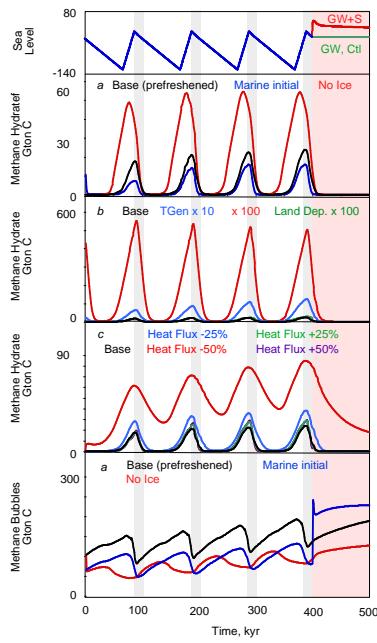
**Fig. 1.** Thermodynamics of hydrate and ice. Top) Colors are salinities, which range from fresh if there is no solid phase, to saltier as the freezing point depression of the solid phase follows the in situ temperature.

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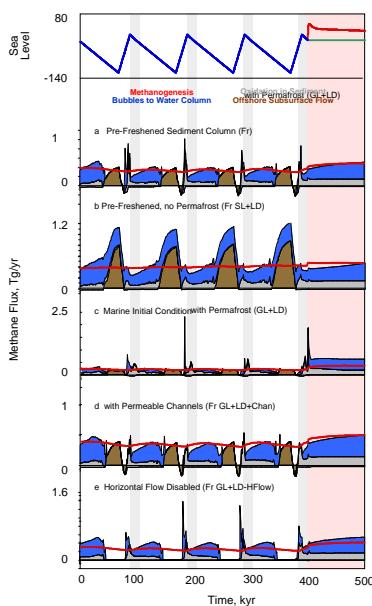
**Fig. 2.** Sensitivities of the hydrate stability zone. Impact of the competition between ice and hydrate phases (a-d), and the geothermal temperature gradient (e-f). When ice is included as a potential solid

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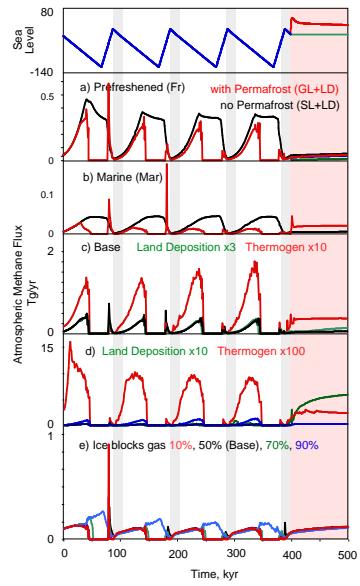
**Fig. 3.** Glacial cycle of methane hydrate inventory on the continental shelf. a) Effects of salt and ice. b) Sensitivity to methaneogenesis rates. c) Sensitivity to the column temperature gradient. d) Glac

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**Fig. 4.** Glacial / interglacial cycle of methane fluxes on the continental margin of the model. Sea level at top, grey regions indicate interglacial intervals, pink the Anthropocene. a-e) Cumulative methane f

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**Fig. 5.** Methane fluxes to the atmosphere. Sea level at the top, interglacial intervals in vertical grey bars, the Anthropocene in pink. a) From a pre-freshened initial condition, with and without permafrost

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