The Response of Marine Clathrates to Climate Change: Beyond the "Clathrate Gun"

Understanding Subsurface, Ocean, and Atmospheric Processes to Assess Climate Consequences

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DOE Methane Hydrates Program-NETL
OBER-IMPACTS
LBNL Laboratory-Directed Research and Development

Introduction and Purpose

Questions that need to be answered quantitatively:

1. Could rising water temperatures affect methane hydrates?
2. What controls the fate of the methane?
3. How much hydrate carbon could reach the atmosphere? At what rate?
4. Should we worry about rapid release and rapid feedbacks?

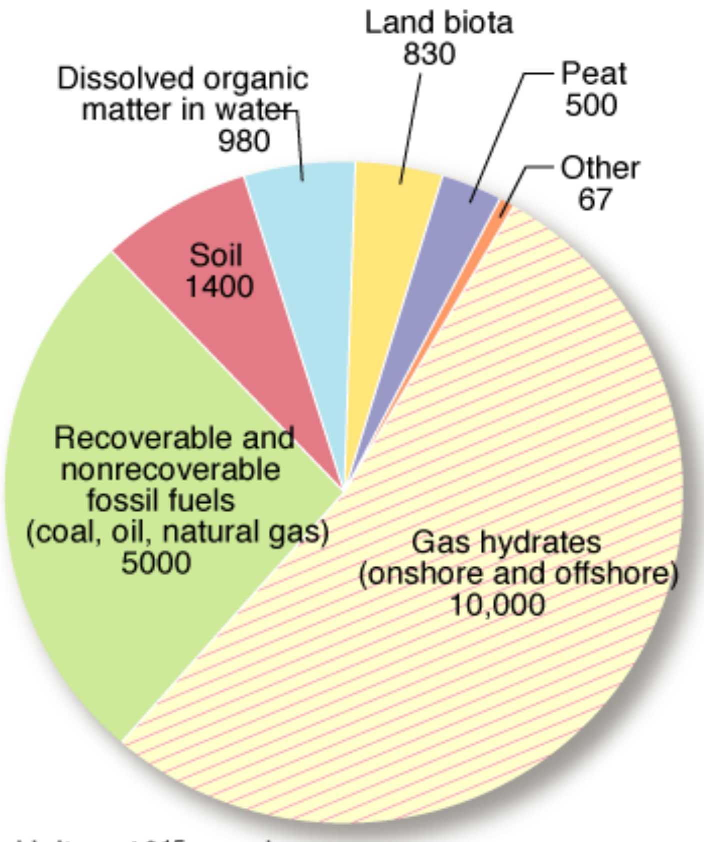
Global Organic Carbon Distribution + Gas Hydrates

- Hydrates store huge amounts of methane
- Huge deposits in permafrost and in the oceans (oceans >> permafrost)

- Potential energy resource
    - DOE Methane Hydrates Program
    - High-saturation oceanic & permafrost hydrates can be produced with current technology
    - Oil companies are interested
    - Sophisticated reservoir models have been developed

- "Consensus value" (10KGt) developed in the 90's (Gornitz & Fung, Kvenvolden)
- Recent studies suggest higher and lower values are possible
    - Sandler (2005): 74,000 Gt (74,000,000 Tg)
    - Archer, Milkov, Wallmann: <5,000 Gt (5,000,000 Tg)

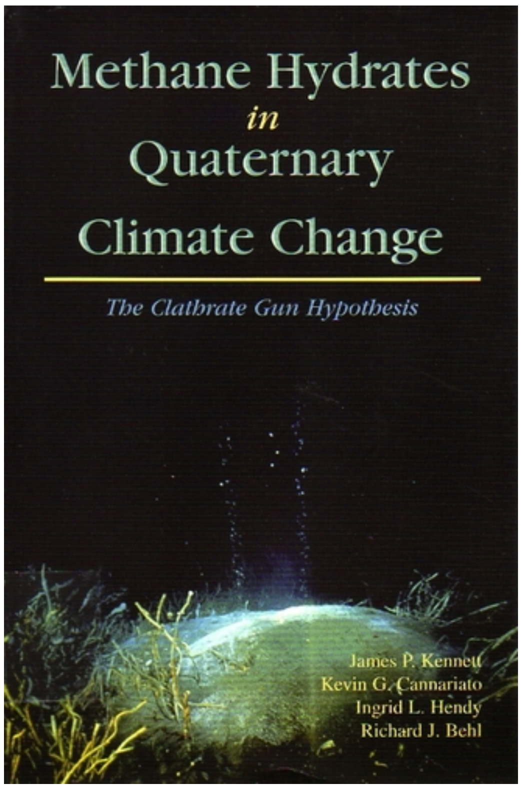
- Huge potential climate forcing, if unstable under warming conditions (in Gt (1,000 Tg) quantities)



Units = 10^{15} g carbon

Global Organic Carbon Distribution + Gas Hydrates

- "Clathrate Gun" Hypothesis and related disaster scenarios
- The quality varies



Methane-driven oceanic eruptions and mass extinctions

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ABSTRACT

Focusing on the Permian-Triassic boundary, ca. 251 Ma, I explore the possibility that mass extinction can be caused by an extremely fast, explosive release of dissolved methane (and other dissolved gases such as carbon dioxide and hydrogen sulfide) that accumulated in the oceanic water masses prone to stagnation and anoxia (e.g., in silled basins). The mechanism of the explosive release is the same as in the Lake Nyos disaster of 1986, i.e., a water-column eruption caused by the interplay of buoyancy forces and exsolution of dissolved gas. The eruption brings to the surface deep anoxic waters that cause extinctions in the marine realm. Terrestrial extinctions are caused by explosions and conflagrations that follow the massive release of methane (the air-methane mixture is explosive at methane concentrations between 5% and 15%) and by the eruption-triggered floods. This scenario accounts well for the available data, and may be relevant to other phenomena.

Keywords: mass extinctions, methane, Permian-Triassic boundary.

INTRODUCTION

The history of life is punctuated by mass extinctions, but their causes remain obscure. Still missing is a satisfactory answer to the question posed by Raup (1991, p. 195), "Did we choose a safe planet?" Extraterrestrial causes have attracted the most attention, but "there is no reason why all catastrophes on Earth should have been induced by bolide impact. As yet we know too little about the workings of our planet to dismiss Earth-induced catastrophes" (Hallam and Wignall, 1997, p. 242). Here I explore one possible mechanism of the latter: oceanic eruption, driven by exsolution of methane dissolved in the water column.

METHANE IN THE OCEAN WATER COLUMN

Methane, CH_4, is continuously produced beneath the ocean floor. Most of this methane is consumed by archaea and bacteria in the upper layer of sediments; the rest escapes into the overlying water column as bubbles. (For present purposes, it is immaterial whether some part of this methane flux results from dissociation of methane hydrates.) The rising bubbles diminish in size and finally disappear as methane dissolves in the seawater (Hovland et al., 1993). In a well-oxygenated (or anoxic but sulfate rich) water column, dissolved methane, as well as the sinking organic matter from the surface waters, is oxidized by microbes. But unlike the rising bubbles of methane or the sinking particles of organic matter, which can traverse the entire water column in a few days, oxygen molecules or sulfate ions can be delivered to the water column only by fluid flow (or diffusion, which is very slow). In stagnant water masses, therefore, the oxidation potential of the water column will be eventually overwhelmed by the flux of sinking organic matter, plus the flux of methane bubbles from the seafloor. There is strong evidence in the geological record that dissolved methane may escape oxidation in the water column (Thomas et al., 2002). Under such conditions, methane that dissolves in the water column will accumulate in it as time proceeds.

Evidence of such accumulation exists both in direct measurements and in the geological record. The only long-term series of the former, in the Cariaco Basin, shows that methane concentration in the deep waters of the basin is increasing with time, roughly linearly (Figs. 6d and 7 of Scranton et al., 2001). The microfossil carbon isotope data from the Santa Barbara Basin sediment core show that high levels of dissolved methane were present periodically in the water column (Kennett et al., 2000). This has been confirmed by a microbial-biomarker study (Hinrichs et al., 2003), and is likely to be representative of oceanic regions prone to stagnation and anoxia, such as silled basins or deep-water masses isolated by topography and Taylor columns[1]. (Such regions are likely to have sizes below the resolution of ocean circulation models used in biogeochemical studies; e.g., Hotinski et al. [2001].) The time scale of the meridional overturning circulation, $\sim 10^3$ yr, has little relevance for the water masses that do not participate in it; these can only be mixed by turbulence resulting from breaking of the internal gravity waves (ultimately due to tides and winds). The corresponding vertical (diapycnal) turbulent diffusivity K is typically $\sim 10^{-5}$ m^2 s^{-1}, and can be as low as 0.5×10^{-6} m^2 s^{-1} (Gregg et al., 2003); the latter translates into $K = 16$ m^2 yr^{-1}. This means that it may take a million years for turbulent mixing to penetrate vertically through $(Kt)^{1/2} = 4$ km (t being time). (The tracer-based estimates of the age of water masses are controversial [Wunsch, 2002] and are not used here.) In stagnant water masses, accumulation of dissolved methane may thus continue for very long times. Assuming that dissolved methane can accumulate to high concentrations, let us explore the consequences.

Consider a water column with stable density stratification due to the temperature and/or salinity gradients. Methane carried by a rising bubble will dissolve in the surrounding water as long as the concentration of methane already dissolved in it is less than the saturation value (solubility) for the local temperature T and pressure P; here saturation means equilibrium with respect to gaseous methane at the same T and P, i.e., with respect to methane inside the bubble. The solubility of methane in seawater is low (Handa, 1990); in terms of mole fraction, solubility at $T = 25$ °C and $P = 1$ bar is $\sim 2 \times 10^{-5}$. However, solubility is nearly proportional to pressure (Henry's law), and also increases as temperature drops, so that at $T = 5$ °C and $P = 400$ bar (depth 4 km), the predicted value of solubility is 4.3×10^{-3}.

METASTABILITY AND ERUPTION

A liquid subject to gravity and completely or partially saturated with dissolved gas is, thermodynamically, in a metastable state. Consider for clarity the case when the concentration of the dissolved gas is only slightly below saturation throughout, and thus increases downward in accordance with Henry's law. Then locally there is no tendency for the dissolved gas to exsolve (to form bubbles), in spite of the fact that nuclei are abundant in seawater. (Exsolution would lead to a slight increase in free energy: below saturation, the chemical potential of the gas species is lower in solution than in the free gas phase.) At the same

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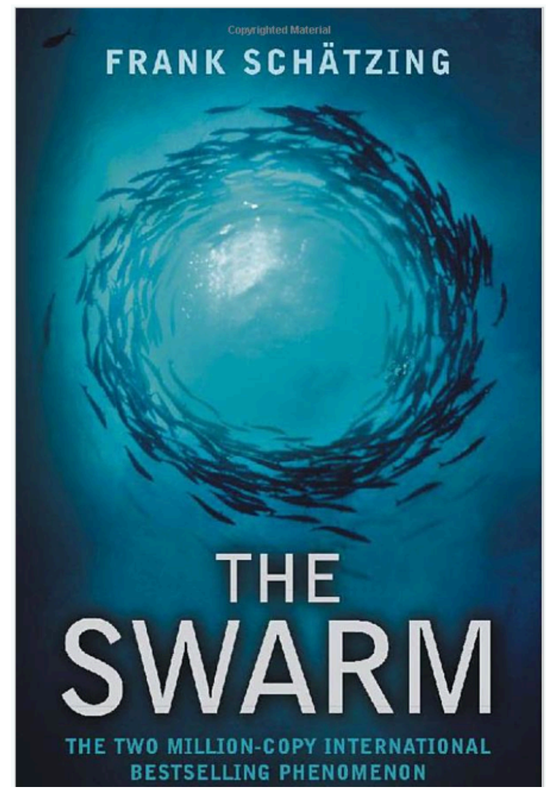
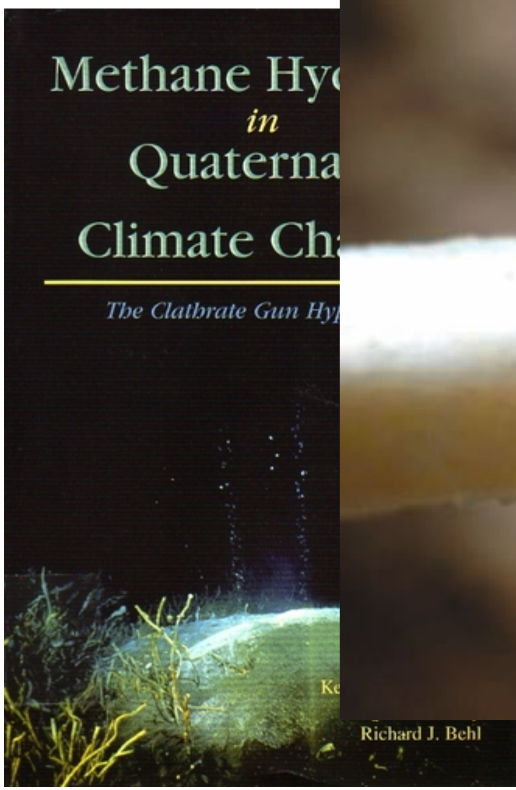
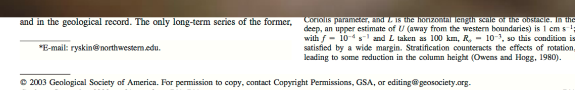
[1]In a rotating fluid, conservation of potential vorticity leads to formation of Taylor columns over bumps or depressions, the fluid trapped inside a Taylor column either being stagnant or recirculating slowly along closed streamlines. The necessary condition for the Taylor column formation is the smallness of the Rossby number $R_o \equiv U/fL$, where U is the flow velocity scale, f is the Coriolis parameter, and L is the horizontal length scale of the obstacle. In the deep, an upper estimate of U (away from the western boundaries) is 1 cm s^{-1}; with $f = 10^{-4}$ s^{-1} and L taken as 100 km, $R_o = 10^{-3}$, so this condition is satisfied by a wide margin. Stratification counteracts the effects of rotation, leading to some reduction in the column height (Owens and Hogg, 1980).



Global Organic Carbon Distribution + Gas Hydrates

- “Clathrate Gun” Hypothesis and related disaster scenarios
- Quality varies




and in the geological record. The only long-term series of the former,

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Coriolis parameter, and L is the horizontal length scale of the obstacle. In the deep, an upper estimate of U (away from the western boundaries) is 1 cm s⁻¹; with f = 10⁻⁴ s⁻¹ and L taken as 100 km, R_o = 10⁻³, so this condition is satisfied by a wide margin. Stratification counteracts the effects of rotation, leading to some reduction in the column height (Owens and Hogg, 1980).

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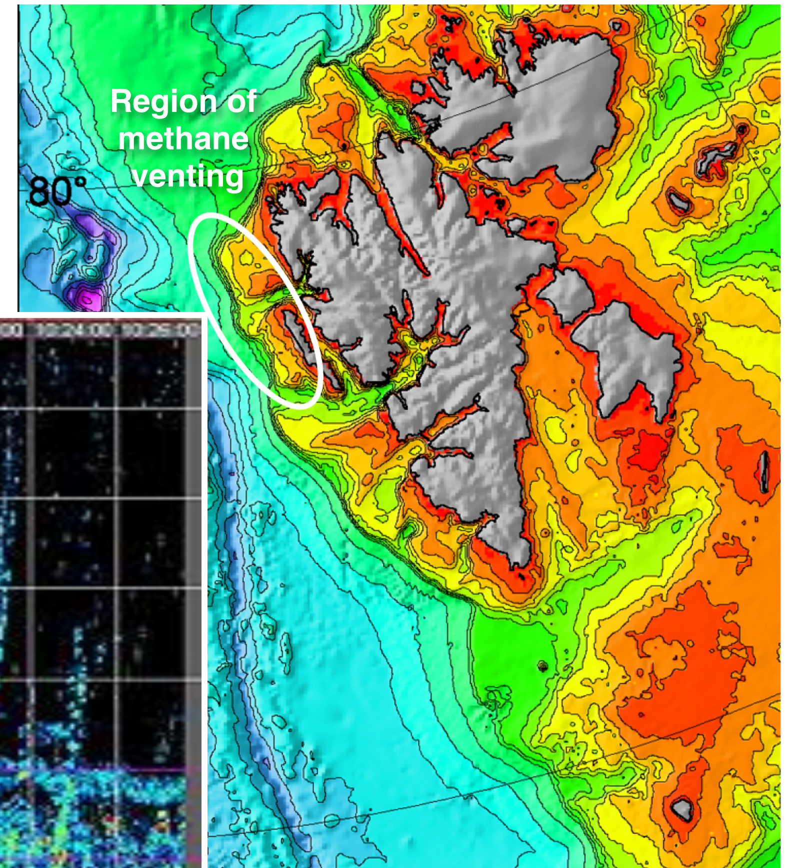
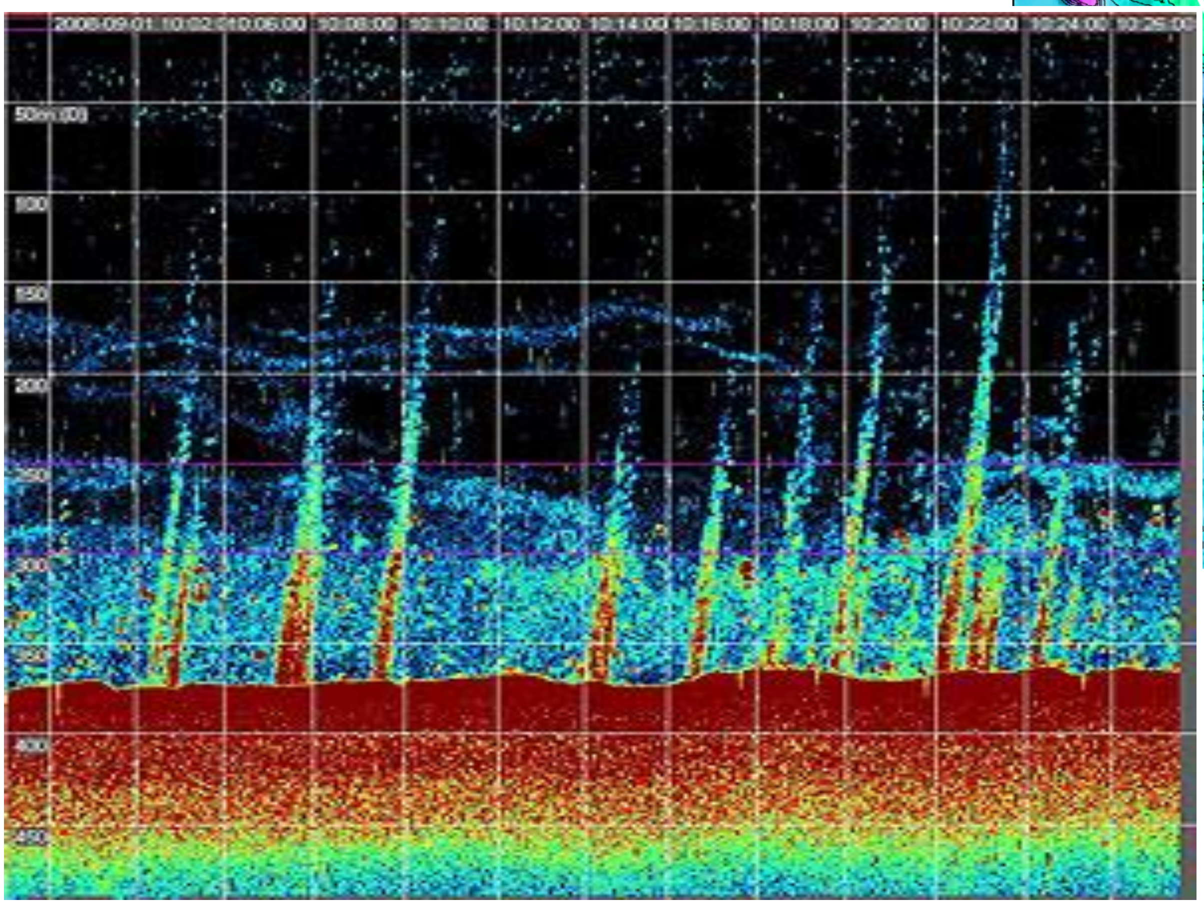
Global Organic Carbon Distribution + Gas Hydrates

- Most hydrate is deep and low-saturation
- Continental margins are the key
- Evidence is hard to find
- Are we seeing anything now?





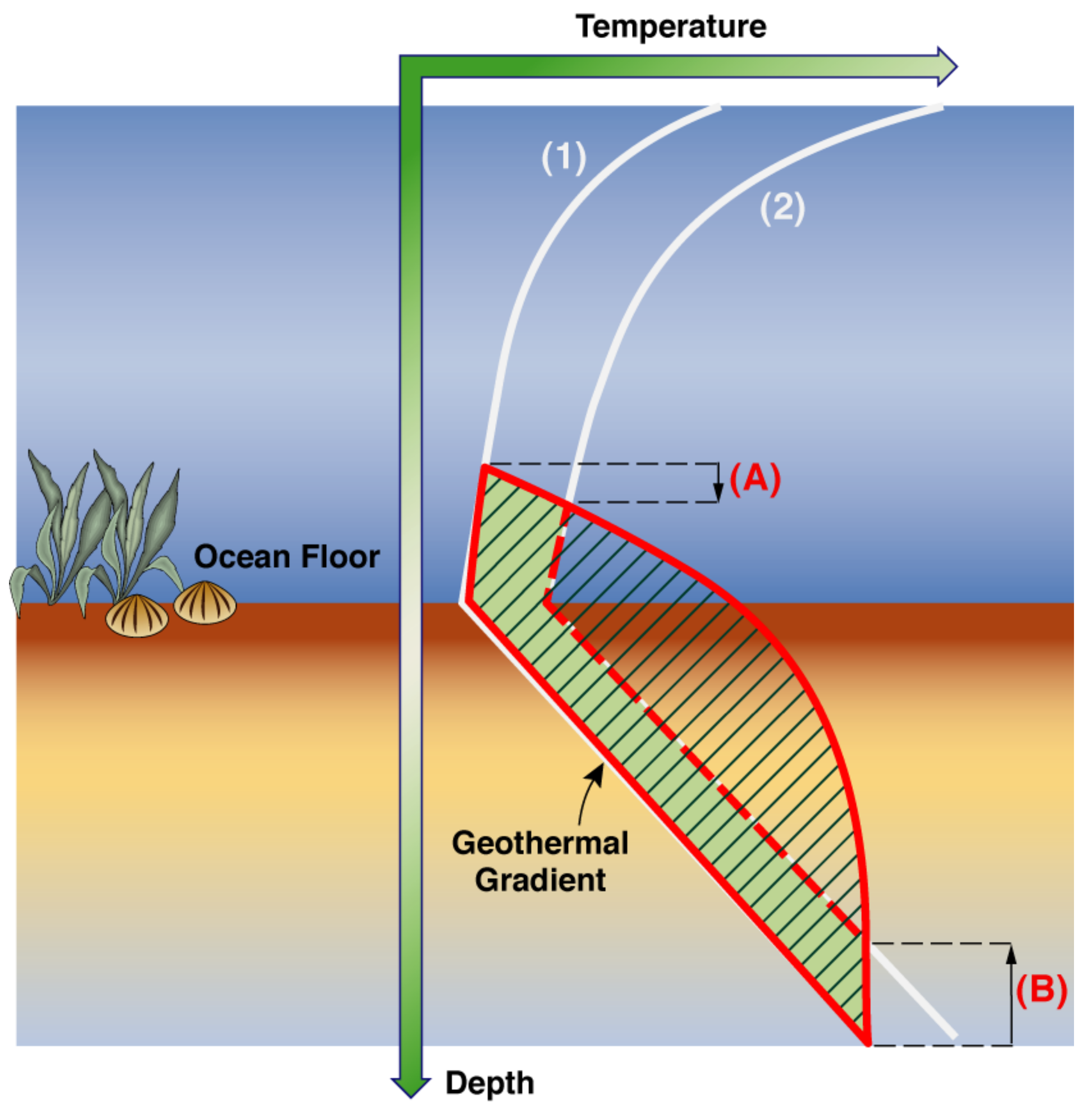
Oceanic Gas Hydrates: Dissociation

Climate change alters ocean temperature (and geothermal gradient)

Decreases hydrate stability region

Methane release to ocean by hydrate dissociation

What happens between (1) and (2)?



Oceanic Gas Hydrates: Dissociation

Climate change alters ocean temperature (and geothermal gradient)

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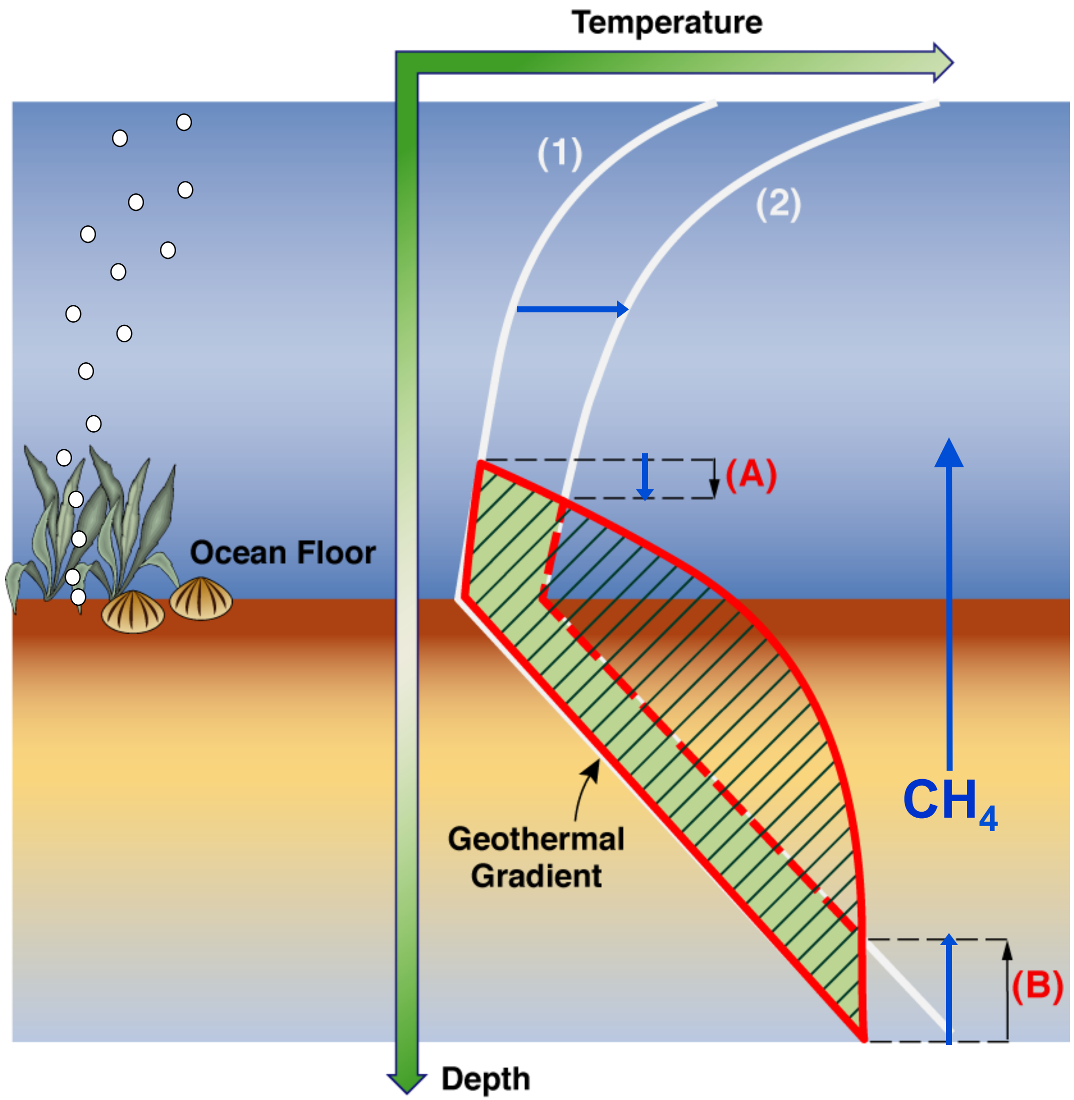
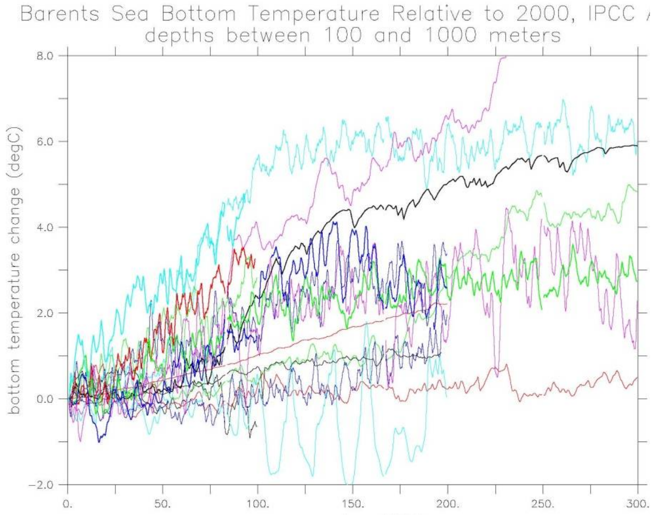
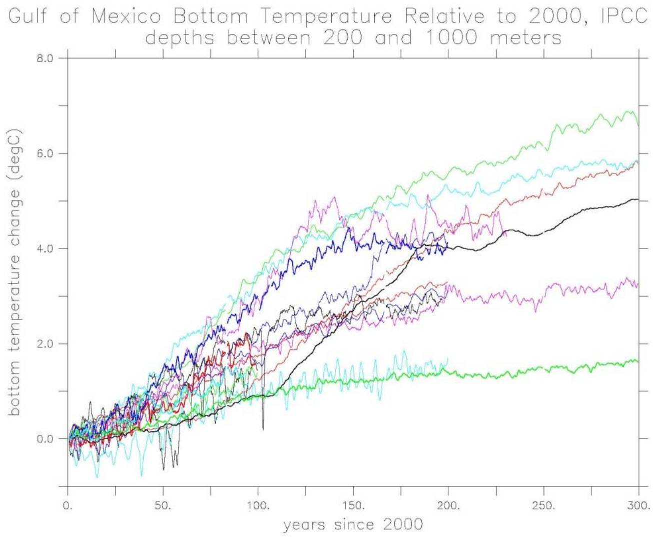
What happens between (1) and (2)?

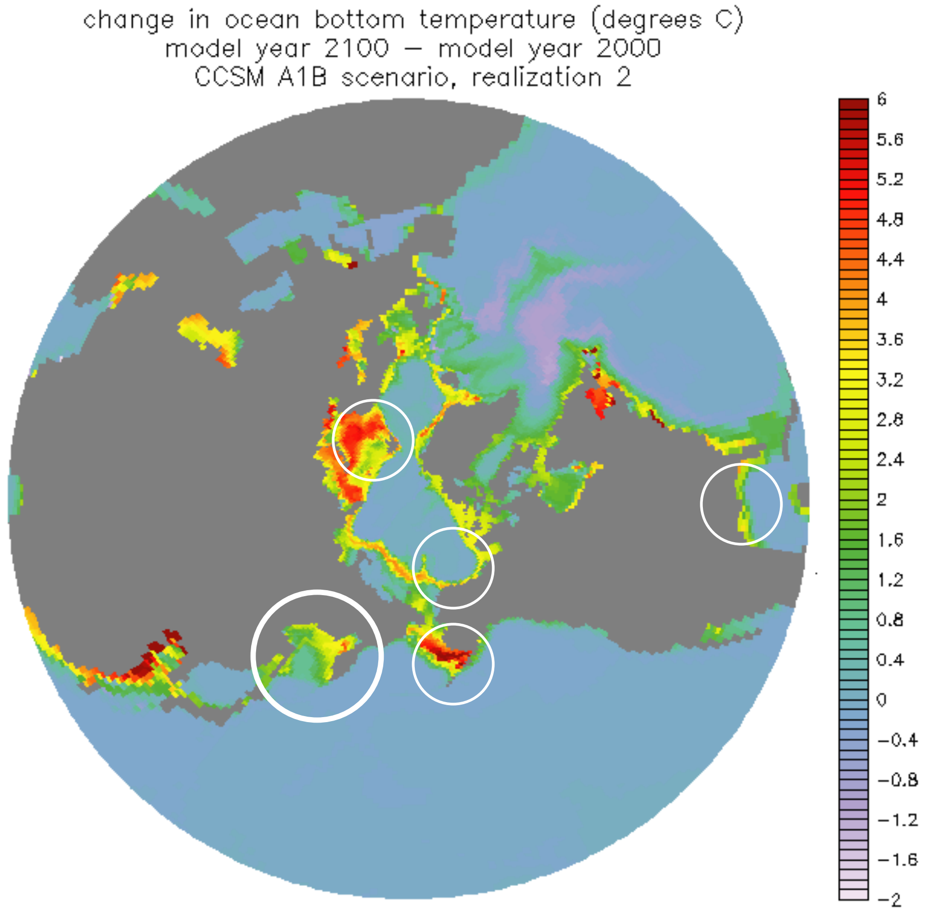
What is the fate of the methane?



Oceanic Gas Hydrates: Dissociation





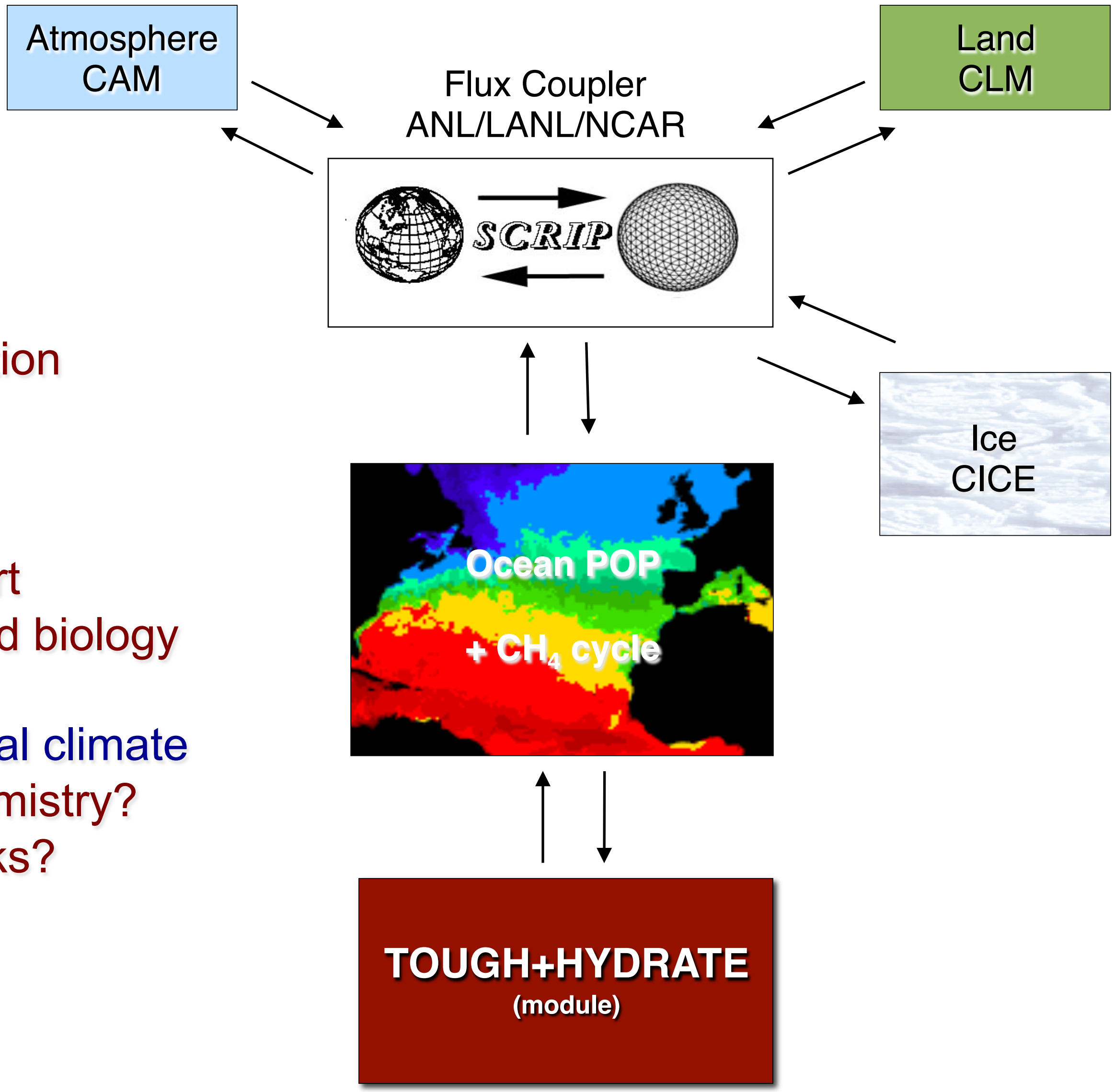


Outline

1) Sub-seafloor
   - Hydrate dissociation
   - Fluid transport

2) Ocean water column
   - Methane transport
   - Geochemistry and biology

3) Atmosphere and global climate
   - Atmospheric chemistry?
   - Positive feedbacks?



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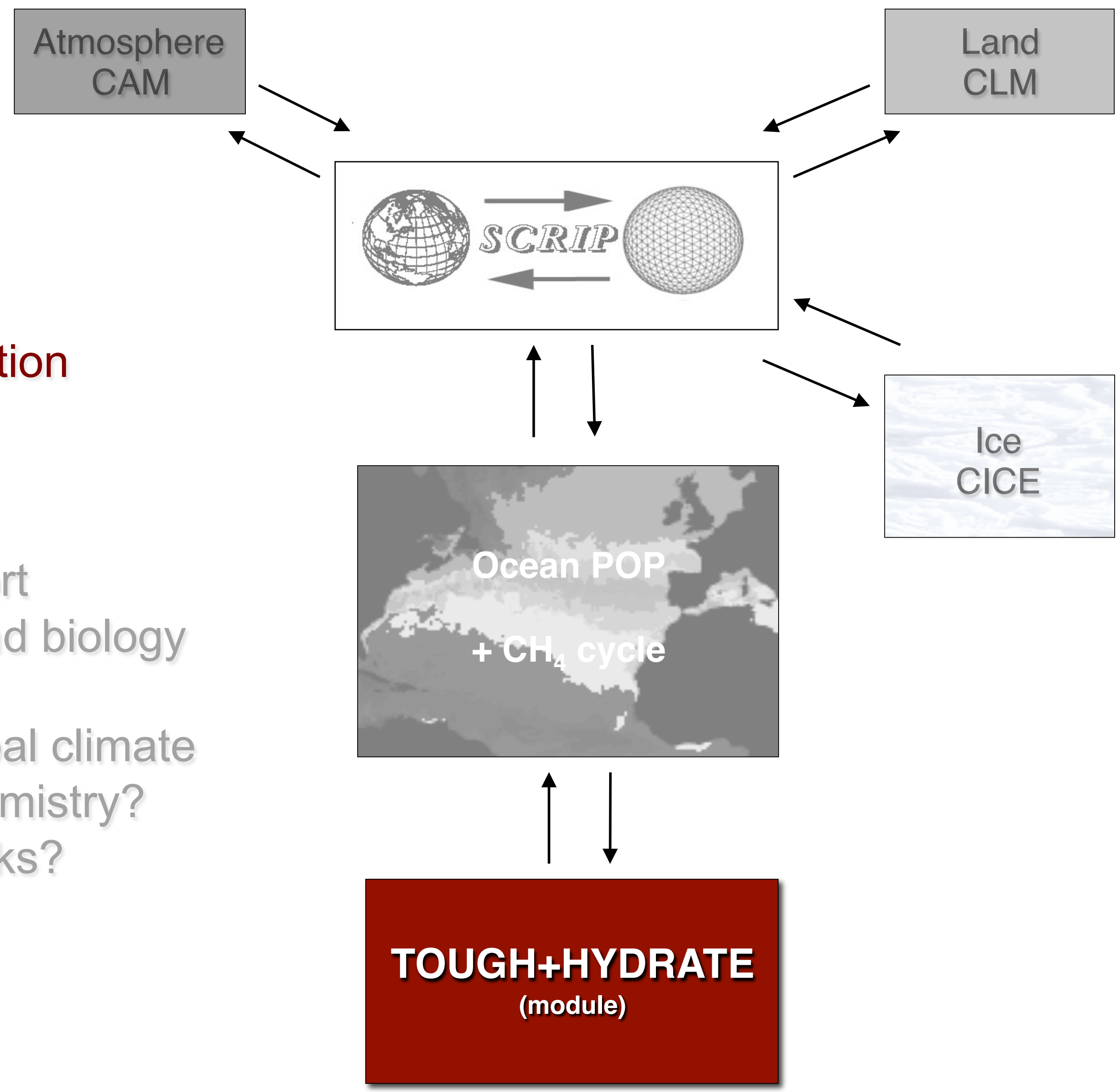


The Numerical Model

TOUGH+HYDRATE code (Moridis *et al.*, 2005; 2008; 2012):

- A complete 3D subsurface simulator for non-isothermal hydrate dissociation/ formation, CH_4 flow & transport, and phase behavior in porous media systems
- Child of codes used for hydrology, YMP, geothermal, carbon sequestration
- Validated for commercial hydrate gas production from permafrost deposits and lab experiments (extremely complex thermodynamics)

Components

(1) H_2O
(2) CH_4
(3) Hydrate
(4) Salt
(5) Inhibitor
(6) Heat

Phases

(1) Aqueous
H_2O, CH_4, salt, I

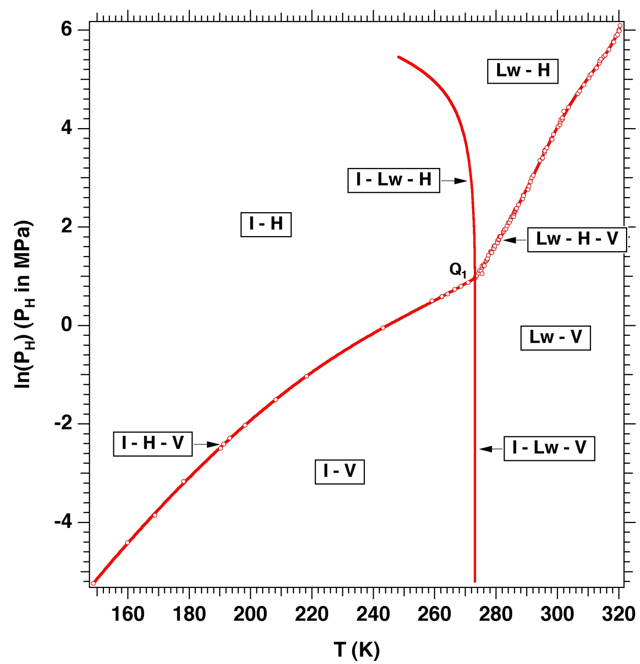
(2) Gas
CH_4, H_2O, I

(3) Solid-Hydrate
$CH_4.N_mH_2O$

(4) Solid-Ice
H_2O

30+ possible phase combinations

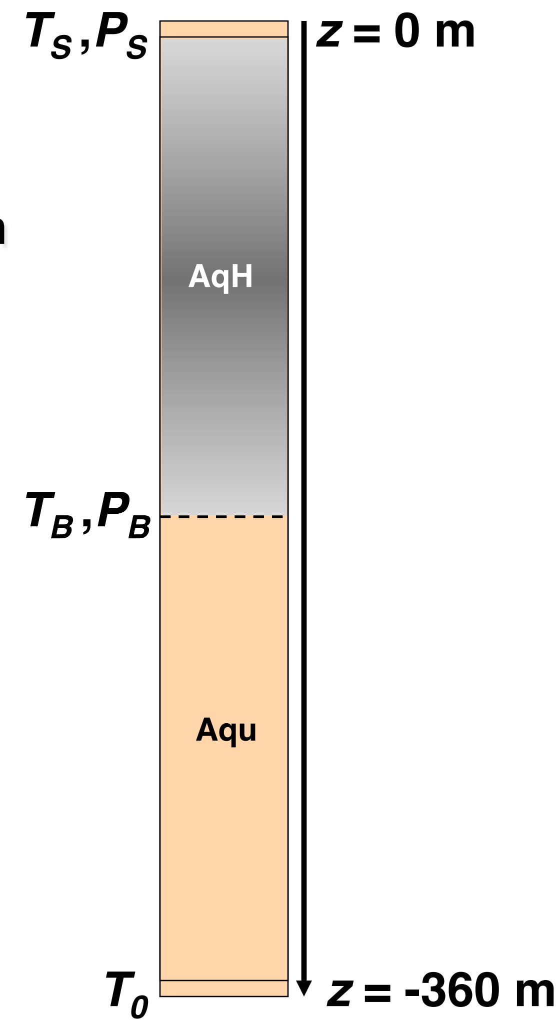
Real *P-T* relationships



1D Hydrate Stability/Dissociation

- 1D sediment column (from thermal, chemical, hydrostatic equilibrium)
- Assume hydrate exists within the stability zone
- No free gas: only look at gas generated from hydrates
- Sparse biogenic hydrate ~1%-3 %vol (up to 1%-9% found in nature)
- Expose to 1 °C to 5 °C warming over 100 yr

- Multiple kinds of hydrates tested:
  - Deep ocean[1,2] - 1000 m, $T_s = 4$ °C – stable (no release)
  - GoM[1,2] - 570 m, $T_s = 6$ °C - unstable
  - Arctic shelf[1,2] - 320 m, $T_s \sim 0.4$ °C - unstable
  - Arctic shelf - 390 m, $T_s \sim 0.0$ °C – unstable
- Rising sea levels don't make much of a difference



[1]Reagan, M.T. and G.J. Moridis, Oceanic gas hydrate instability and dissociation under climate change scenarios, *Geophys. Res. Lett.*, **34**, L22709, doi: 10.1029/2007GL031671, 2007.

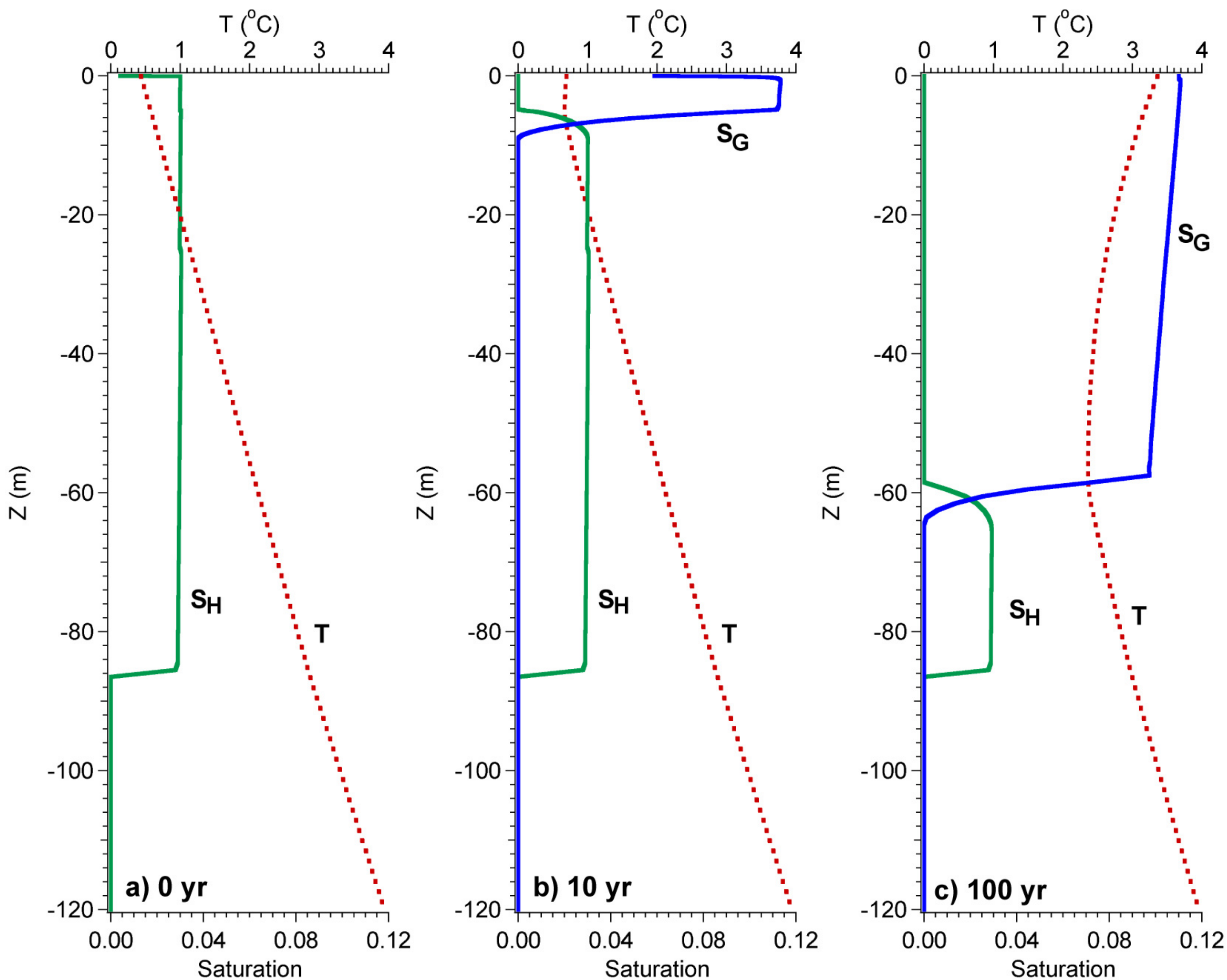
[2]Reagan, M.T. and G.J. Moridis, The dynamic response of oceanic hydrate deposits to ocean temperature change, *J. Geophys. Res. Oceans*, **113**, C12023, doi:10.1029/2008JC004938, 2008.

1D Hydrate Stability/Dissociation

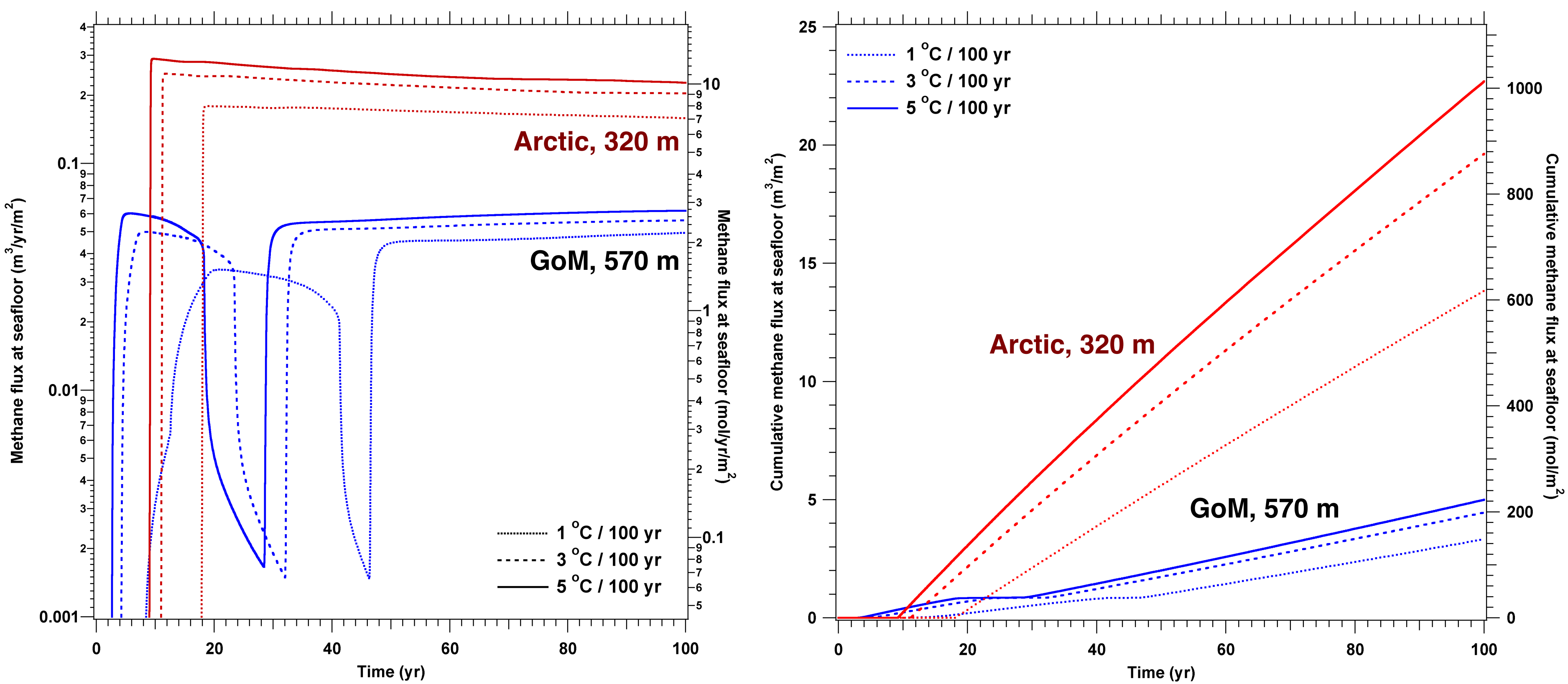
ΔT = +3 °C, 320m

- Thick hydrate layer
- Dissociates from top
- Sharp T front
- 1/3 of the deposit remains at t = 100 yr

- Dissociation continues with no further warming
- Remaining hydrate dissociates by t = 250-300 yr (with no further change in T)



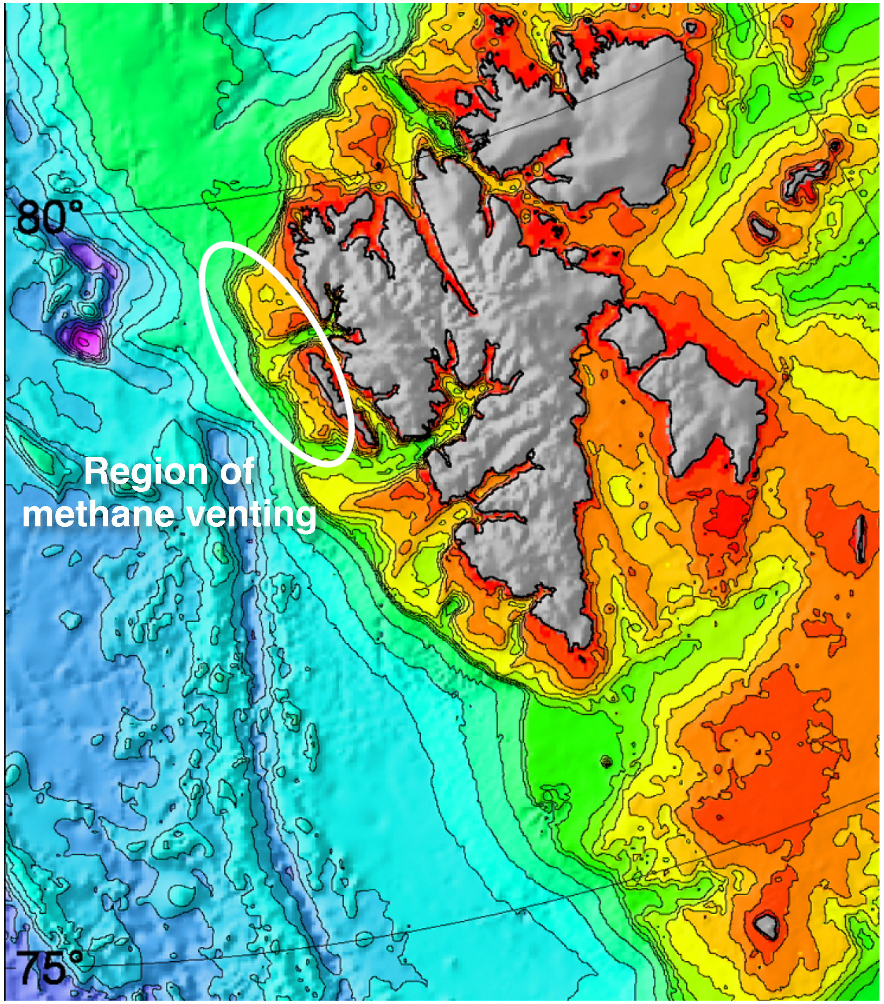
1D Hydrate Stability/Dissociation



- Peak methane fluxes: 40 g/yr/m² (GoM), 176 g/yr/m² (Arctic)
- Spread globally: 560-2140 Tg/yr CH_4 (0.5 – 2 Gt) released into the ocean (Lamarque, *GRL*, 2008)

2-D Hydrate Dissociation Model

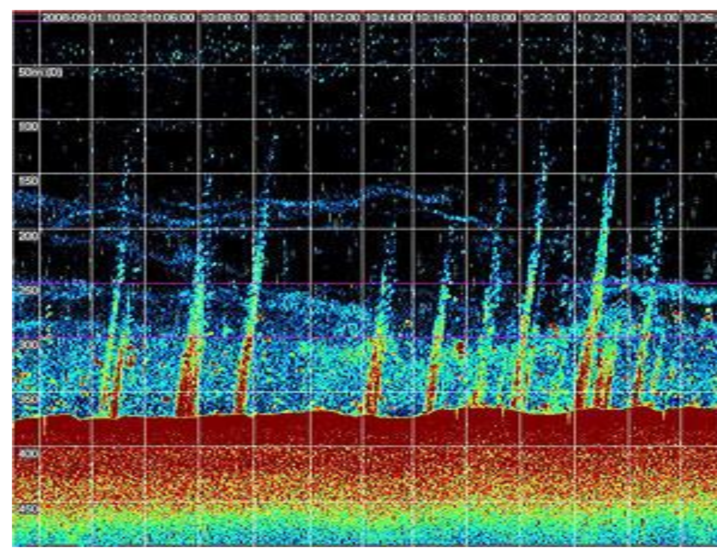
from NOAA/IBCAO (http://www.ngdc.noaa.gov/)



4. Westbrook, G.K., *et al.*, Escape of methane gas from the seabed along the West Spitsbergen continental margin *Geophys. Res. Lett.*, **36**, L15608, doi: 10.1029/2009GL039191, 2009.

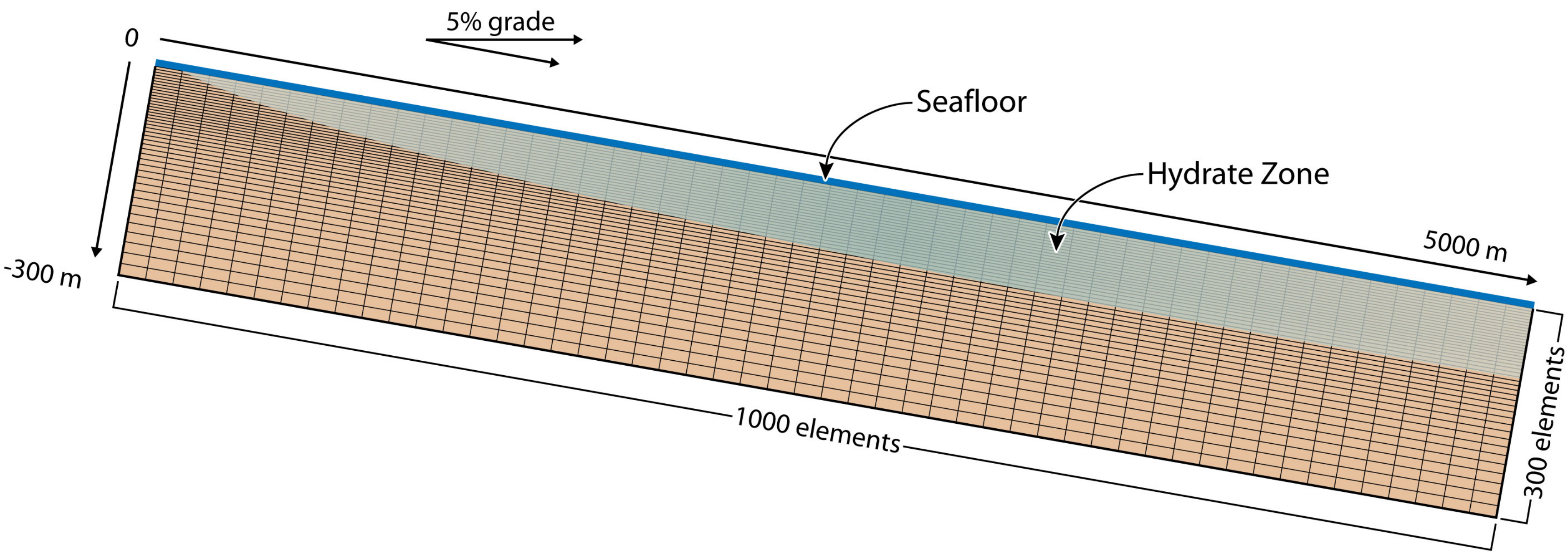
- Methane plumes reported west of Svalbard at the upper limit of a receding GHSZ[4]
- Measured warming, partly due to ocean current shifts (end of the Gulf Stream!)
- Plumes seem to be moving downslope

- Could shallow hydrates alone produce such plumes?
- How much methane could be released on short timescales?



2-D Hydrate Dissociation Model

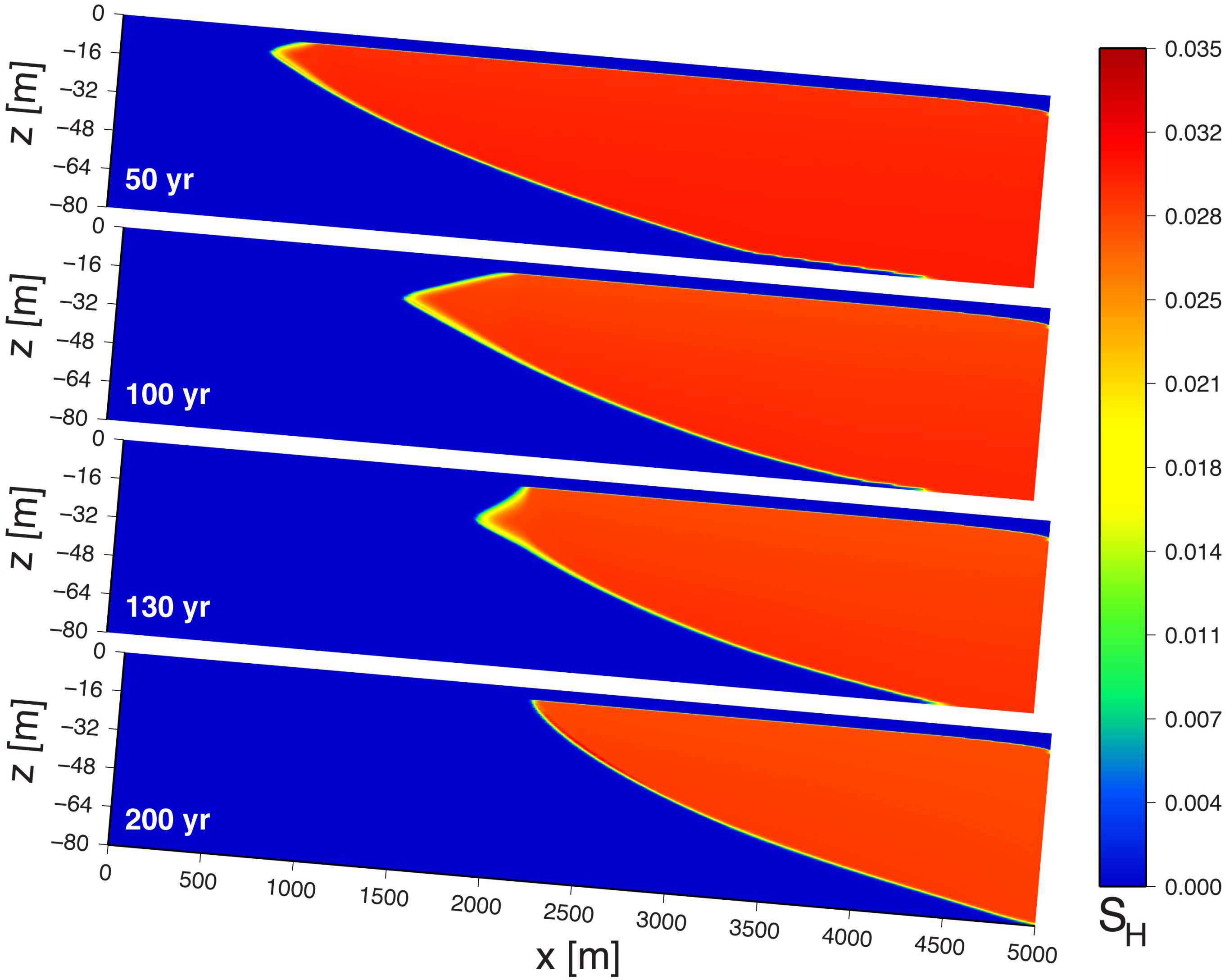
- 2-D system represented by a 300 x 1000 x 1 = 300,000 element mesh, fine discretization
- 5% grade (20:1), capturing seafloor depths from 300m to 550 m
- Equilibrated to thermal, chemical, hydrostatic equilibrium; uniform hydrate (3%) within the hydrate stability zone
- Use parallel TOUGH+HYDRATE (pT+H) to solve fully coupled system as seafloor temperature increases, reflects various past and future warming scenarios[5]



[5]Reagan, M.T. et al., "Contributions of Oceanic Gas Hydrate Dissociation to the Formation of Arctic Ocean Methane Plumes," J. Geophys. Res. Oceans, 116, C09014, 2011.

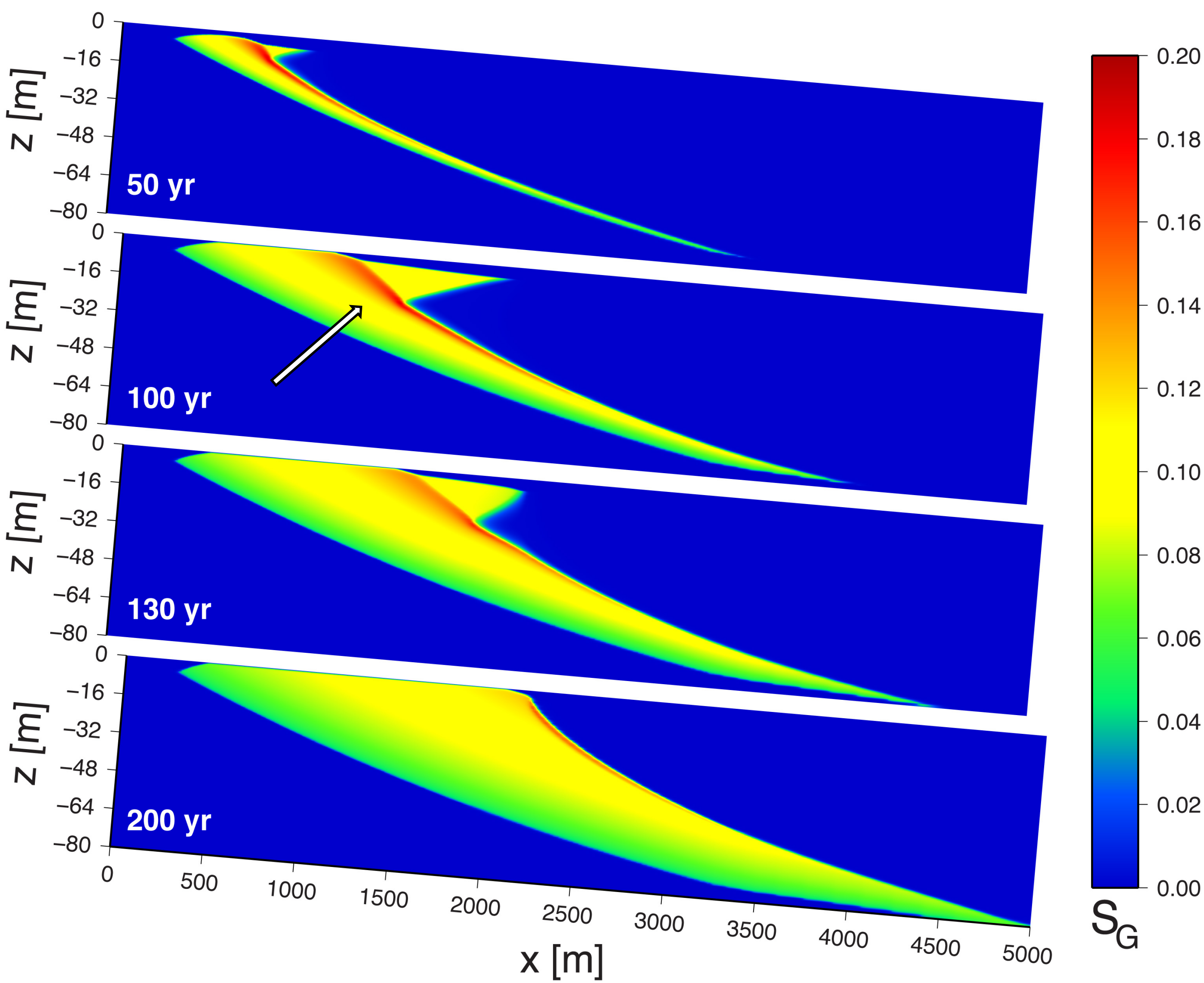
2-D Hydrate Model: Rapid Change

- A linear change of 3°C/ 100 yr imposed for 100 yr, then *T* held constant
- By 100 yr, dissociation proceeds >1000 m downslope
- By 200 yr, dissociation has moved ~2,000 m downslope
- Some hydrate reforms along the bottom of the GHSZ



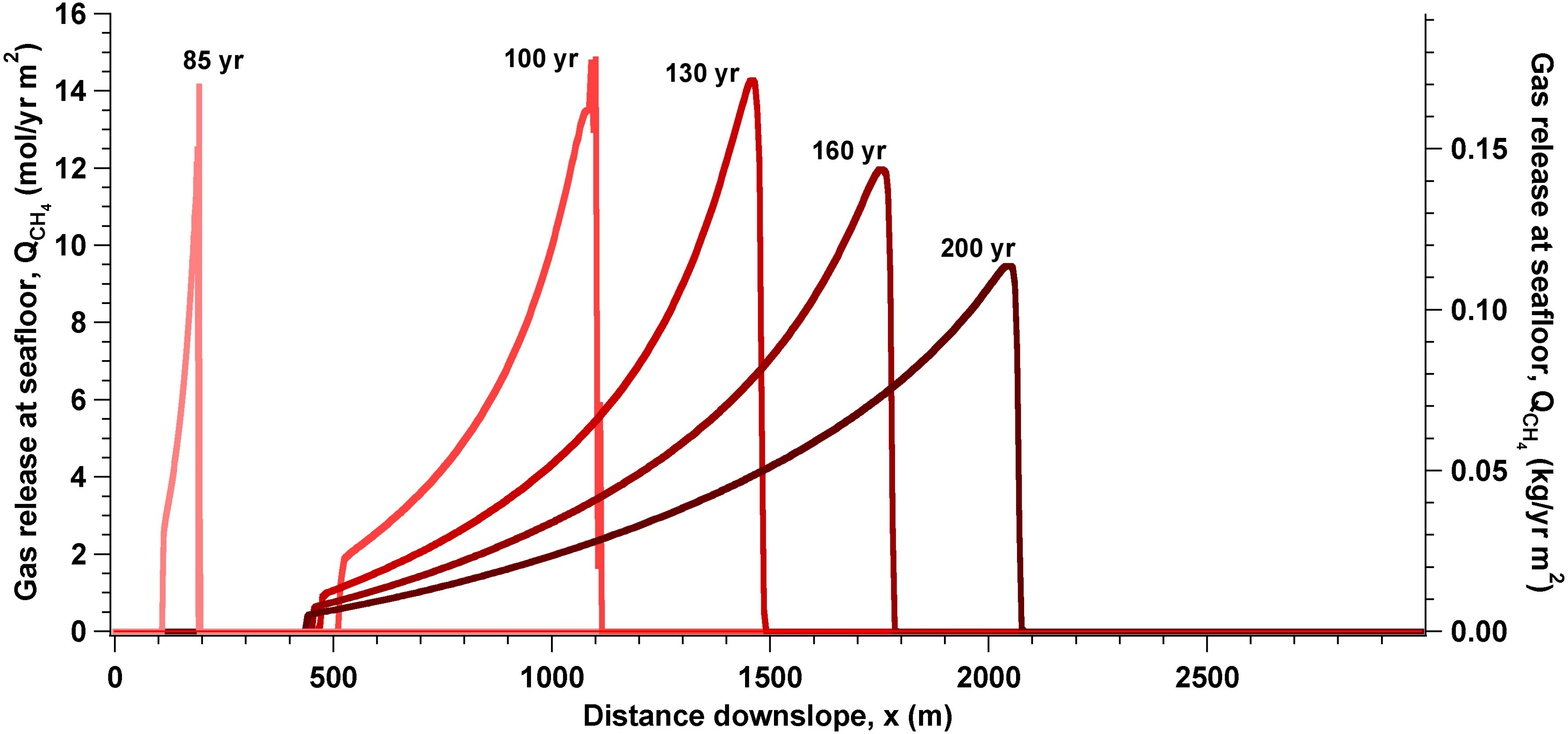
2-D Hydrate Model: Rapid Change

- A linear change of 3°C/ 100 yr imposed for 100 yr, then *T* held constant
- A "plume" of high gas saturation forms at upper limit of dissociating hydrates
- Plume focused by the remaining hydrate layer
- Plume reaches seafloor and again moves downslope within the sediments

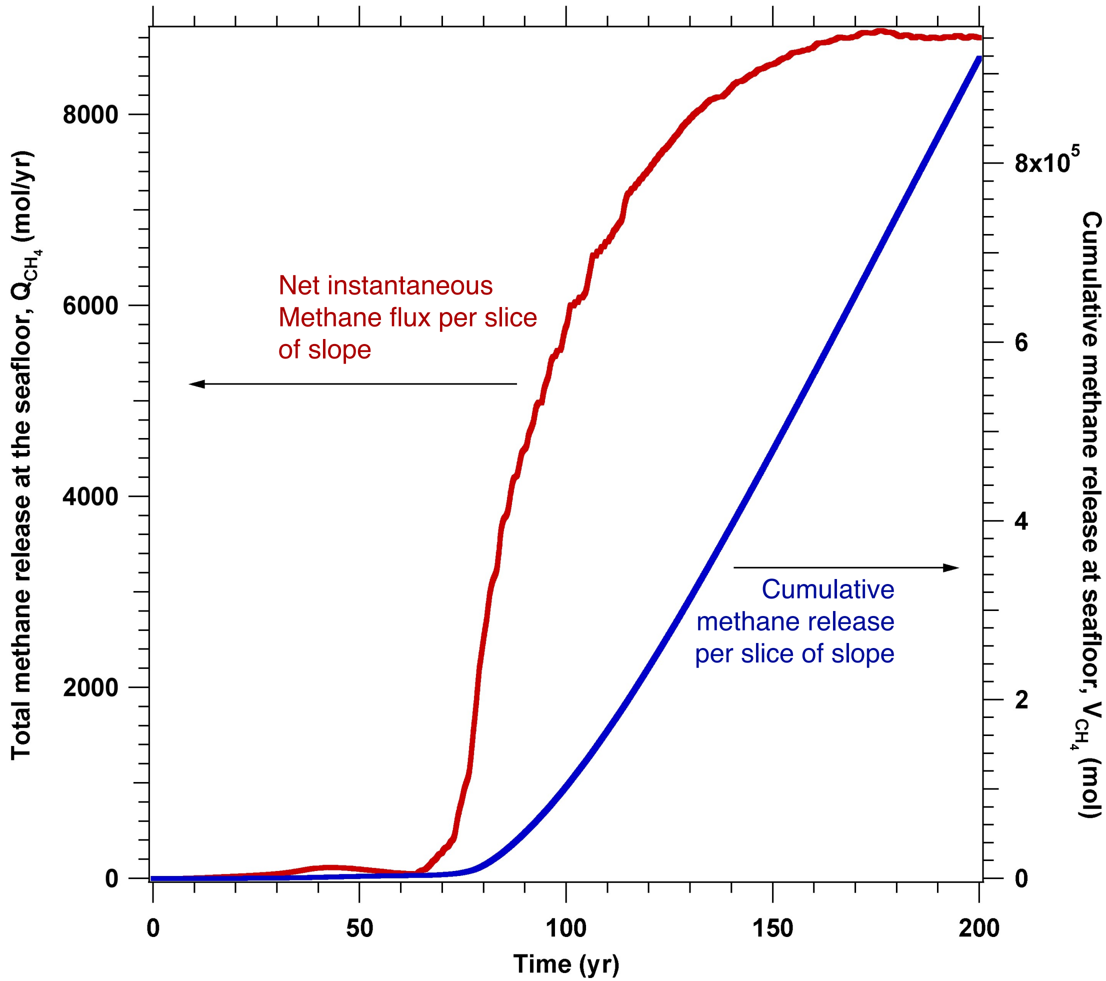


2-D Hydrate Model: Rapid Change

- Record localized fluxes along the seafloor boundary during system evolution
- Gas fluxes are mol/yr CH_4 per m^2 of seafloor at position *x*
- Localization and movement of maximum CH_4 release agrees with observations



2-D Hydrate Model: Rapid Change



Results are per m of slope width

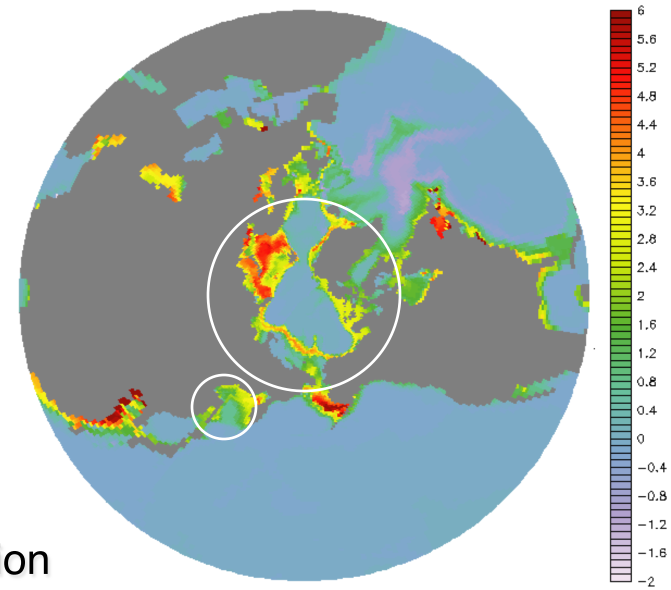
Over 30km of active slope, that's 0.4 Tg from just one patch

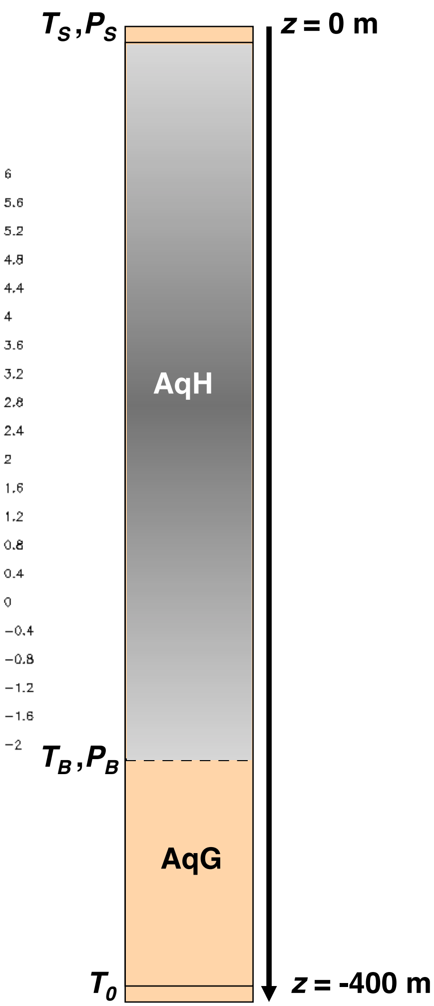
Integration: Basin-Scale Assessments

Integrate 1-D columns across Arctic bathymetry!

- Noted that transport is almost entirely vertical in the 2-D system
- Use real depths, T, conditions
- Okhotsk: T_s = 0 °C - 2 °C
- Arctic: T_s = 0.5 °C - 1 °C

- Apply different possible changes
- ΔT = 1, 3, 5, 7 °C/100 yr, or $\Delta T = f(z)$
- 100 yr warming, then T_s = constant



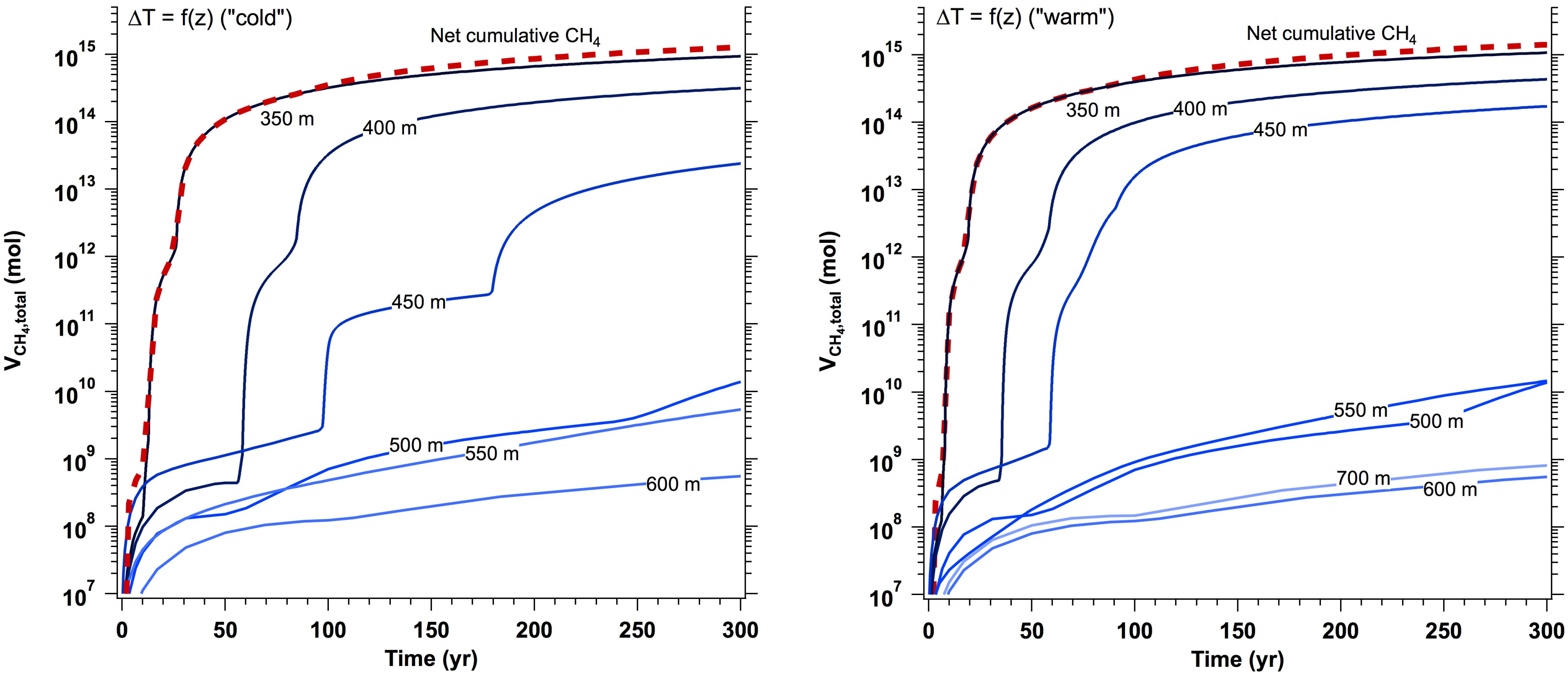


- Simulate CH_4 release vs. t at each location
- Fluxes will be a function of depth, T_s, ΔT
- Perform the release simulations on 40-min grid, 25 m depth increments
- Integrate total methane release/flux over bathymetry
- Estimate basin-scale CH_4 emission

Integration: Arctic Ocean

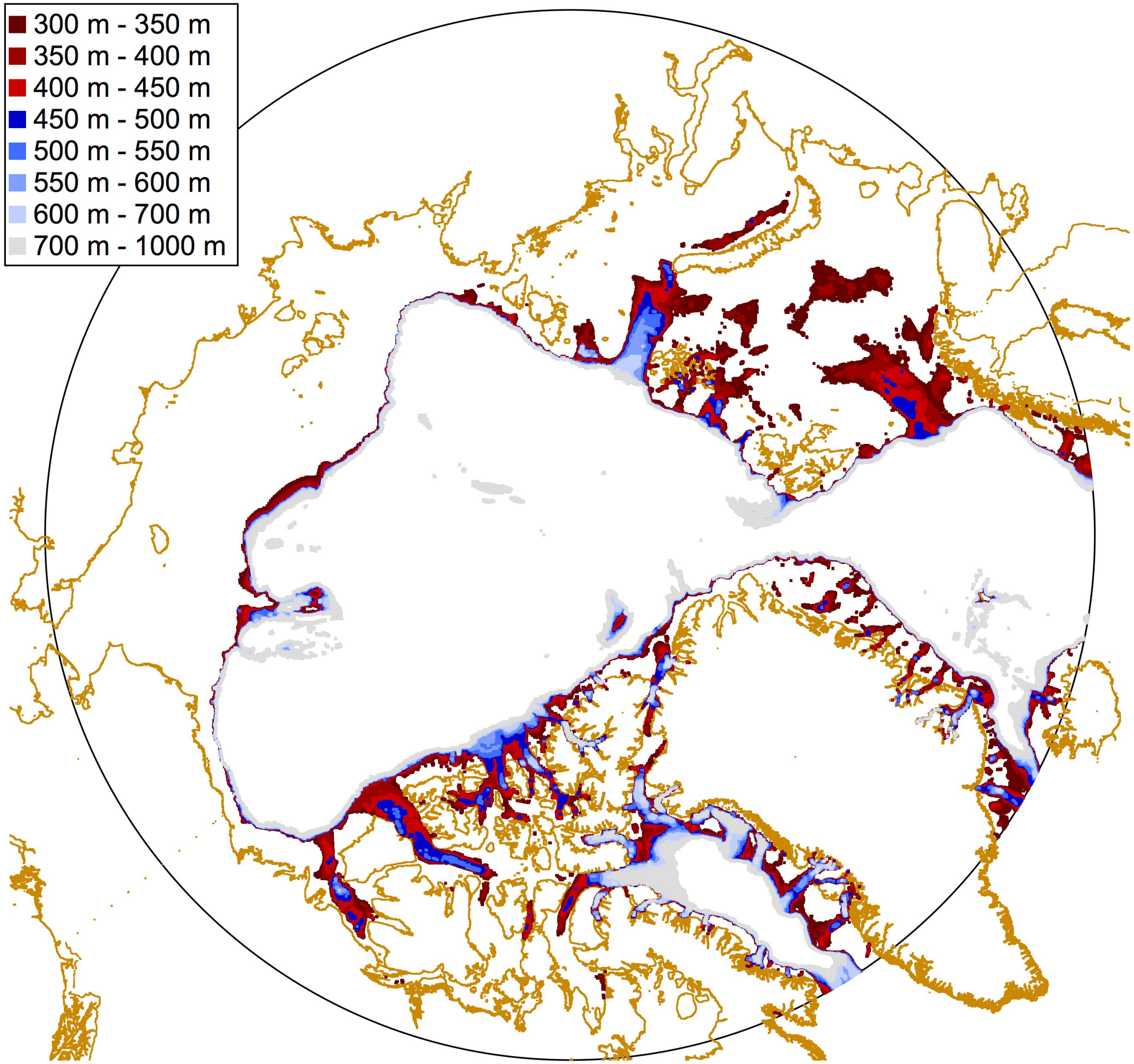
Integration: Arctic Ocean

Cumulative release (V_{CH4}) vs. depth



- Instability confined to a narrow band near the top of the GHSZ
- Up to 6,400 – 9,000 Tg CH_4 at $t = 100$ yr

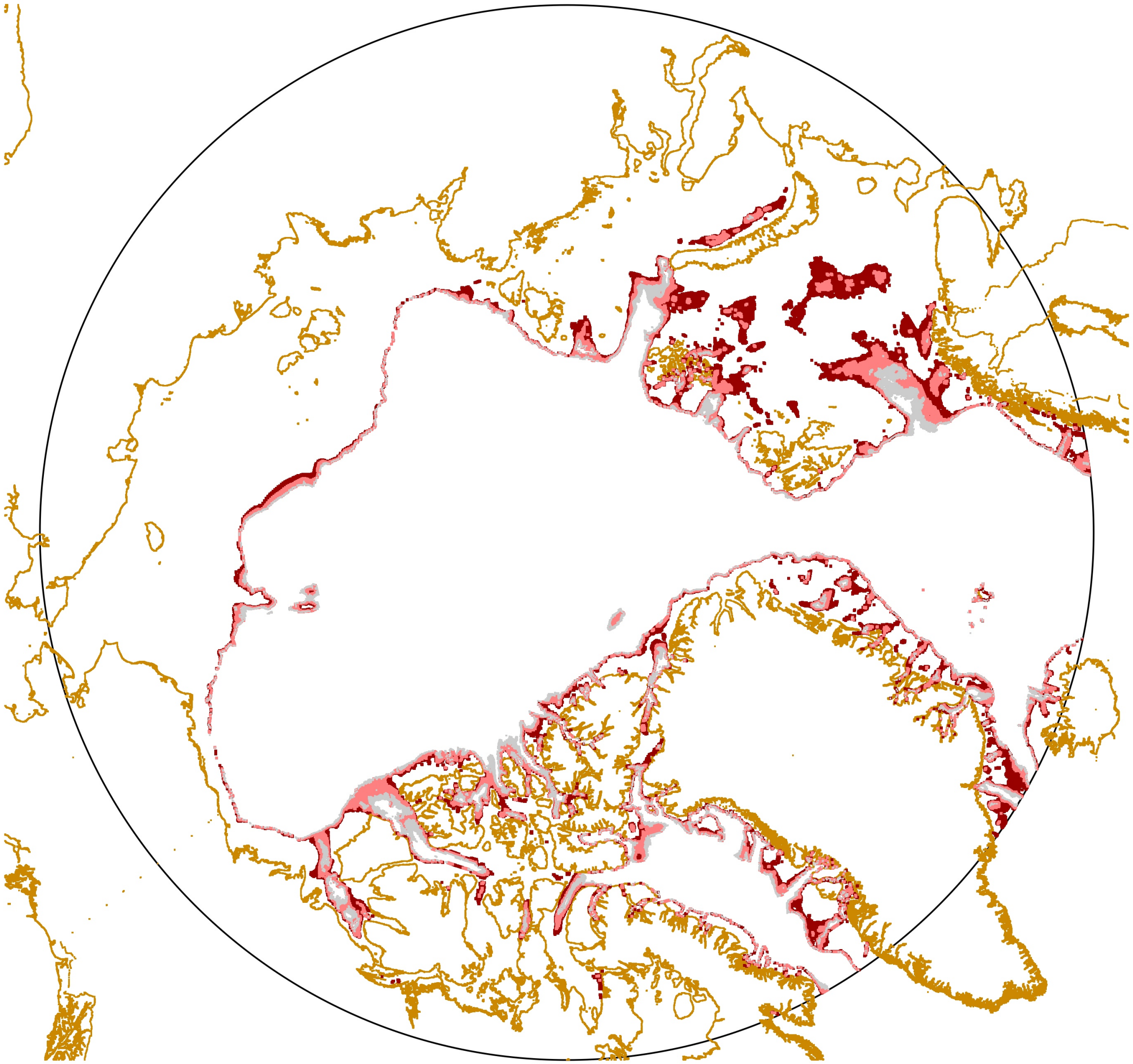
Integration: Arctic Ocean



Depth contours, coloring suggesting areas of potential destabilization (reds) vs. low-flux areas (blues)[6]

[6]Reagan, M.T. et al., "Constraints on the Extent of Gas Hydrate Dissociation in Response to Climate Change," in review for Geophysical Res. Lett., 2012.

Integration: Arctic Ocean

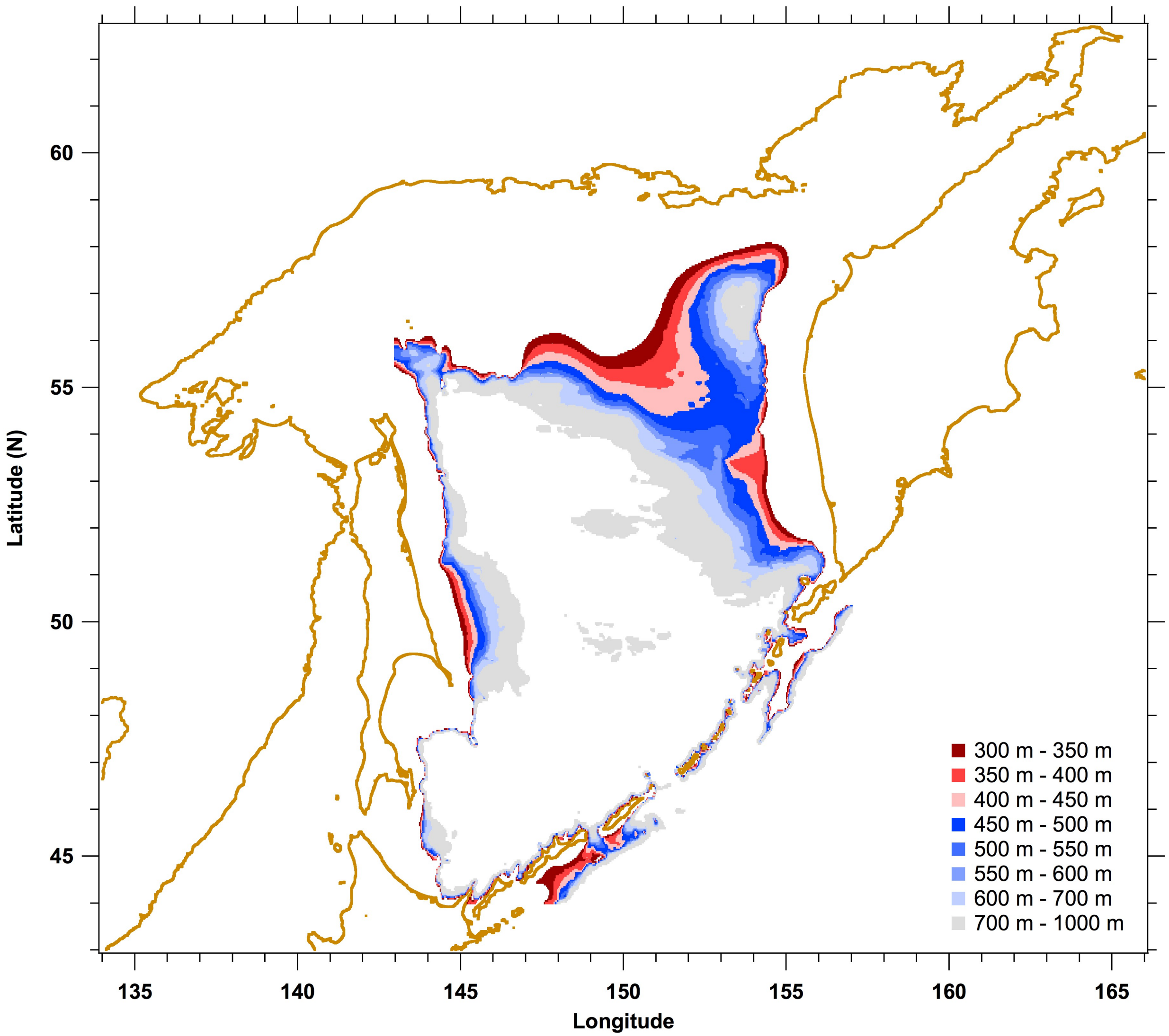


Regions realistically capable of generating gas plumes

[6]Reagan, M.T. et al., "Constraints on the Extent of Gas Hydrate Dissociation in Response to Climate Change," in review for Geophysical Res. Lett., 2012.

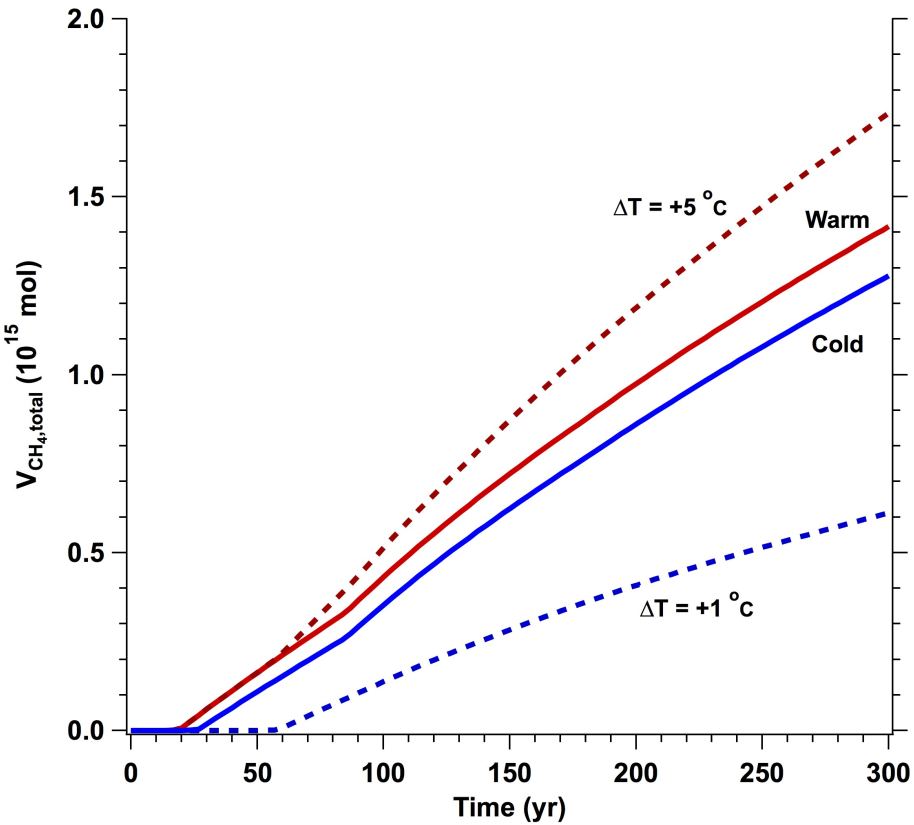
Integration: Sea of Okhotsk

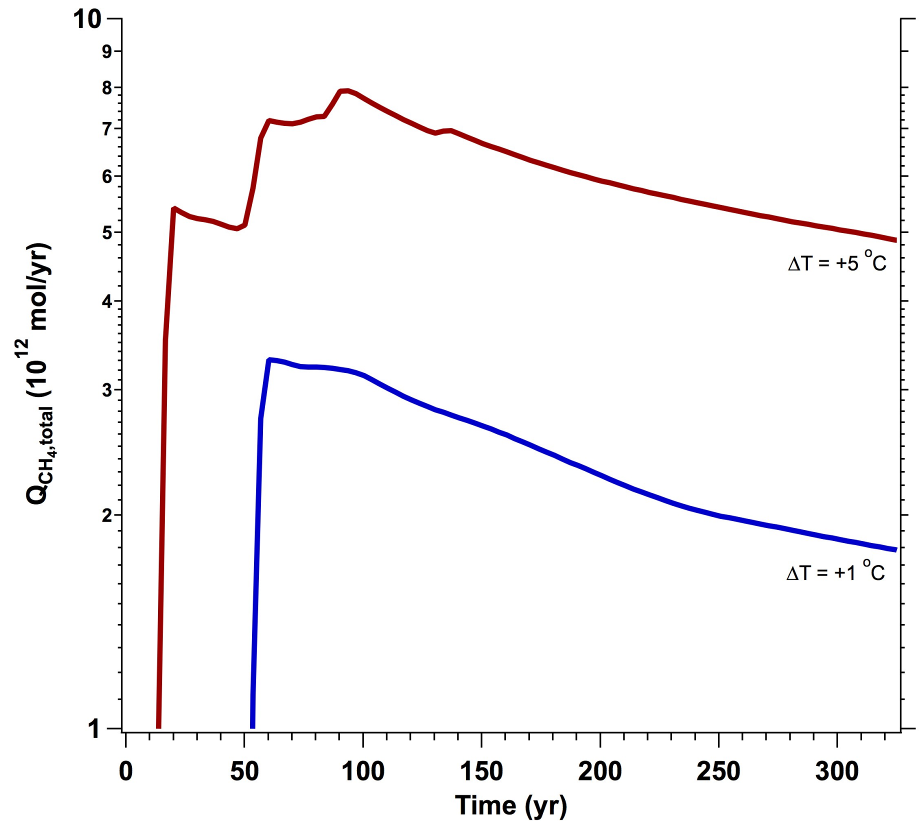
Depth contours, coloring suggesting areas of potential destabilization (reds) vs. low-flux areas (blues)



Integration: Totals

Cumulative release (*V*) and net flux (*Q*), upper and lower limits





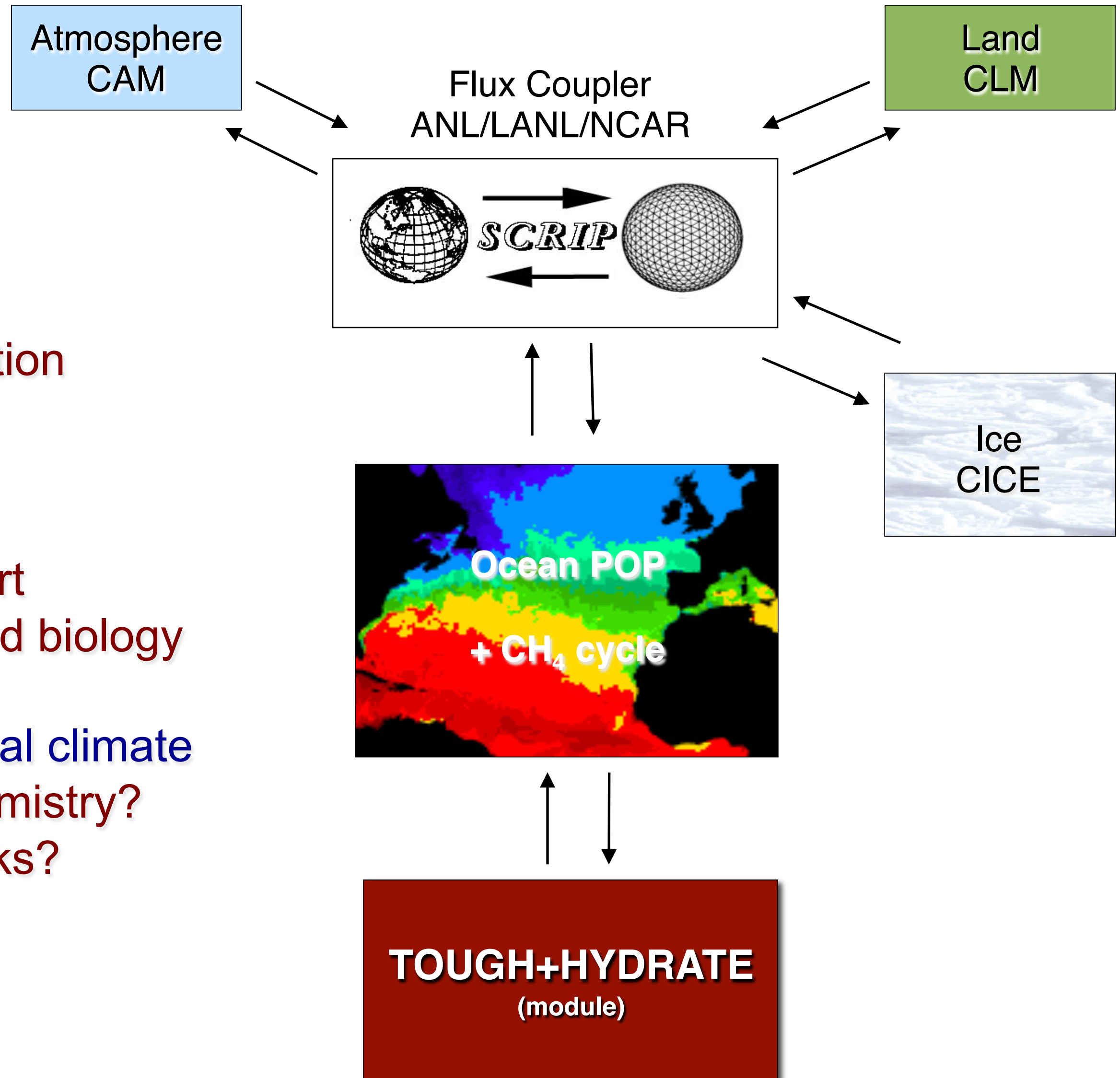
- Scenarios: +5°C, +1°C, warm (1°C - 5°C as f(*z*)), cold (1°C - 3°C as f(*z*))
- Short-term: 1,696 – 3,296 Tg CH_4 @ 30 yr, 5,120 - 11,520 Tg @ 100 yr (Okhotsk included) or about ~ 1 Gt/yr for a few centuries

Outline

1) Sub-seafloor
    - Hydrate dissociation
    - Fluid transport

2) Ocean water column
    - Methane transport
    - Geochemistry and biology

3) Atmosphere and global climate
    - Atmospheric chemistry?
    - Positive feedbacks?



Outline

1) Sub-seafloor
   - Hydrate dissociation
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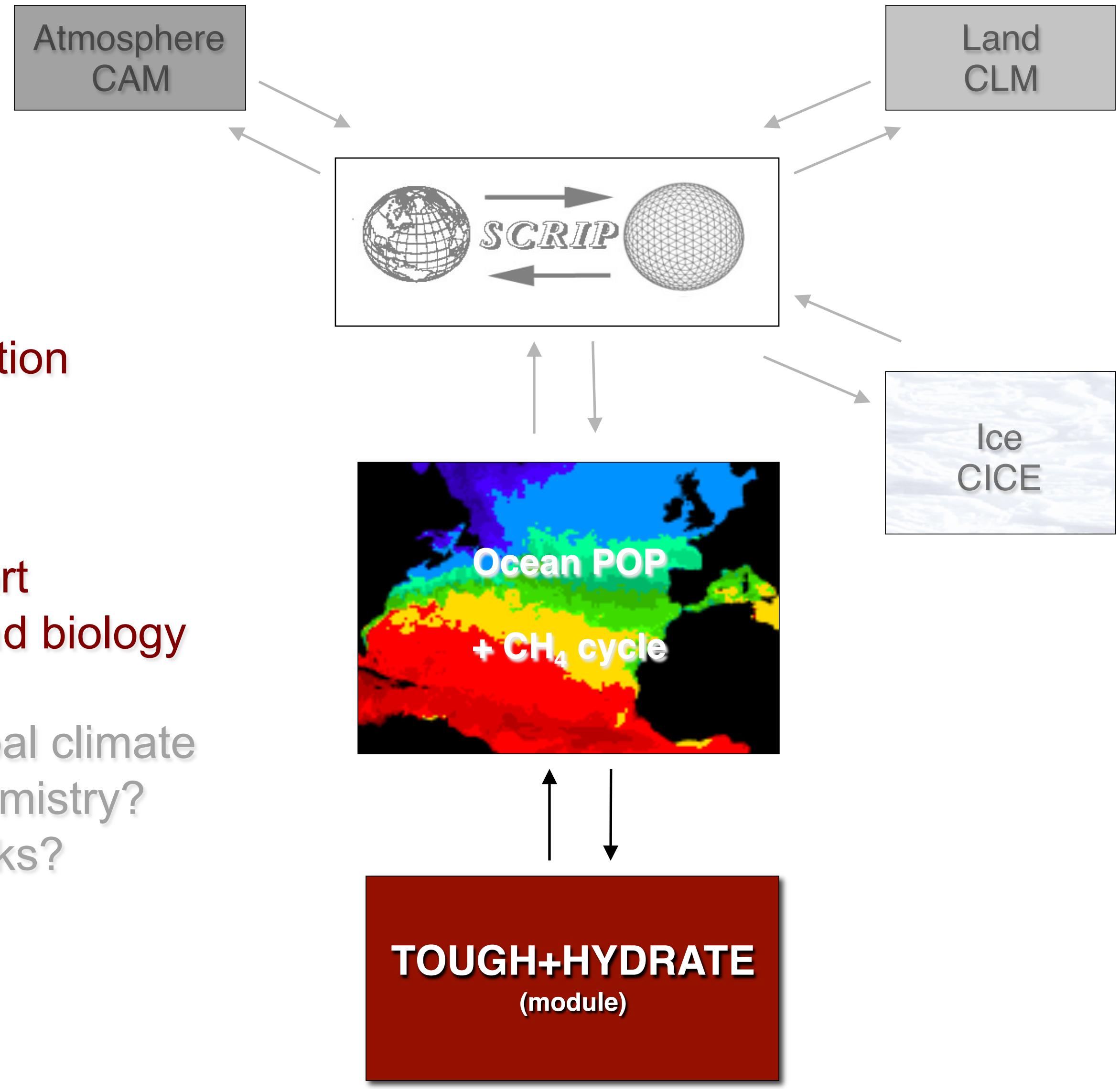
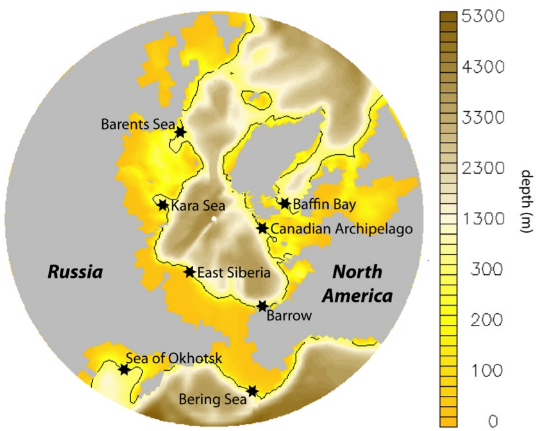


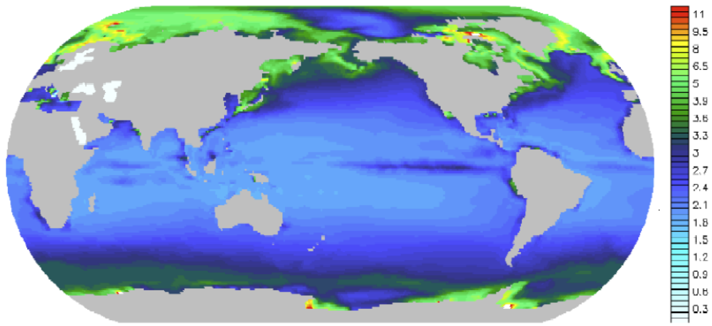
Coupled Ocean Modeling & Biochemistry

- POP is the CESM ocean model
- Extended to consider methane biogeochemistry in the water column[5,6]
- A background methane cycle creates a baseline for methane release calculations[6]
- Localized methane releases from hydrates inserted into POP[5] (fully dissolved*)

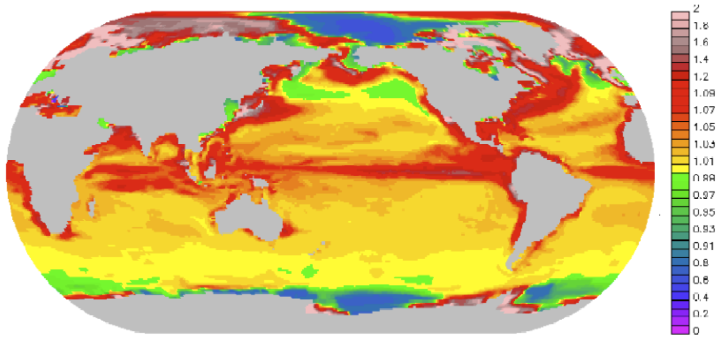
  *Plume physics forthcoming



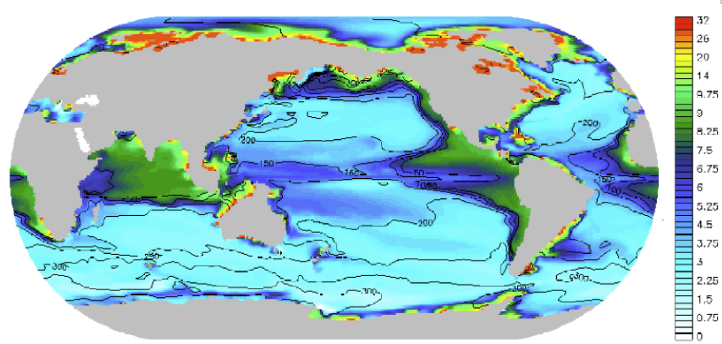
CH_4 Surface Concentration (nanomolar)



CH_4 Surface Saturation Ratio



CH_4 150m Concentration (nanomolar) with O_2 contours

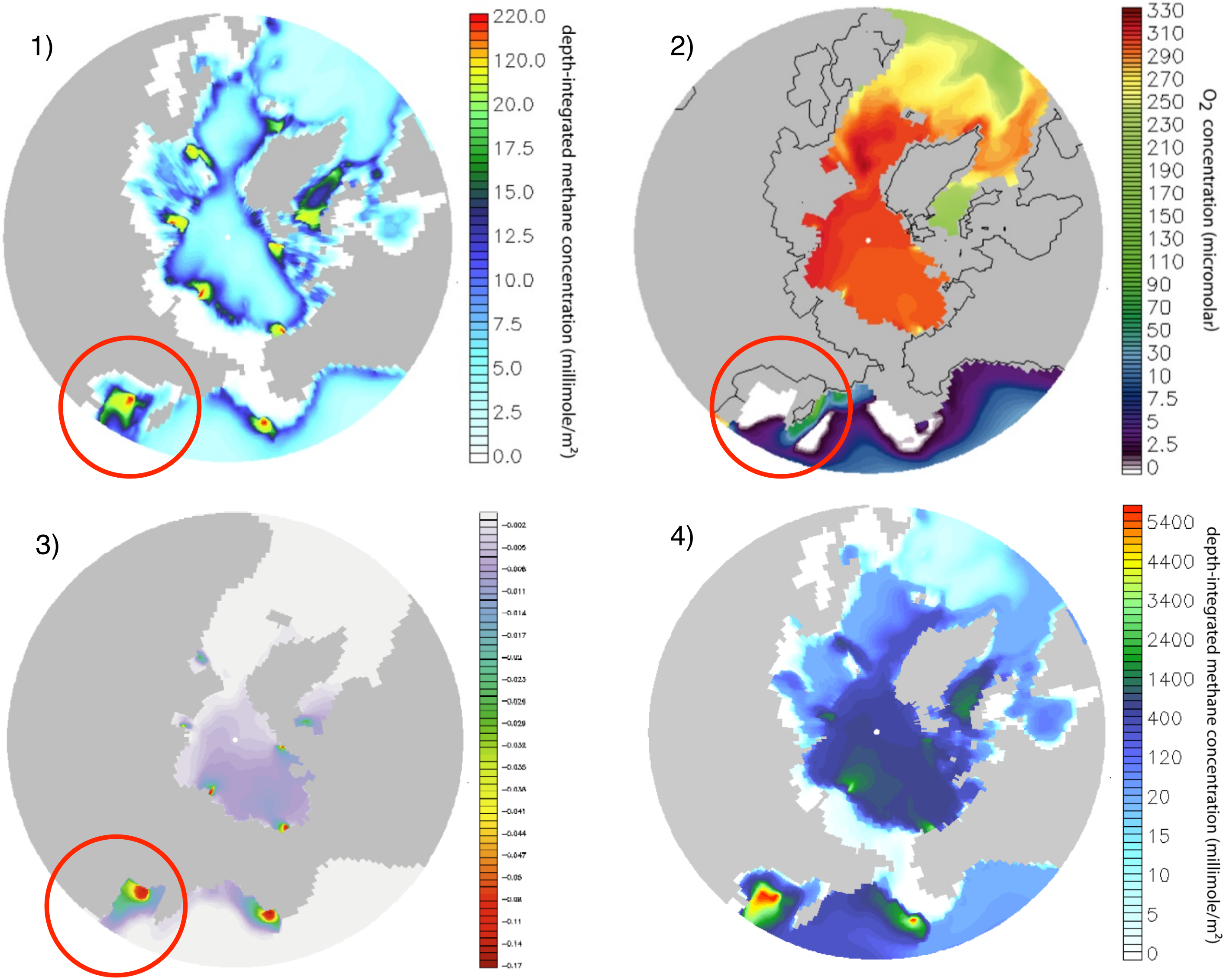


[5]Elliott, S.M., Maltrud, M., Reagan, M.T., Moridis, G.J., Cameron-Smith, P.J., "Geochemistry of Clathrate-Derived Methane in Arctic Ocean Waters," *Geophys. Res. Lett.*, **37**, L12607, 2010.

[6]Elliott, S.M., Maltrud, M., Reagan, M.T., Moridis, G.J., Cameron-Smith, P.J., "Marine Methane Cycle Simulations for the Period of Early Global Warming," *J. Geophys. Res. Biog.*, **116**, G01010, 2010.

Coupled Ocean Modeling & Biochemistry

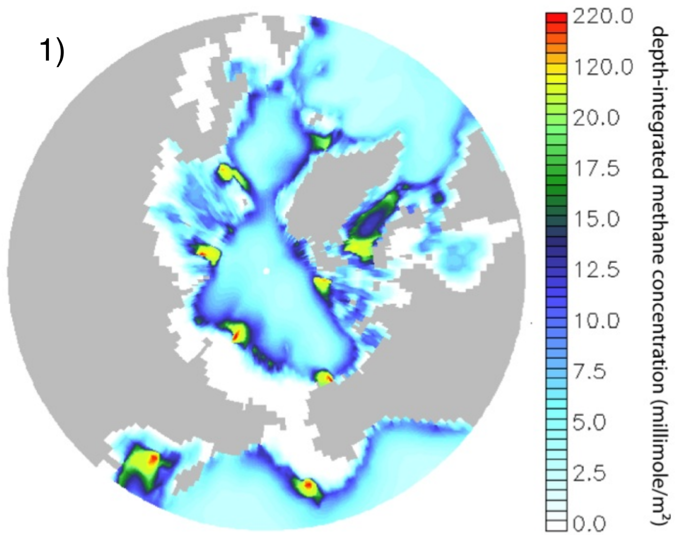
***t* = 30 yr:**



Coupled Ocean Modeling & Biochemistry

***t* = 30 yr:**

1)



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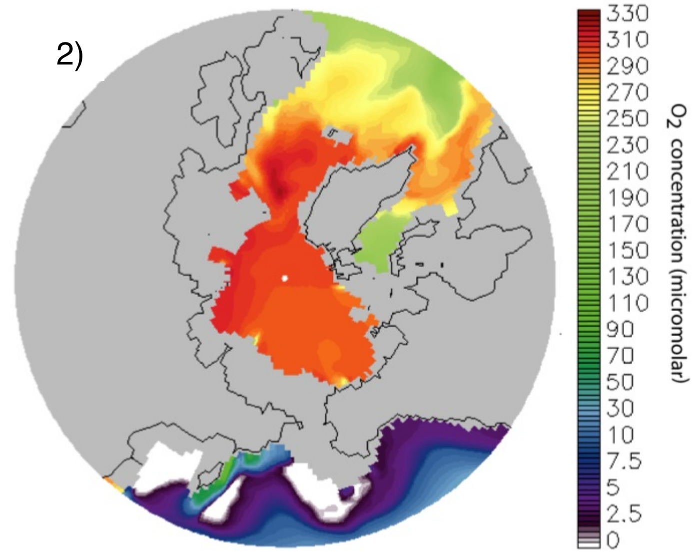

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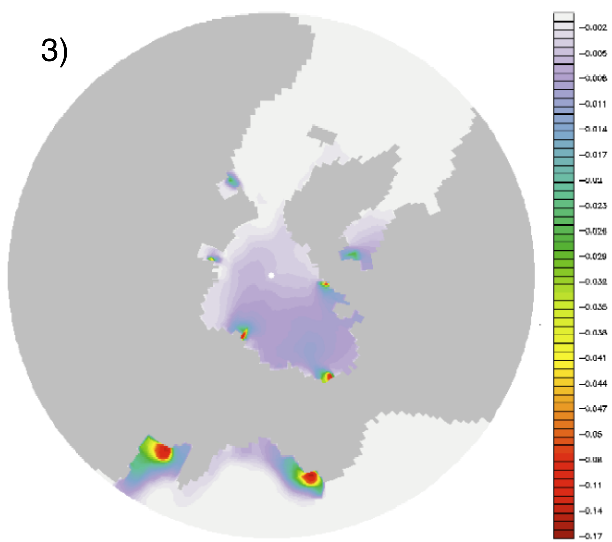

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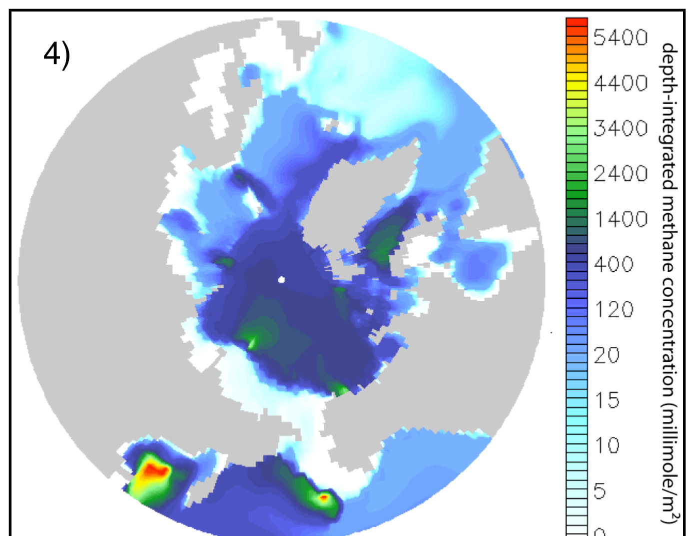

~60% Transfer to atmosphere!

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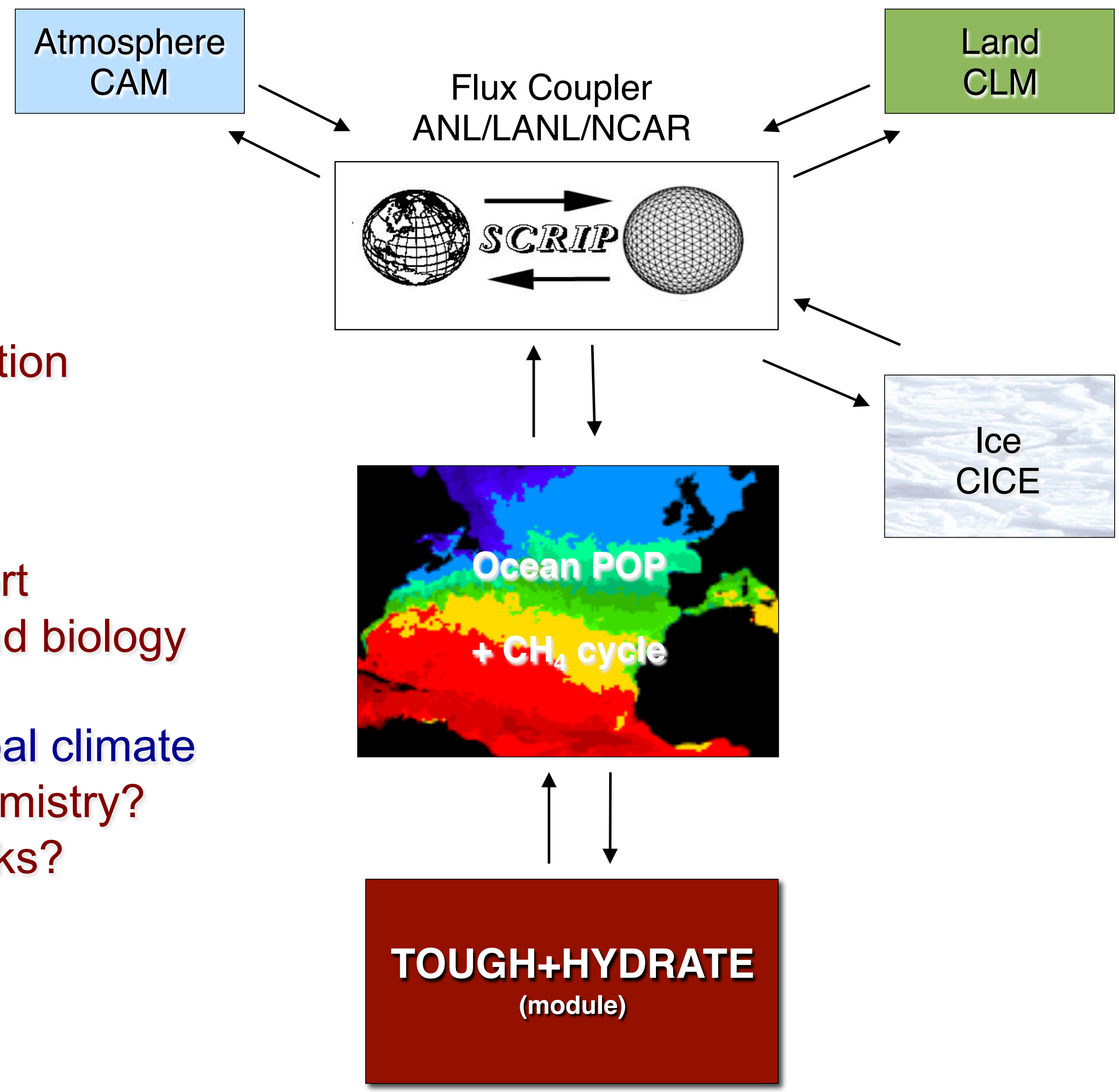

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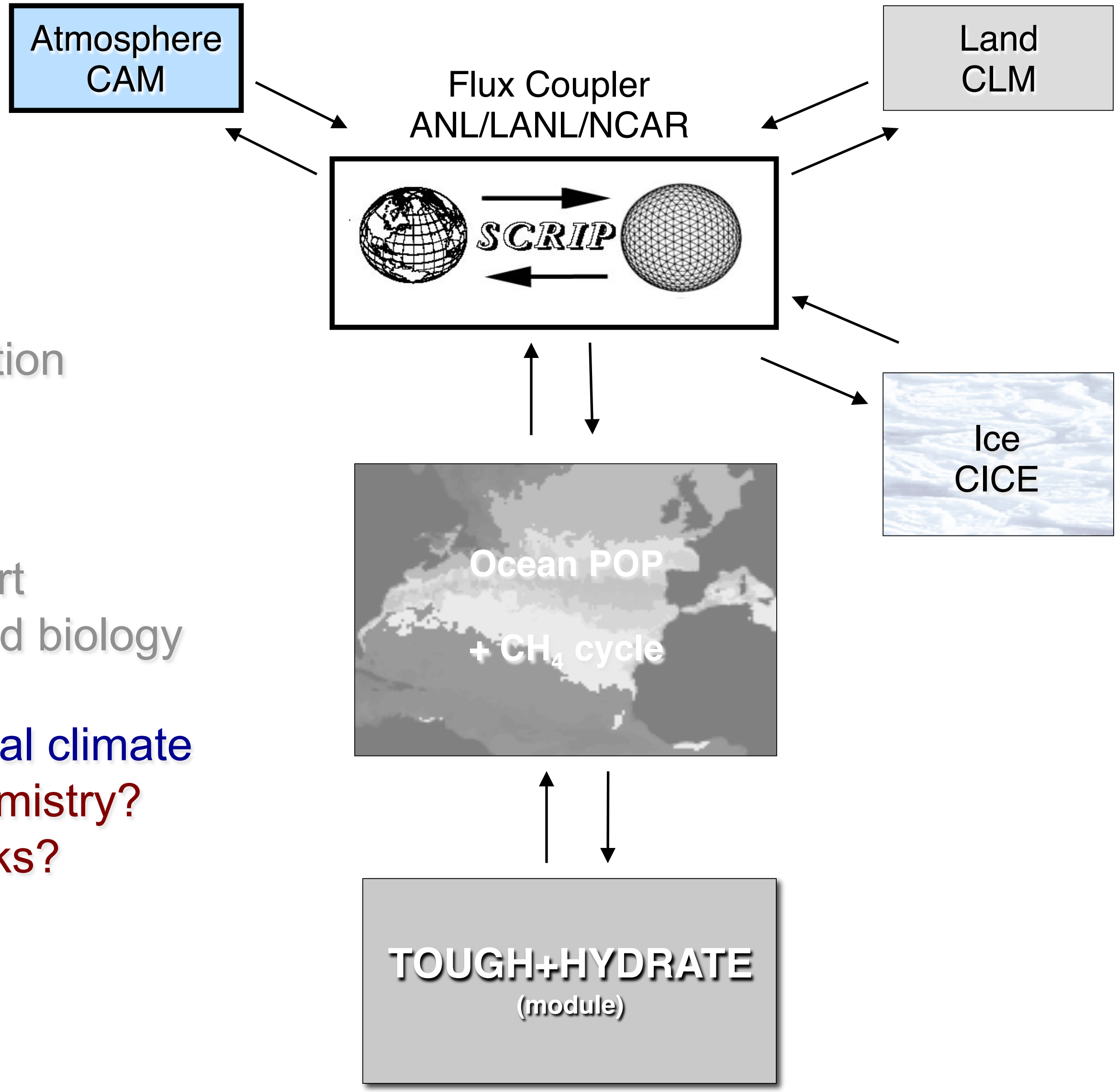
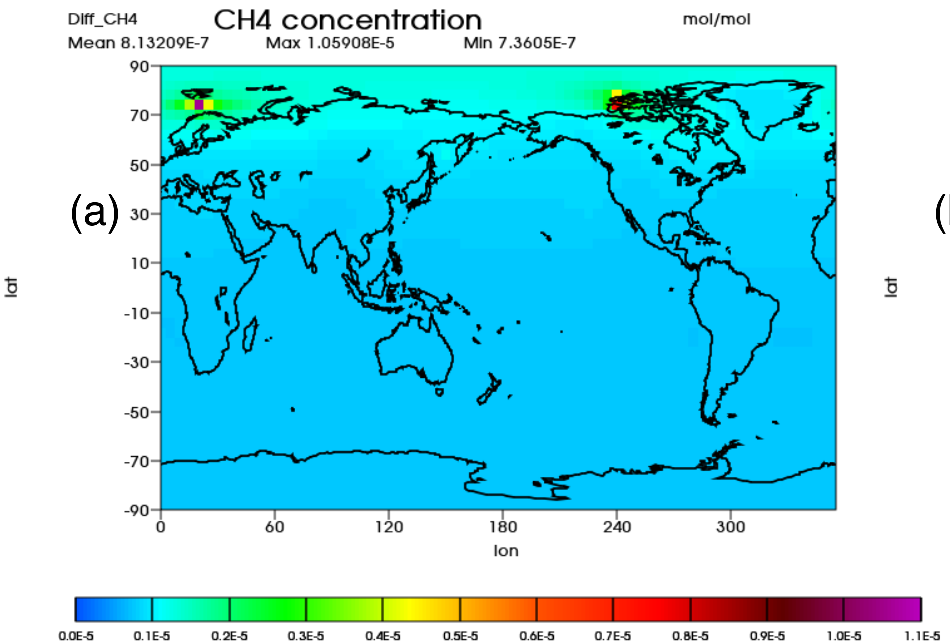
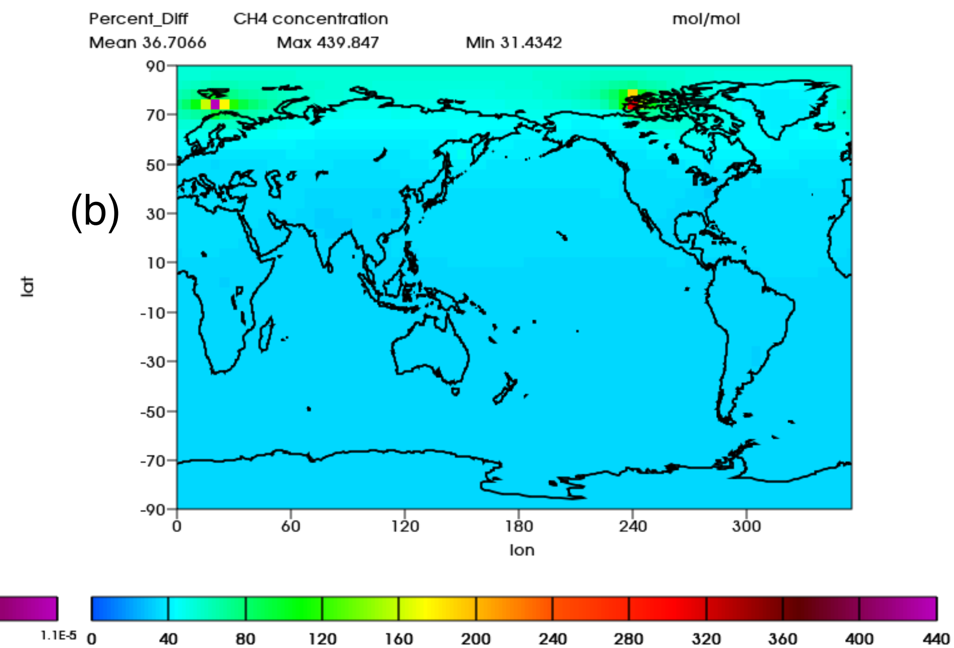


Coupled Atmospheric Chemistry

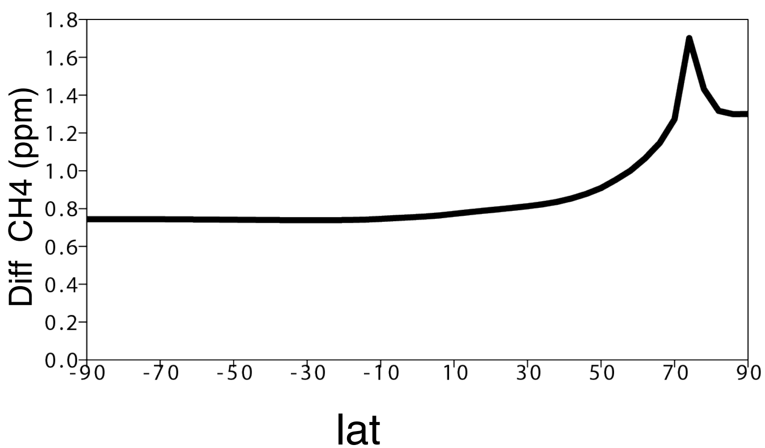
(a)



(b)



(c)



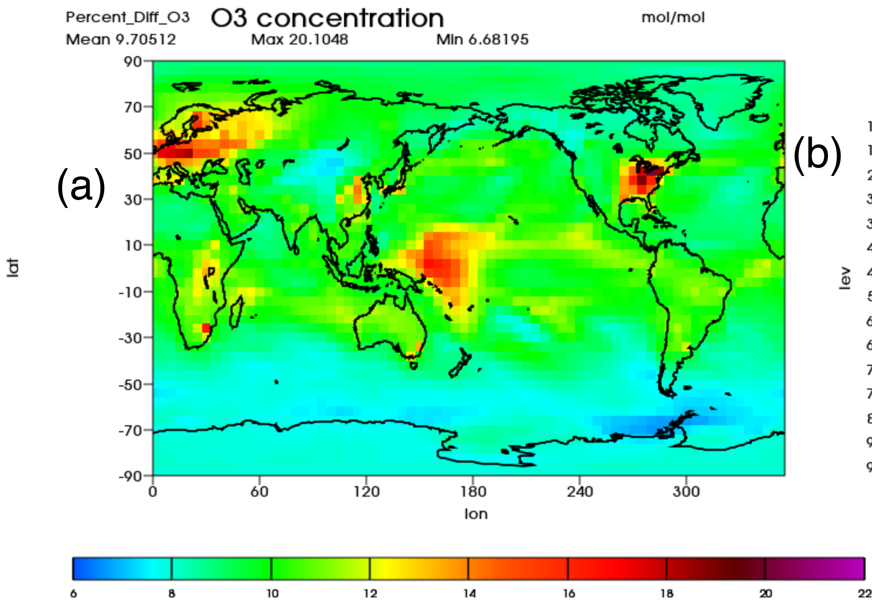
(a) Difference in surface CH_4 concentration relative to control

(b) Percent Difference in CH_4 concentration relative to Control

(c) Difference in surface CH_4, zonal mean

Coupled Atmospheric Chemistry

(a)



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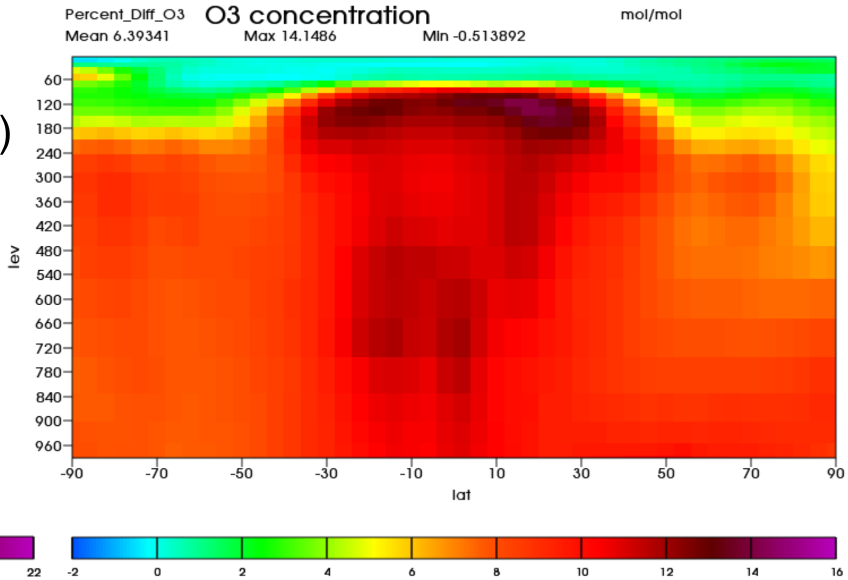
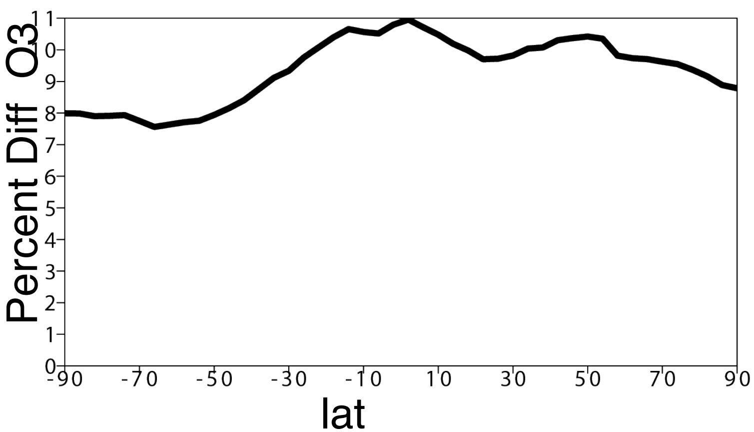


(c)



(a) Percent difference in surface ozone relative to control
(b) Percent difference in atmospheric ozone (zonal mean)
(c) Percent difference in surface ozone (zonal mean)

Interesting: ozone layer

Conclusions

- Shallow hydrates can release significant methane rapidly, but not explosively!

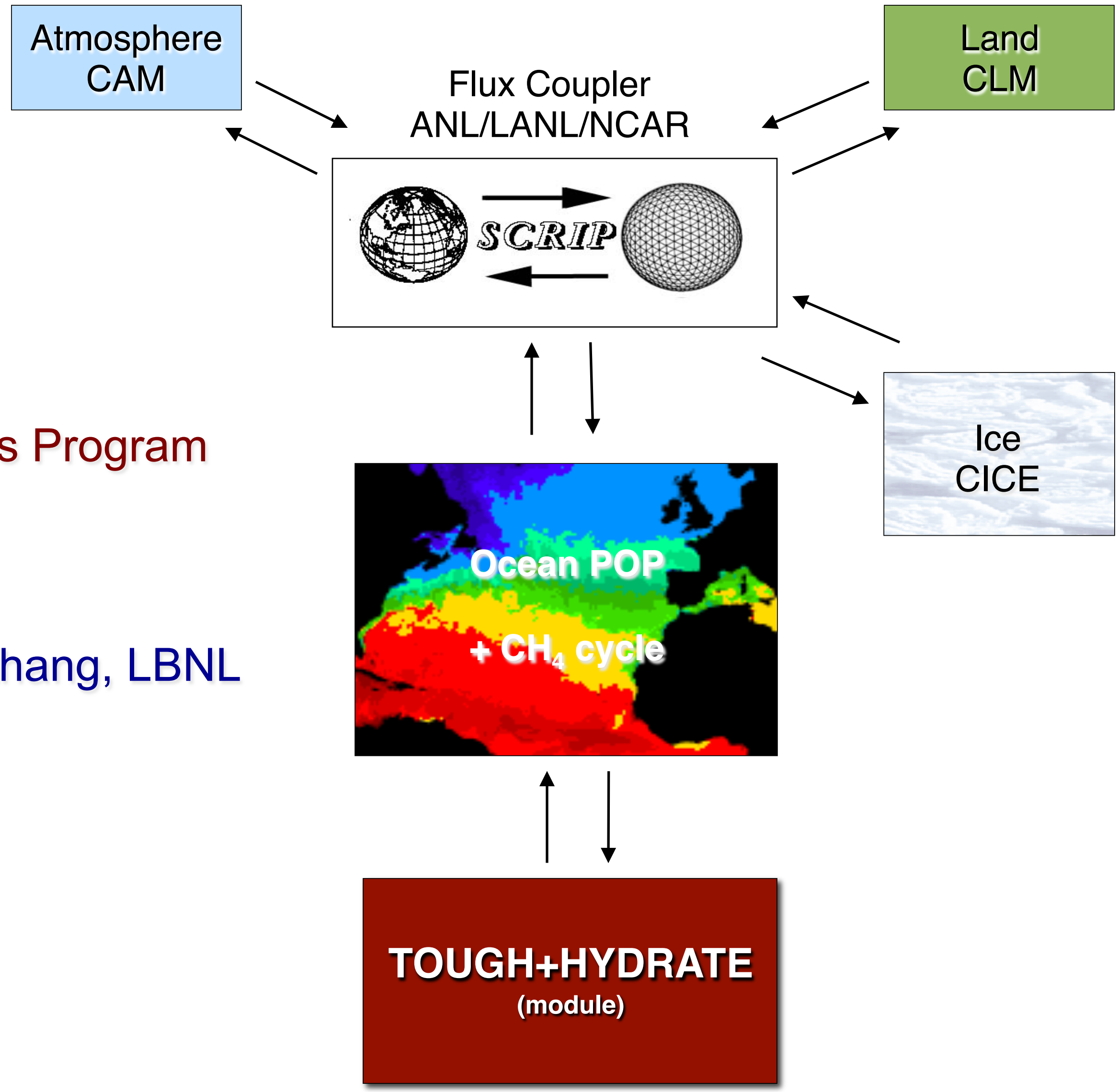
- The vast majority of deep hydrates are stable, in the short term, but the methane release potential is still large

- Methane is relevant to ocean (and atmospheric!) chemistry, not just as a contributor to total atmospheric CO_2
- Limited instability/release can feed biochemical/chemical changes in the ocean and atmosphere, before climate effects are considered
- Resource limitations overturn assumptions about methane oxidation

- New coupled seafloor-ocean-atmosphere calculations under way (with plume physics, extended biochemistry, higher resolution) leading to a coupled global model… and better estimates!

Conclusions

Wrap-up



Thanks to:

- DOE Methane Hydrates Program
- OBER-IMPACTS

- Katie Boyle and Keni Zhang, LBNL