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Estimates of the inventory and vulnerability of the methane hydrate reservoir in the ocean are based on a one-dimensional modeling formulation [*Davie and Buffett*, 2001] [*Bhatnagar et al.*, 2007; *Buffett and Archer*, 2004; *Reagan and Moridis*, 2007]. Methane is produced by in-situ respiration of organic matter or by diffuse upward fluid flow. Hydrate forms within the stability zone when pore water CH_4 concentrations exceed equilibrium, and it is ultimately buried deeply enough that the local temperature exceeds the melting temperature, driving the methane into the dissolved and possible gas phases.

We begin with a brief description of a representative one-dimensional model. The input factors that control the hydrate column model include water depth and temperature, and the depth-dependent rate of methane production, which itself depends on the concentration and reactivity of organic carbon in the sediment. Organic carbon concentrations in our formulation come from the Muds model of the early diagenesis reaction zone (the top meter of the sediment column) [*Archer et al.*, 2002]. Muds in turn is driven by organic carbon rain rates to the sea floor, based on a fit to observed sediment respiration rates as a function of depth [*Buffett and Archer*, 2004], and bottom water oxygen concentrations. Advection of the pore fluid has a strong impact on the abundance of methane, which collects in the sediment column. We have parameterized the advection of pore fluid as a binary function of margin classification, active or passive. The hydrate column model was run to steady state under conditions to fill a three-dimensional array of results, in the parameter space of water depth, ocean temperature, and bottom water oxygen concentration. The hydrate model is applied within regions of passive and active margins by interpolation into the results array using these parameter values (depth, T, O_2).

We assess the climate sensitivity of ocean hydrates using a climate system model CLIMBER-2 [*Ganopolski et al.*, 2001; *Petoukhov et al.*, 2000]. The model includes a 2.5-dimensional statistical-dynamical atmosphere with a coarse spatial resolution of 10° in latitude and 51° in longitude. The ocean consists of three zonally averaged basins with a latitudinal resolution of 2.5° and 20 unequal vertical levels. The ocean carbon cycle model includes an oceanic biogeochemistry model, with phosphate-limited biota [*Brovkin et al.*, 2002], and a deep-ocean carbonate sediment model [*Archer*, 1991]. The model is constructed to simulate the interactions between carbon and climate on multi-millennial time scales [*Brovkin et al.*, 2007].

ETOPO5 bathymetry is used to calculate the sea floor area associated with each ocean grid point in CLIMBER. The temperature and oxygen fields from CLIMBER are used to define an initial (steady-state) methane inventory for each location. As the ocean temperature evolves in a time-dependent simulation, the altered temperature field is used to calculate what the steady state methane inventory would be, given the deep ocean temperature lagged by 1000 years to account for the slow process of heat diffusion into the sediment column. When the sediment column warms, if the bubble volume fraction

of the pore space upon melting exceeds a critical value of 2.5% (a poorly known but critical parameter), then the sediment column is allowed to release enough methane to bring it to its warmer steady state inventory. We call this quantity "releasable methane". If the bubble volume upon melting does not exceed critical, the methane is retained in the sediment column. After the initial spin-up, changes in the ocean oxygen concentrations are not allowed to impact the hydrate inventory, because it takes millions of years for surface sediment to reach the methanogenesis zone. Similarly, we do not allow a buildup of methane in response to cooling, as for example in the period after the peak warming, because it takes millions of years for methanogenesis to supply methane.

The model was subjected to CO_2 emission scenarios of moderate (1,000 GtC) and large scale (5,000 GtC) taken from [*Archer and Brovkin*, 2007]. Simulations without methane release are labeled as Fossil Fuels in Figure 2. For each emission scenario, two extreme scenarios are considered, one with complete methane oxidation and consequent CO_2 dissolution in the water column, (hydrates as CO_2) and the other assumes that the released methane reaches the atmosphere, where it oxidizes to CO_2 with a ten-year time constant (hydrates as CH_4). In the later scenario, the radiative effect of methane is calculated in terms of an equivalent CO_2 concentration following Shin et al. [2003].

The model ultimately releases 450 Gton C of methane in response to 1000 Gton C of fossil fuels, or 600 Gton C of methane after 5000 Gton C of fossil fuels. For the first few thousand years of the simulations, the climate impact of the melting hydrate depends on whether methane gas reaches the atmosphere. Methane is released over a time period of several thousand years, warming the atmosphere by about 0.4-0.5 °C in response to either fossil fuel CO_2 release scenario. As the excess methane concentration decreases after a few thousand years, the accumulated CO_2 from methane oxidation, either in the ocean or in the atmosphere, acts to perpetuate a warming of about this same magnitude for the entire 10-kyr duration of the simulations.

The fundamental limitation to this calculation is that many of the processes that govern the distribution of methane hydrate in the ocean are more complicated than a one-dimensional modeling framework can capture. Bubbles of methane migrate horizontally through porous sediment layers such as sandy turbidites. Hydrate concentration at Blake Ridge seems highest at topographic highs, suggestive of subsurface bubble migration. Pore fluid flow is governed by processes in at least two dimensions, such as the pressure gradients associated with the continental slope [*Dugan and Flemings*, 2000] or an accretionary wedge [*Wang*, 1994].

The potential for methane escape is limited by several critical but poorly known parameters. First is simply the global inventory of methane below the sea floor. An estimate of the methane inventory made by computation in isolation would have little predictive power, because of the many poorly known parameters that go into such a calculation. However, a model that is as mechanistic as possible will provide some guidance in interpolation of sparse data into larger-scale inventories.

Second is the possibility or likelihood of methane escape from the sediment column in the event of hydrate melting. Gas migration through a porous medium is very sensitive to the volume fraction of the gas. If the fraction is too low, the gas migration will be limited

by capillary effects or by the viscosity of the fluid if bubbles are small enough to pass unimpeded through the sediments. (The viscosity of the fluid is a factor of 1000 smaller than the viscosity of the gas, the latter being relevant if methane gas forms an interconnected phase.) If only the most concentrated gas reservoirs escape to the ocean floor, then it is very important to simulate the distribution of hydrate into deposits of higher or lower concentration. A one-dimensional model formulation for hydrates neglects the type of deposits, such as on topographic highs or as focused by subsurface porous channels, where hydrate is present at highest concentrations [*Dallimore and Collett*, 2005; *Trehu et al.*, 2004a].

Organic carbon concentrations deep in the sediment column are implicitly inferred from the concentration in the surface sediments, neglecting the possibility that the sea floor may have been at a different depth millions of years ago, when the sediments in the current methanogenesis zone were originally deposited. The availability and flux of methane from deeper in the sediment column requires knowing something about the temperature and hence the depth of the sediment column.

One-dimensional modeling formulations were a good place to start with modeling hydrates, because much of the variability in hydrate concentration is indeed governed by overlying ocean temperature and sediment surface organic carbon concentrations. However, when looking at the real world, more and more of the hydrate reservoir seems to consist of "special cases" for which one-dimension is inadequate.

We propose to develop a two-dimensional, basin scale model for the deep sediment biosphere with methane dynamics. The model would be the next step toward integrating methane hydrates into the global carbon cycle, by giving us a better picture of the distribution of hydrates on the sea floor, and their vulnerability to warming of the deep ocean. The model would be used to simulate four archetype regions of the world's ocean: the Atlantic passive margin of the U.S. east coast, exemplified by Blake Ridge, an accretionary wedge system exemplified by Hydrate Ridge, the Arctic shelf and slope system, and the Gulf of Mexico.

A preliminary demonstration version of the model has been built and will be described here with preliminary results. The model is formulated on an arbitrarily-spaced depth and distance coordinate system. The vertical coordinate can follow the depositional layers of a system undergoing sediment accumulation, the layers draping over each other and ultimately over an arbitrarily time-varying depth of bedrock. The horizontal coordinate system can be manipulated in a time-dependent way to simulate uniform thickening of the sediment column, as in an accretionary wedge.
Fluid flow follows Darcy's law in response to the pore fluid excess pressure gradient. The pressure formulation of the model is based on a constitutive equation in which the excess pore fluid pressure can be calculated from the porosity [*Athy*, 1930; *Rubey and Hubbert*, 1959]. Surface sediments have very high porosity, but as they become buried, they undergo greater loading from the sediment column above, and the excess pressure drives the fluid out, allowing the sediment column to relax toward the porosity at which the sediment is able to bear the lithostatic load. Currently the porosity / pressure

relationship is treated as reversible in the model, but we plan to distinguish an "unloading" porosity / pressure pathway [*Audet and Fowler*, 1992] which would apply in the case of hydrate melting to produce bubbles which increase the overall porosity of the sediment.

Organic carbon concentrations are predicted as a function of water depth and a water column O_2 concentration. The current model configuration has a uniform "bioavailable fraction" (25%) of the organic carbon concentration fermenting to produce H_2, at a rate which increases by a factor of 3.5 for each 10 °C of warming, until rates fall at temperatures near 50 °C [*Conrad and Schuetz*, 1988]. The H_2 either reduces SO_4^{2-} if it is available or it produces CH_4 from CO_2 if SO_4^{2-} is depleted [*Hoehler et al.*, 1998]. Thermogenic methane is produced at temperatures of 80 – 120 °C, acting on the entire carbon content of the sediment, not just the bio-available fraction. The time constants for biogenic and thermogenic organic carbon degradation are currently determined, by model tuning to the methane and organic carbon distributions, to values of 300 million years and 30 million years, respectively. The model simulates isotopic fractionation of carbon and hydrogen isotopes in methane and dissolved inorganic carbon by treating parallel tracers for the different isotopes, with specified fractionations at key chemical transformations, following [*Whiticar*, 1999]. Alkalinity and $CaCO_3$ production will provide further comparison points with deep sea porewater data.

The model can simulate a 25 by 25 point grid over a time scale of 10 million years in a few hours or a day of computer time. One of the early tasks of the project will be to implement message-passing parallelism using MPI, partitioning the model domain in the horizontal, to facilitate interactive model development and higher-resolution simulations. We have experience writing and debugging MPI parallelism on our linux cluster equipped with Myrinet networking hardware for fast, low-latency message-passing computation.

There are several important barriers that must be overcome in this research. First, many of the relevant physical processes are poorly understood. By greatly expanding the list of geophysical and geochemical parameters that are predicted and compared with observations, we expect to constraint these poorly understood processes using all available data. We also explicitly account for structure differences between the major archetype scenarios and include a representative geological history for each region. These additions should improve our ability to compare physical processes across the different regions.

The modeling effort described here will improve our understanding of hydrates in the natural environment. Specifically, we expect to improve our estimates of the hydrate inventory, including both the spatial distribution and local concentration. This information is essential for predicting the response of hydrate to climate change. Inventory estimates are also important for assessing the economic viability of gas hydrate as a hydrocarbon resource. We also expect to improve our understanding hydrates as a component of the deep carbon cycle. Deliverables from this project include maps of the hydrate inventory and the locations that are most vulnerable to future climate change. We

will also make all of the observations we use to constrain the model and will make the computer codes available to other researchers.