Transport - reaction modeling of marine gas hydrate deposits - global results

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Introduction

We have developed a multi-1D numerical model of gas hydrate formation and dissolution processes in anoxic marine sediments and, by this model, we have estimated the new global gas hydrate inventory (BURWICZ E. B. et al., 2011). The reaction-transport model contains various chemical compounds (solid organic carbon, dissolved methane, inorganic carbon, and sulfates, gas hydrates, and free methane gas). The rates of POC degradation, anaerobic methane oxidation, sulfate reduction, and methanogenesis are kinetically controlled. Gas hydrate stability zone (GHSZ) is defined as a combination of pressure, temperature, and (to a smaller degree) salinity conditions. The lower boundary of the GHSZ is defined as the intersection of gas hydrate and methane gas solubilities.
The diffusion equations are solved using a fully-implicit finite-differences method, while all transport processes are resolved by a Semi-Lagrangian scheme. Global input data sets ($1°x1°$ resolution) were compiled from various oceanographic, geological and geophysical sources. The entire model was implemented in Matlab.

Numerical model

Reference frame
We consider a reference frame which extends from the seafloor to the bottom of the GHSZ plus 50m of Free Gas Zone lying directly beneath. This implies that the spatial location of the upper boundary is fixed and does not follow sediment burial which results in a net downward migration of deposited sediments. This fixed lower boundary results in the advective loss of system components through the bottom of the modeling domain.

Boundary and initial conditions
We assume constant concentrations of dissolved chemical species on top of sediment column. Burial velocities at zero depth (w_0) are functions of water depth (Holocene simulation). In a second set of model runs (Quaternary simulation), w_0 values are enhanced along continental margins. Sediment pore space was initially filled by pore fluids of a constant salinity. According to multi-1D approach, pressure regimes are calculated separately for each sediment bin as hydrostatic values considering ambient water and sediment depths. Temperature profiles are set according to the bottom water temperature and heat flow data.

Compaction and advection velocities
Sedimentation and compaction processes imply, in the chosen reference frame, a continuous downward movement of sediment grains with respect to the seafloor (Eq. 1):

$$w(z) = \frac{-w_0(1-\phi_0)}{(1-\phi)} \tag{1}$$

Sediment compaction results in pressurization and expulsion of pore fluids carrying dissolved chemical species which allows us to use an analytical expression (Eq. 2) for pore fluid flow:

$$\upsilon(z) = \frac{-w_0(1-\phi_0)\cdot\exp(z-B/\lambda)}{1-\phi_0\cdot\exp(-B/\lambda)} \tag{2}$$

Basement of each sediment column (B) from the fluid velocity equation was set to a value adequate for depths where porosity reaches the level of 20 % and thus, compaction processes become negligible.

Governing equations for solid and dissolved compounds
Two major phases essential for hydrate formation were considered: pore fluids containing chemical species and solids including sediment grains and POC. Transport of both phases was solved as an advection process occurring via sediment burial with solid (w) and fluid (υ) velocities. Source terms contain time and depth-dependent rates of chemical reactions. Eq. 3 describes mass conservation of solid species, whereas Eq. 4 stands for mass conservation of solutes:

$$(1 - \varphi) \cdot \frac{\partial G}{\partial t} = -\frac{\partial((1-\varphi) \cdot w \cdot G)}{\partial z} + (1 - \varphi) \cdot R \tag{3}$$

$$\varphi \cdot \frac{\partial C}{\partial t} = -\frac{\partial(\varphi \cdot \upsilon \cdot C)}{\partial z} + \frac{\partial(\varphi \cdot D_s \cdot \frac{\partial C}{\partial z})}{\partial z} + \varphi \cdot R \tag{4}$$

Source terms
A key reaction is the degradation of organic matter (POC) which follows the kinetic approach developed by Wallmann (WALLMANN K. et al., 2006) which assumes the decrease in organic matter reactivity with depth and age of sediments. POC is degraded via microbial sulfate reduction until the dissolved sulfate pool in ambient pore waters is depleted. Below the sulfate penetration depth, POC is microbially decomposed into methane and CO_2. Upward diffusing dissolved methane is consumed by anaerobic oxidation within the sulfate-methane transition zone.

Results and discussion

The total amount of methane carbon from hydrates is estimated to be ~8.3 Gt (low sedimentation scenario, Holocene boundary conditions) and ~900 Gt C (equivalent to ~2 x 10^{15} m^3 CH$_4$ (STP), high sedimentation scenario, Quaternary boundary conditions).

Distance to continents	Total area covered by margins	Total amount of hydrates
Quaternary boundary conditions:		
400 km	89.347 million km^2	959 Gt C
500 km	106.70 million km^2	819 Gt C
Holocene boundary conditions		8.3 Gt C

Tab. 1: Gas hydrate accumulations under Holocene and Quaternary boundary conditions

Comparatively, the world's conventional gas endowment estimated at 2.567 TBOE (Trillion Barrels of Oil Equivalent), equivalent to 436.4 x 10^{12} m^3 of natural gas (USGS WORLD ENERGY ASSESSMENT TEAM, 2000), is at least a few times smaller than the global inventory calculated in our Quaternary simulation.

References

Burwicz E. B., Rüpke L. H., and Wallmann K., 2011. Estimation of the global amount of submarine gas hydrates formed via microbial methane formation based on numerical reaction-transport modeling and a novel parameterization of Holocene sedimentation. *Geochimica et Cosmochimica Acta*.

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