



New global estimates of marine gas hydrate accumulations based on POC degradation and reaction-transport modeling

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This study provides new estimates for the global methane hydrate inventory based on reaction- transport modeling. A multi-1D model for POC degradation, gas hydrate formation and dissolution is presented. The novel model contains an open three-phase system of two solid (organic carbon, gas hydrates), three dissolved (methane, sulfates, inorganic carbon) and one gaseous (free methane) compounds.

The model computes time-resolved concentration profiles for all compounds by accounting for chemical reactions as well as diffusive and advective processes. The reaction module builds upon a kinetic model of POC degradation based on the approach of Wallmann K. et al., 2006. Various chemical reactions such as organic carbon decay, Anaerobic Oxidation of Methane, methanogenesis, and sulfate reduction are resolved using time and space dependent kinetic constants. The solid (and gaseous) phase is buried via sediment deposition and compaction. Fluid expulsion from compacting sediments results in a relative upward migration of dissolved species with respect to the solid phase. Chemical species dissolved in pore waters are able to diffuse through entire sediment profile adequate to their molecular diffusion coefficients. Gas hydrate and free gas formation occur if the concentration of dissolved methane exceeds the pressure, temperature, and salinity-dependent solubility limits of hydrates and/or free gas.

Global input grids have been compiled from a variety of oceanographic, geological and geophysical data sets. Bathymetry, bottom water temperatures and salinities are extracted from an Ocean Circulation Model (OCM) simulation run in the ORCA_R025 configuration (Barnier B. et al., 2006) and represent a combination of ETOPO1 and GEBCO data sets. Geothermal gradients are based on the heat flow database provided by International Heat Flow Commission (IHFC). Sediment thicknesses are implemented according to NOAA data. Global TOC distribution is compiled from wide range of sediment cores data from Seiter K. et al., 2004.

We find that the global distribution of methane hydrates does not correlate in a simple way with the thickness of the hydrate stability zone but is a complex function of all input and model parameters. Prominent gas hydrate provinces are found offshore Central America where sediments are rich in organic carbon and in the Arctic Ocean where low bottom water temperatures stabilize methane hydrates. Our new total estimates of the world's marine hydrate inventory formed due to POC degradation give a number of $\sim 3 \times 10^{15} \text{ m}^3$ of CH_4 (at STP conditions). These findings are in good agreement with previous studies based on direct observations (Milkov A. V., 2004) and show that numerical modeling is a valuable tool for studying the worldwide distribution of methane hydrates.

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Seiter K. et al., 2004. Organic carbon content in surface sediments-defining regional provinces. *Deep-Sea Research I* **51**, 2001-2026.

Wallmann K. et al., 2006. Kinetics of organic matter degradation, microbial methane generation, and gas hydrate formation in anoxic marine sediments. *Geochimica et Cosmochimica Acta* **70**, 3905-3927.