Main controls on gas hydrate deposits
in marine environment - development
and application of numerical models

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Dean
I hereby confirm that apart from the supervisor’s guidance the content and design of the essay is all my own work. The thesis has not been submitted either partially or as part of a doctoral degree to another examining body. Some parts of the thesis have been published as scientific papers in the international scientific journals as indicated at the beginning of each chapter. The thesis has been prepared subject to the Rules of Good Scientific Practice of the German Research Foundation.

Kiel, 10.06.2015

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ZUSAMMENFASSUNG

Abstract

This study investigates the controlling parameters and processes of gas hydrate formation, preservation, and dissolution in marine sediments on global and regional scales using newly developed and applied numerical simulation tools. The main motivation for this work was 1) the absence of converging estimates on global gas hydrate deposits in marine environments and their fate under global warming, 2) the lack of basin-scale studies resolving for gas hydrate formation and dissolution processes in environments experiencing salt tectonics, tectonic faulting, and rapid sedimentation, and 3) a need to develop a multi-phase numerical model that uses an adaptive mesh approach coupled with biochemical reaction solvers in order to account for local sediment heterogeneity and fluctuations in depositional regimes affecting gas hydrate formation. The outcome of this work is relevant for new global gas hydrate assessment (estimated here at ~1,000 Gt C from in-situ CH₄ formation) and climate studies investigating the fate of gas hydrates under global warming. Our results suggest that ~140-410 Mt C and ~54 Mt C will be released within the next 500 years from the Arctic and the Blake Ridge regions, respectively affecting the carbon balance between marine sediments and the ocean-atmosphere coupled system. However, a total reduction in gas hydrate volume will not exceed 0.03% within the next 100 years. Volumetric rates of deep methane fluxes responsible for gas hydrate and free gas co-existence within the gas hydrate stability zone (GHSZ) of the Blake Ridge sediments were estimated at 1.6·10⁻¹¹ kg s⁻¹ m⁻² (CH₄ mass flux). A basin-scale gas hydrate/free gas recycling process at the base of the GHSZ (2.6 Ma - present), which leads to high (>80 vol. %) gas hydrate saturations in the Green Canyon region of the Gulf of Mexico, was identified by 3D numerical simulation. Finally, the global volume of microbial habitat available for microorganisms was estimated at 3.04·10⁸ km³ of marine sediments and 8.10⁻⁷ km³ of sedimentary pore water. Moreover, we concluded that the rate of organic matter biodegradation within the sub-oceanic sediments oscillates at ~361 T C yr⁻¹ for Holocene and ~11 Tg C yr⁻¹ for Pleistocene.
EXTENDED ABSTRACT

Gas hydrates (also known as clathrate hydrates) are crystalline ice-like solid compounds containing gas molecules (also called a guest molecule) locked within the water cage-like structure (host structure). Guest molecules, of which the most common is methane, are stabilizing the already existing hydrogen-bonded water molecules to form a gas hydrate. Due to their physicochemical composition, gas hydrates are very sensitive to pressure, temperature, and, to a smaller degree, salinity changes. The stability field of gas hydrate (commonly called as the Gas Hydrate Stability Zone- GHSZ) within marine sediments is predominantly present in low-temperature and high-pressure regions (e.g. high-latitude areas), whereas the occurrence of gas hydrates depends strongly on the supply of gas. Dynamic response of gas hydrate deposits to rising bottom water temperatures which might lead to shrinkage of the stability zone resulting in immediate dissociation, poses questions about sub-seafloor and slope stability, as well as the potential gas hydrate impact on global climate change in both past geological epochs and in the future.

Since many anticipated prominent gas hydrate deposits are not available for drilling and direct sampling, it is essential to broaden our knowledge by using numerical modeling tools. State-of-the-art numerical tools not only allow for precise stability calculations and for investigating gas hydrate dynamic behavior in porous media but also provide biochemical reaction solvers which help to understand the role of e.g. anaerobic methane oxidation (AOM) and its impact on gas hydrate distribution within marine sediments. These tools can be further used to extrapolate our knowledge into the regions not available for direct scientific campaigns and thus, give preliminary answers to some of the major questions in the gas hydrate research: how much is still out there? How are they responding to the changing climate? What are the rates of current seafloor methane release due to the melting hydrates? How much is accessible for the potential gas recovery?

To evaluate global amounts of gas hydrates stored within marine settings, a complex global modeling approach is needed. Previously suggested numbers did not converge into a clear
picture and were derived from variety of sources (e.g. region-to-region extrapolation, theoretical investigations). By constructing a new multi-1D Finite Differences (FD) model based on consistent global data sets and a new parameterization of Holocene sedimentation rates, we were able to conclude that global gas hydrate accumulations contain a minimum of about 1000 Gt C formed by only in-situ microbial methane production (Chapter 1). Due to the presence of gas hydrate deposits formed by methane-rich pore fluids and free methane gas ascending to the Gas Hydrate Stability Zone from great depths (e.g. Hydrate Ridge, offshore Oregon situated on the active continental margin), this number should be considered as a minimum estimate of the total gas hydrate storage.

To better understand the dynamic interplay between gas hydrates and free gas phases, a new 1D multi-phase Finite Elements (FE) model was designed to investigate the potential of gas hydrate formation from mixed sources of methane at the Blake Ridge province, offshore South Carolina (Chapter 2). It has been confirmed in the course of this study that compaction-driven fluid flow only is, most likely, not sufficient to create measured gas hydrate concentrations and therefore, free gas migration through the GHSZ is necessary to explain observed gas hydrate concentrations. Modeling scenario being the closest to reproduce exact parameters determined at the Site (e.g. P-T conditions, compaction curve, rate of seafloor pore fluid expulsion, and geochemical species gradients) assumes pore fluid entry mass of 5.9·10^{-9} \text{ kg s}^{-1} \text{ m}^{-2} (1.6·10^{-11} \text{ kg s}^{-1} \text{ m}^{-2} of \text{ CH}_4) through the lower boundary of modeling domain and results in seafloor net pore fluid velocities of about 6.3·10^{-12} \text{ m s}^{-1}, gas hydrate and free gas concentrations of 3.8 – 4.4 vol. % and 7.3 vol. %, respectively which stays in a good agreement with the measured data and suggests a potentially mobile free gas phase being actively transported upwards into the GHSZ.

Accounting for local geological features such as sedimentary layer discontinuities, tectonic faults and spatial sediment heterogeneity was always challenging in numerical modeling of complex gas hydrate provinces. Previously published modeling studies were suffering from a lack of a regional context of pore fluid and gas migration on the basin scale which
strongly limited interpretation of the results and comparison to the existing data acquired via borehole drilling, pore water sampling and seismic studies. To analyze a full-scale complexity of the Green Canyon gas hydrate province, Gulf of Mexico, we have constructed a 3D numerical model using the PetroMod™ software by Schlumberger that covers roughly 32 km by 14 km modeling domain (X- and Y- direction) extending vertically from the present-day seafloor down to the Jurassic basement (about 14,500 meters below the sea-level with water depth oscillating around 2,000 meters). As a result, we were able to investigate gas hydrate-related processes such as: thermogenic gas generation at great depths and its further migration towards the GHSZ, gas hydrate formation due to gas hydrate-free gas recycling process at the base of the GHSZ throughout the history of the basin, salt tectonics and associated thermal phenomena in sediments (Chapter 3). As a result, numerically-obtained present-day gas hydrate resources estimated by this study fully correlate with well data in the region and provide important insights on sub-salt gas migration pathways and their influence on gas hydrate formation in the supra-salt Pleistocene reservoir sediments.

Due to high sensitivity of numerical modeling approaches to the starting parameters, modeling techniques, and the variety of commonly accepted mathematical formulations describing marine sedimentary basins, a comprehensive study on gas hydrate formation controls including the CH₄ solubility limits, seafloor organic matter availability, sediment compaction, GHSZ thickness, fluid and gas bubble ascent, rates of methanogenesis and kinetics of gas hydrate formation was conducted (Appendix 1). Moreover, it has been concluded that over 44×10⁶ km³ of pore water is trapped within the present-day marine stability zone of gas hydrates. A total inventory of gas hydrates derived from this study suggests that more than minimum 455 Gt C is presently stored within sub-oceanic sediments which combined with, presented here, estimation on the Holocene seafloor accumulation rates of about 140 Tg C yr⁻¹ serves a base for further investigation on the evolution of currently present world-wide gas hydrate deposits. Furthermore, this study
contributes to the discussion on the potential co-existence of dissolved and gaseous form of methane within the GHSZ and its potential release to the oceanic system.

In the context of seafloor methane seeps and venting structures commonly observed at continental margins, it is important to look precisely at the potential response of melting gas hydrate deposits to the climate change. Two modeling examples of regional (high-latitude Arctic region; Appendix 2) and global (Appendix 3) response to anthropogenic warming are presented here. Using ocean circulation climate model coupled with rates of GHSZ shrinking led towards the conclusion of rather limited methane gas release within the next hundred years from melting hydrate deposits in the Arctic region with a rate of about 162 Mt CH$_4$ per year (see Appendix 2) which remains lower than the present anthropogenic methane input to the atmosphere. As a comparison, global study of potential methane release performed by detailed transient temperature analysis confirms a minor impact of the global climate change on the total gas hydrate inventory suggesting a reduction of about 355 ± 23.5 Mt C within the next 100 years (see Appendix 3) out of the total 1146 Gt C estimated therein. Additionally, a detailed response of certain oceanic regions to global warming of bottom waters suggest that the Blake Ridge site, offshore South Carolina, and the Arctic will be the mostly affected ones with gas hydrate accumulations reduced within the next 500 years by 54 ± 5 Mt C, and between 140 and 410 ± 30 Mt C, respectively.

Taking into account the important role of microbial organisms in methanogenic processes in oceanic settings, there was a need to estimate the volume of marine sediments acting as habitat for microorganisms and the rates of microbial activity (Appendix 4). Based on combined data sets of sediment thickness, heat flow and bottom water temperatures, it is suggested that about 3.04·10$^8$ km$^3$ of sub-oceanic global marine sediments is presumably available for microorganisms to live. Moreover, the total volume of sedimentary pore water was estimated as 8.10·10$^7$ km$^3$ which exceeds the one of the Southern Ocean. Despite the fact that the life extent in marine sediments is extremely difficult to estimate, it is known that activity levels of microbes strongly depend on temperature ranges. Although there are
examples of microbes being active in extreme temperatures (laboratory microbial growth stays within the temperature range of -15 to 122°C, however, microorganisms have been found in more extreme environments of -196°C or >250°C) and settings (e.g. highly toxic, anoxic), most of their activity falls into a moderate temperature range of 0 - 20 °C to 40 - 60 °C. Keeping that in mind, we give a number of $1.76 \times 10^8$ km$^3$ of marine sediments (58 % of the total) within temperature range of 0 – 40°C available for appropriate microbial habitation and remaining $1.28 \times 10^8$ km$^3$ lying within >40°C limit (42 % of the total). Availability of organic carbon as a driving force for microbial activity was calculated with reactive-continuum model. It was concluded that the rate of organic matter biodegradation within the sub-oceanic Holocene sediments oscillates around 361 T C yr$^{-1}$. On the contrary, the rate of OM degradation in thick and more abundant Pleistocene sediments was estimated at only 11 Tg C yr$^{-1}$ which gives important perspective on the marine carbon cycle and the rates of microbial activity therein.
CONTENTS

Zusammenfassung..............................................................................................................VII

Abstract ..........................................................................................................................IX

Extended abstract .........................................................................................................XI

Contents .........................................................................................................................XVII

List of Figures ................................................................................................................XXIII

List of Tables ................................................................................................................XXVII

Introduction ..................................................................................................................XXIX

   Motivation ..................................................................................................................XXIX

   State-of-the-art in gas hydrate research ...................................................................XXXII

      History and early experiments .............................................................................XXXII

      First in-situ deposits and global perspective ......................................................XXXIII

      New technologies – numerical modeling ..............................................................XXXVII

   Outline of the Thesis ..................................................................................................XLIII

References ......................................................................................................................XLV

Chapter 1: 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 ..............................................................1

   Abstract ......................................................................................................................1

1. Introduction ................................................................................................................2

2. Input data ..................................................................................................................4

3. Mathematical model ................................................................................................9

   3.1. Introduction .......................................................................................................9

   3.2. Reference frame ...............................................................................................10

   3.3. Compaction and advection velocities ..............................................................11

   3.4. Governing equations for solid and dissolved compounds ................................14

   3.5. Reactions .........................................................................................................16

4. Gas hydrate and free gas formation .........................................................................18

5. Numerical procedure ...............................................................................................21

6. Results and discussion ............................................................................................22

   6.1. Global gas hydrate distribution .......................................................................22

   6.2. Controls on gas hydrate formation ..................................................................27

7. Conclusions ..............................................................................................................29

Acknowledgments ........................................................................................................31

Appendix A. Supplementary data ................................................................................31

XVII
## Contents

References......................................................................................................................... 34

**Chapter 2: A new numerical solver for a multiphase flow at marine porous sediments—new application and insights on gas hydrate formation and free gas co-existence from the Blake Ridge Site** ................................................................. 39

Abstract.............................................................................................................................. 39
Introduction.......................................................................................................................... 40
Mathematical model.......................................................................................................... 43
  Introduction...................................................................................................................... 43
  Governing equations........................................................................................................ 44
  Source terms – bio-chemical reactions........................................................................... 51
  Temperature...................................................................................................................... 53
Numerical model................................................................................................................. 54
  Reference frame.............................................................................................................. 54
  Initial conditions.............................................................................................................. 57
  Solution algorithm.......................................................................................................... 58
Blake Ridge Site 997 description....................................................................................... 59
  Geological setting............................................................................................................ 59
  Co-existence of gas hydrates and free gas at Site 995 and 997...................................... 60
Site 997 characterization.................................................................................................... 62
  Previous numerical modeling approaches of the Blake Ridge Site 997......................... 64
  Modeling scenarios for the Blake Ridge Site 997........................................................... 66
Results and discussion........................................................................................................ 68
Conclusions........................................................................................................................ 79
References.......................................................................................................................... 80

**Chapter 3: New gas hydrate and free gas estimates from Green Canyon Site, Gulf of Mexico, based on basin-scale multiphase modeling** ................................................................................. 85
Abstract.............................................................................................................................. 85
Introduction.......................................................................................................................... 87
  Geological setting and basin evolution........................................................................... 87
  Stratigraphy....................................................................................................................... 89
  Salt tectonics and related faulting systems...................................................................... 91
  Presence of gas hydrates................................................................................................. 93
  Petroleum geology of the region..................................................................................... 95
  Source rock locations and characterization................................................................... 95
Modeling approach.............................................................................................................. 96
  Introduction...................................................................................................................... 96
Input parameters ...................................................................................................................... 97
Surface maps and age assignment ......................................................................................... 97
Lithology, facies definitions and sediment properties .......................................................... 99
Salt tectonics ......................................................................................................................... 101
Faults ..................................................................................................................................... 102
Boundary conditions ........................................................................................................... 103
Simulation .............................................................................................................................. 106
Migration method .................................................................................................................. 106
Gas hydrate formation from biodegradation module ............................................................. 107
Hydrocarbon generation kinetics .......................................................................................... 108
Results .................................................................................................................................. 108
Burial history ......................................................................................................................... 108
source rocks productivities and hydrocarbon generation ...................................................... 110
Predicted gas hydrate accumulations .................................................................................... 112
Uncertainties ......................................................................................................................... 116
Conclusions ........................................................................................................................... 118
Acknowledgments ............................................................................................................... 119
References ............................................................................................................................. 120

Summary and conclusions .................................................................................................... 123

Appendix 1: The Global Inventory of Methane Hydrate in Marine Sediments: A Theoretical Approach .................................................................................................................. 127
Abstract ................................................................................................................................ 127
1. Introduction ......................................................................................................................... 128
2. Accumulation of particulate organic carbon at the seafloor .............................................. 128
   2.1. Holocene POC accumulation rates ............................................................................. 129
   2.2. Quaternary POC accumulation rates ....................................................................... 132
   2.3. Cenozoic – Cretaceous POC accumulation rates ...................................................... 133
3. Microbial degradation of organic matter and methane formation in marine sediments .... 134
4. Thickness of the gas hydrate stability zone ....................................................................... 143
5. Solubility of methane in sedimentary pore fluids ............................................................ 149
6. Sediment compaction, fluid flow and gas ascent ............................................................. 150
7. Controls on gas hydrate accumulation in marine sediments ........................................... 157
   7.1. Reference case ............................................................................................................. 158
   7.2. Effects of POC concentration, burial velocity and GHSZ thickness on gas hydrate accumulation ................................................................................................................. 162
7.3. Effects of sediment compaction on gas hydrate accumulation...........................................166
7.4. Effects of fluid and gas flow on gas hydrate accumulation.................................................170
7.5. Effects of POC degradation kinetics on gas hydrate accumulation.....................................171
8. Constraining the global methane hydrate inventory in the modern ocean.............................178
9. Accumulation of gas hydrates under PETM boundary conditions........................................184
10. Conclusions and open questions............................................................................................185
List of symbols and abbreviations used in the contribution.......................................................187
Acknowledgements.....................................................................................................................188
References......................................................................................................................................188

Appendix 2: Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification ...........................................................................................................................193
   Abstract......................................................................................................................................193
   Introduction.................................................................................................................................194
   Temperature Evolution in the Mid-depth Arctic Ocean.............................................................194
   Impact on Methane Hydrate Stability and Ocean Acidification...............................................197
   Conclusions...............................................................................................................................201
   Acknowledgements...................................................................................................................201
   References....................................................................................................................................202

Appendix 3: Modeling the fate of methane hydrates under global warming..............................205
   Abstract......................................................................................................................................205
   1. Introduction............................................................................................................................206
   2. Data and Methods ................................................................................................................211
      2.1. Model configurations.....................................................................................................211
      2.2. Stability analysis of gas hydrates..................................................................................213
   3. Results....................................................................................................................................217
      3.1. Present-day climate conditions.....................................................................................217
      3.2. Future climate conditions..............................................................................................220
   4. Discussion...............................................................................................................................227
   5. Conclusion..............................................................................................................................230
   Acknowledgments......................................................................................................................230
   References....................................................................................................................................231

Appendix 4: Global marine sediments as microbial habitats: Distribution of water, organic carbon, temperature, and pore space in marine sediments.................................................237
   Abstract......................................................................................................................................237
   1. Introduction............................................................................................................................238
2. Size ............................................................................................................................................... 241
3. Porosity........................................................................................................................................ 245
4. Temperature .................................................................................................................................. 249
5. Sedimentary organic matter ........................................................................................................... 254
   5.1. Quantification of organic matter degradation and burial in Holocene and Pleistocene Marine Sediments .................................................................................................................. 257
   5.2 3-D global distribution of organic matter in marine sediments .............................................. 262
6. Discussion .................................................................................................................................... 266
   6.1 Pore water ................................................................................................................................. 267
   6.2 Temperature ............................................................................................................................. 268
   6.3 Quaternary organic matter ...................................................................................................... 270
   6.4 Before the Pleistocene ............................................................................................................. 272
7. Concluding remarks ....................................................................................................................... 276
Acknowledgements ........................................................................................................................... 277
References cited .................................................................................................................................. 277
Acknowledgments ............................................................................................................................... 283
Curriculum Vitae ............................................................................................................................... 285
LIST OF FIGURES

Introduction:
Fig. I Pure methane hydrate phase diagram ................................................................. XXXIII
Fig. II Methane gas hydrate stability field in marine sediments .................................... XXXV
Fig. III The Gas Hydrate Stability Zone thickness ......................................................... XXXVI
Fig. IV World- wide locations of recovered and inferred gas hydrate deposits ............... XXXVII
Fig. V Risks associated with gas hydrate vulnerability to the oceanic warming .......... XXXIX
Fig. VI Gas hydrate production techniques ..................................................................... XLI

Chapter 1:
Fig. 1 Burial velocity of Holocene surface sediments ....................................................... 6
Fig. 2 An example of compaction-driven solid and fluid components movement within sediment column ................................................................................................. 12
Fig. 3 Global distribution of gas hydrates under Quaternary sedimentation conditions ...... 23
Fig. 4 Predicted thickness of the gas hydrate stability zone (GHSZ) ................................. 24
Fig. 5 Predicted filling of pore space by gas hydrate in the high sedimentation scenario ...... 27
Fig. 6 Relationship between gas hydrate stability zone (GHSZ) thickness and gas hydrate concentration for high sedimentation scenario .................................................. 28
Fig. 7 TOC concentration at the surface as function of sedimentation rate ..................... 29
Fig. EA-1 Bathymetry data extracted from an Ocean General Circulation Model (OGCM) simulation run in the ORCA_R025 configuration .................................................. 31
Fig. EA-2 Salinity data extracted from an Ocean General Circulation Model (OGCM) simulation run in the ORCA_R025 configuration .................................................. 32
Fig. EA-3 Bottom water temperature data extracted from an Ocean General Circulation Model (OGCM) simulation run in the ORCA_R025 configuration .................................. 32
Fig. EA-4 Heat flow data provided by the International Heat Flow Commission (IHFC) ...... 33
Fig. EA-5 A combined set of global sediment thicknesses ............................................. 33
Fig. EA-6 POC concentrations in surface sediments ...................................................... 34
Fig. EA-7 Global sedimentation rate data obtained from a novel parameterization of Holocene sedimentation ................................................................. 34

Chapter 2:
Fig. 1 Schematic illustration of the reference frame concept used in the model ............... 55
Fig. 2 Bathymetric map of the Blake Ridge region .......................................................... 60
Fig. 3 Scenario 1 modeling results ................................................................................. 69
Fig. 4 Scenario 2 modeling results ................................................................................. 70
Fig. 5 Scenario 2a modeling results .............................................................................. 71
Fig. 6 Scenario 2b modeling results .............................................................................. 72
Fig. 7 Change in the GHSZ thickness over simulation time for scenario 2 .................... 73
Fig. 8 Scenario 3 modeling results ................................................................................. 74
List of Figures

Fig. 9 Scenario 4 modeling results ................................................................. 76
Fig. 10 Scenario 5 modeling results ................................................................. 77

Chapter 3:
Fig. 1 Bathymetry map of the A) Gulf of Mexico with a focus on B) the Northern Gulf of Mexico and C) the Green Canyon area ................................................................. 88
Fig. 2 Litho-stratigraphy of the Northern Gulf of Mexico ............................................. 90
Fig. 3 Simplified interpretation of post-tectonic structures and salt deposits in the Northern part of the Gulf of Mexico ............................................................................. 92
Fig. 4 Stratigraphy and geometry of the 3D modeling domain ........................................ 99
Fig. 5 Porosity data from drill wells GC955-H, GC955-Q, and GC-955-I, plotted with preliminary porosity calculations ............................................................................. 101
Fig. 6 Location of faulting structures interpreted within the modeling domain from seismic data ........................................................................................................ 103
Fig. 7 Paleo-water depth and paleo-heat flow trends used in the modeling study .............. 104
Fig. 8 A set of 2D heat flow maps calculated from the McKenzie crustal rifting model ....... 105
Fig. 9 Burial history plot extracted from the JIP Leg II drill site location ........................ 109
Fig. 10 Oil and thermogenic methane generation from Tithonian, Oxfordian, and MCU source rocks ........................................................................................................... 110
Fig. 11 Total gas hydrates distribution within Pleistocene sediments of the Green Canyon province (3D view) ................................................................................... 114
Fig. 12 Total gas hydrates distribution within uppermost Pleistocene sediments of the Green Canyon province .................................................................................. 115

Appendix 1:
Fig. 1 Concentration of particulate organic carbon (POC) in Holocene surface sediments 129
Fig. 2 Accumulation rate of POC in Holocene surface sediments .................................. 131
Fig. 3 Accumulation rate of POC in Quaternary sediments .......................................... 133
Fig. 4 Accumulation of POC over the last 150 Myr ...................................................... 134
Fig. 5 Fraction of buried POC entering the methanogenic zone .................................. 138
Fig. 6 Fraction of POC converted into methane carbon within the methanogenic zone of continental margin sediments ................................................................. 141
Fig. 7 Phase diagram for methane hydrate (structure type I) for sulfate-free seawater with a salinity of 35 ........................................................... 144
Fig. 8 Down-core change in porosity, thermal conductivity of bulk sediment and temperature in typical continental margin sediments ................................................. 147
Fig. 9 Thickness of the gas hydrate stability zone calculated from global heat flux data .... 148
Fig. 10 Solubility of methane in marine sediments deposited at 2000 m water depth .......... 150
Fig. 11 Burial velocity of pore fluids (v_b) and solids (w_b) in marine sediments subject to steady-state compaction ............................................................... 152
Fig. 12 Velocity of Darcy fluid flow at lithostatic pressure (uL) in marine sediments as function of intrinsic permeability ................................................................. 154
Fig. 13 Relative permeability of gas and buoyancy-driven gas flow in fine-grained marine sediments as function of gas saturation ........................................... 157
Fig. 14 Concentrations of dissolved inorganic carbon, dissolved methane, particulate organic carbon and methane hydrate saturation in the reference model run ................................................................. 160
Fig. 15 Concentrations of dissolved sulfate and dissolved methane in surface sediments calculated in the reference model run .............................................................................. 160
Fig. 16 Effect of POC concentration and burial velocity on methane hydrate accumulation in marine sediments .................................................................................. 163
Fig. 17 Effect of GHSZ thickness on methane hydrate accumulation in marine sediments ............ 163
Fig. 18 Gas hydrate inventories within the GHSZ calculated by individual runs of the transport- reaction model and with the transfer function for the same set of parameter values .... 164
Fig. 19 Controls on gas hydrate accumulation as predicted by the transfer function .......... 165
Fig. 20 Effect of sediment compaction on gas hydrate accumulation ........................................ 166
Fig. 21 Porosity, burial velocity of sediments (wB) and pore waters (vB) applied in the reference case and in margin sediments with complete compaction ......................... 167
Fig. 22 Effect of POC concentration and burial velocity on methane hydrate accumulation in continental margin sediments experiencing complete compaction .............. 168
Fig. 23 Gas hydrate inventories calculated by individual runs of the transport- reaction model and with the transfer function for fully compacting margin sediments .......... 169
Fig. 24 Controls on gas hydrate accumulation as predicted by the transfer function for margin sediments subject to complete compaction .............................................. 170
Fig. 25 Effect of fluid flow and gas flow on gas hydrate accumulation ...................................... 171
Fig. 26 Kinetic controls on gas hydrate accumulation ............................................................. 172
Fig. 27 Dissolved sulfate and methane profiles at age = 100 kyr .................................................. 172
Fig. 28 Concentrations of dissolved inorganic carbon, dissolved methane, particulate organic carbon and methane hydrate saturation calculated by integrating the kinetic rate laws .......... 174
Fig. 29 Model results for ODP site 799A .............................................................................. 178
Fig. 30 Global distribution of methane hydrate in marine sediments calculated by applying low compaction and Quaternary burial velocities ........................................ 180
Fig. 31 Global distribution of methane hydrate in marine sediments calculated by applying complete compaction and Quaternary burial velocities .......................................... 180
Fig. 32 Concentrations of dissolved inorganic carbon, dissolved methane, particulate organic carbon and methane hydrate saturation calculated for the modern ocean and the PETM .......... 185

Appendix 2:

Fig. 1 (a) Map of the time-mean (1985-2004) bottom water temperatures in the ocean hindcast simulation and (b) ensemble-mean trend in (in °C per 100 years) in the climate model simulation under CO2 increase ............................................................................. 195
List of Figures

Fig. 2 Variability of temperatures in the hindcast simulation, shown by monthly and inter-annually filtered temperatures .......................................................... 196
Fig. 3 (a) Changes in thickness of the GHSZ caused by temperature increase of the ensemble mean of the global warming, (b) phase diagram of methane hydrate as a function of pressure and temperature (c) Volumetric GHSZ thickness changes north of 60°N as a function of time .... 198
Fig. 4 Changes in pH due to the release of 50% of the methane from hydrates within the first 100 years .................................................................................. 200

Appendix 3:
Fig. 1 Schematic of a typical continental shelf margin depicting the present-day area of gas hydrate stability ......................................................... 207
Fig. 2 Global estimates of methane hydrate inventories ........................................ 210
Fig. 3 Global map of the gas hydrate stability zone thickness under present-day climate conditions .......................................................... 218
Fig. 4 Present-day global distribution of methane hydrates in marine sediments calculated for Quaternary sedimentation rates ................................................................ 219
Fig. 5 Global distribution of the ensemble mean trend in bottom water temperatures over the next 100 years ................................................................. 220
Fig. 6 Global map of the predicted thickness of the gas hydrate stability zone calculated under steady-state conditions .................................................. 221
Fig. 7 The predicted change in the distribution of methane hydrates under steady-state conditions .............................................................................. 223
Fig. 8 Phase diagrams of methane hydrate as a function of pressure and temperature .................. 224
Fig. 9 Global mean volume change in the GHSZ thickness and global mean change in the methane hydrate inventory as a function of time ........... 225

Appendix 4:
Fig. 1 Global map of marine sediment thickness ........................................... 243
Fig. 2 Illustration of the margin, shelf and abyss domains ................................ 244
Fig. 3 Calculated porosity as a function of sediment depth ................................ 249
Fig. 4 Global Distribution of temperature in marine sediments ..................... 251
Fig. 5 Accumulation rate of particulate organic matter in marine a) Holocene and b) Pleistocene surface sediments .......................................................... 255
Fig. 6 The fraction of total organic carbon, TOC, that exists at the bottom of the (a-c) bioturbated zone, Holocene (d-f) and Pleistocene (g-i) sediment layers relative to the amount of organic matter deposited ...................................................... 263
Fig. 7 Total volumes of bioturbated, Holocene and Pleistocene sediments ........ 265
Fig. 8 Isotopic fractionation of carbon, δ13C, as recorded in marine carbonates .... 273
# List of Tables

## Chapter 1:
- Tab. 1 Depth distribution of sedimentation rates at the Holocene.................................7
- Tab. 2 Global sediment accumulation rates at the seafloor..................................................8
- Tab. 3 Complete list of symbols and parameters used in the model........................................12
- Tab. 4 Details of the chemical reaction rates.........................................................................15
- Tab. 5 Rates of the gas hydrate and free gas formation and dissolution...............................19
- Tab. 6 Change in chemical species concentrations R(X) due to chemical reactions...............19

## Chapter 2:
- Tab. 1 Physical parameters used in numerical simulations......................................................48
- Tab. 2 Geochemical parameters used in numerical modeling for Site 997.............................52
- Tab. 3 Blake Ridge Site 997 characterization...........................................................................63
- Tab. 4 Sedimentation rates at Blake Ridge Site 997.................................................................64
- Tab. 5 Comparison of modeling parameters for five different scenarios...............................78

## Chapter 3:
- Tab. 1 Source rock properties used in the modeling study......................................................96
- Tab. 2 Source rock productivity potential and modeling assumptions used in the study.......108
- Tab. 3 Modeling results on source rock productivities, oil and thermogenic methane generation........................................................................................................111

## Appendix 1:
- Tab. 1 Quaternary POC and methane balance for continental margins.................................142
- Tab. 2 Parameter values and upper boundary conditions applied in the reference case..........158
- Tab. 3 Fluxes at the upper boundary of the model column, depth-integrated rates and carbon inventories calculated in the reference simulation.........................................................161

## Appendix 3:
- Tab. 1 Thickness of the GHSZ and depth of the BSR.............................................................218
- Tab. 2 Volume of sediment within the GHSZ and methane hydrate inventories (present-day estimates and future changes)............................................................................................222

## Appendix 4:
- Tab. 1 Surface area and sediment accumulation rates of selected depth intervals of the global ocean........................................................................................................................................242
- Tab. 2 Volumes of selected water bodies and marine sediment pore water at various temperature intervals..................................................................................................................246
- Tab. 3 Selected values of parameters used to characterize the temperature, porosity and organic matter content of continental margin, continental slope and abyss domains of global marine sediments........................................................................................................248
INTRODUCTION

MOTIVATION

On a scale of millions of years, the Earth has been shaped by powerful, dynamic and complex natural processes which determined the planet’s unique character. A particular compilation of chemical elements defines the Earth’s interior and thus, surface environments. Characteristics of both terrestrial and marine settings are directly related to the complex cycles of the Earth’s basic natural elements: oxygen, carbon, hydrogen, and nitrogen. Specially, biochemical cycle of carbon affects all Earth’s natural systems: lithosphere, hydrosphere, biosphere, and atmosphere and builds a network of subsequent processes responsible for the life sustentation. The balance between losses and gains of carbon-based chemical species drives many important short and long time-scale processes affecting life on Earth, such as naturally-caused and anthropogenic climate change events.

Being a part of the global carbon cycle, gas hydrates received wide scientific and public attention. Gas hydrates are commonly described as ice-like crystalline structures containing various types of mainly hydrocarbon gases and are stable in high-pressure and low-temperature environments. The first documented discovery of gas hydrate structures took place on the Siberian plateau in the 1930s by natural gas miners who noticed an ice-like substance crystallizing and blocking the flow in the gas pipes due to the low surrounding temperatures. The unique structure of gas hydrates serves a base for a fascinating research field that comprises questions about the Earth’s past, present, and future. In the following decades gas hydrate research became an important and weighty topic for scientists, economists, politicians, and the hydrocarbon-related industry part.

Studying gas hydrates incorporates knowledge from the field of geochemistry, geophysics, and biology. The role of gas hydrates in the past geological events that influenced Earth’s climate and thus its bio-diversity was broadly exposed under scientific debate, however, a direct link between past catastrophic events and sudden gas hydrate dissolution coupled with a release of the greenhouse gases stored within their crystalline structure seems to be
unlikely (Archer et al., 2008; Kvenvolden, 1982; Kvenvolden, 1998; Renssen et al., 2004). Nevertheless, past global crises such as Paleocene-Eocene Thermal Maximum (PETM; about 55 Ma ago) or Permian-Triassic extinction event (T-Pr; about 252 Ma ago) show how important it has become to understand in detail the role of gas hydrates in the global Earth’s carbon cycle (Bice and Marotzke, 2002; Buffett and Archer, 2004; Dickens, 2000; Dunkley et al., 2013; Majorowicz et al., 2014) as well as the world’s gas hydrate deposits distribution (Archer et al., 2008; Burwicz et al., 2011; Kvenvolden and Lorenson, 2001; Milkov, 2004; Piñero et al., 2013; Wallmann et al., 2012). Recent natural methane gas venting sites observed at the continental margins and slopes remind about the dynamic character of gas hydrate deposits, most likely vulnerable to the currently observed anthropogenic warming (Bernadt et al., 2014; Burwicz et al., in prep. –b; Kim et al., 2013; Mienert et al., 2005; Thatcher et al., 2013). Gas hydrate dissociation from marine deposits is postulated to be a natural consequence of a global temperature rise (Biastoch et al., 2011; Hunter et al., 2013; Kretschmer et al., accepted; Marin-Moreno et al., 2013; McGuire et al., 2009; Phrampus and Hornbach, 2012; Sasen et al., 2001). In the worst case scenario, gas hydrate response to the ocean warming might lead to destabilization of the ocean floor (similar to the other events in the past, e.g. Santa Barbara Basin formation and the Storegga Landslide; Nixon and Grozic, 2007). The impact of sudden gas release to the ocean might have a great influence on the marine bio-diversity as a direct consequence of increasing ocean acidification. However, recent studies seem to emphasize a rather limited short-scale impact of gas hydrate dissociation on the marine environment and bio-diversity (Biastoch et al., 2011; Kretschmer et al., accepted).

Nevertheless, methane-associated bio-communities remain the main beneficiaries of hydrocarbon gases released from the oceanic floor, and potentially gas hydrate deposits. Studying the sub-surface microbial communities often present in the extreme e.g. high-temperature, low-oxygen and highly acid environments naturally posed the question about the depth extent of the biosphere (Edwards et al., 2011; Reith, 2011; Winghameth et al., 2012). First attempts to quantify marine habitat available for microorganisms and define
the limits of sub-oceanic life’s extension were based on global estimates of the amount of Earth’s living biomass (Colwell and D’Hondt, 2013; Kallmeyer et al., 2012; Whitman et al., 1998). A new approach emphasizes the role of temperature driving microbial activity and aims at estimating the volume of marine sediments and the sediment pore space lying within a given temperature range (Larowe et al., in prep.). Implications from this study comprise further conclusions on deep sub-surface element cycle, energy sources driving microbial activity, and the role of microorganisms in changing, not only adapting, to the environment. Specifically, the role of microbial communities in processing of ore deposits (e.g. leaching out minerals such as copper; Crosby and Bailey, 2012), enhancing porosity generation by producing acid lixiviants (e.g. in limestone reservoirs), and temperature-dependent fossil fuel formation due to hydrocarbon metabolizing proofs the importance of the conducted deep biosphere research.

Microbial and thermogenic methane stored within global gas hydrate deposits remain, potentially, the largest source of hydrocarbon on Earth. A common use of hydrate methane gas as a potential energy resource has been broadly investigated over the last decades (Collett, 2002; Jang and Santamarina, 2011; Moridis et al., 2009). Despite the technical difficulties associated with gas hydrate “mining”, the potential accessibility of hydrocarbon gases stored within gas hydrate accumulations has been noticeable re-shaping the view of the unconventional energy market. Following on that, several attempts of test the possibility of gas hydrate production from natural deposits were conducted (Gamwo and Liu, 2010; Sung et al., 2000). As a consequence, first advanced basin-scale numerical models resolving for organic matter maturation, hydrocarbon expulsion and migration, and, finally, gas storage within potential gas hydrate reservoirs were implemented (Burwicz et al., in prep. –a; Frye, 2008).

Amongst many debates endorsing or questioning postulated influence of gas hydrate accumulations on global climate change and their potential usage as the new energy resource, the importance of conducting advanced gas hydrate research remains unchanged. Understanding long-term cycles present in the Earth’s history helps us to better describe,
model and predict future natural events. Present-day gas hydrate-related hazards, however limited, start from submarine landslides caused by gas hydrate dissociation and potentially leading to damage of the underwater infrastructure (wires, pipelines) and/or scientific equipment and finish on influencing the local microbial communities and environment. Moreover, high energetic potential stored within world-wide gas hydrate deposits requires a constant improvement of our investigating techniques and better understanding of the geological, economical and ecological consequences of our decisions.

STATE-OF-THE-ART IN GAS HYDRATE RESEARCH

HISTORY AND EARLY EXPERIMENTS

The earliest scientific experiments on crystalline gas hydrates were performed in the year 1810 in the laboratory of British chemist Sir Humphrey Davy (Davy H., 1811). Davy’s primary interest/focus was to understand and predict main factors controlling the transition of chlorine into a solid hydrate state. A successful and continuous research brought him to a further understanding of crystallization, dissolution and stability field of the newly discovered substances. Upon this knowledge, a broader and more general view of clathrates research could be established, including early P-T stability diagrams (e.g. Le Chatelier, 1884; Villard, 1888), description of hydrate formed from mixed gases (Cailletet and Bordet, 1882), structural properties (Faraday, 1823; Pierre, 1848), physical properties and composition (e.g. Ditte, 1882; Maumené, 1883; Roozeboom, 1884; Wróblewski, 1882a; Wróblewski, 1882b; Wróblewski, 1882c [first CO₂ hydrate]). By the end of XIX\textsuperscript{th} century, the influence of salt and other ions on the phase boundaries between gas hydrate, solute, and the free gas state was also known and quantified which served a base for a modern P-T phase diagram (Figure I).

First attempts to determine the hydration number (i.e. number of the molecules of water with which a single gas molecule can combine) and distinguish between different cage structures were mostly based on macroscopic methods including hydrate formation heat measurements. The most precise and reliable procedure has been published by Villard in
1896 (Villard, 1896) and became a standard tool helping to predict hydrate phase properties. In order to measure, rather than predict gas hydrate properties, modern microscopic methods- nuclear magnetic resonance (NMR) (Davidson et al., 1977; Garg et al., 1974) and Raman spectroscopy (Tulk et al., 2000; Uchida et al., 1999) were adopted. These direct measurements on gas hydrate crystals allowed determining guest molecule occupancy levels for each known type of hydrate cage structure and gave a new direction to the laboratory experimental research.

Fig. 1. Pure methane hydrate phase diagram with a gas hydrate stability zone shown in blue. Presence of Na\(^+\) and Cl\(^-\) ions can shift the phase boundary to the left (stability zone is shrinking), whereas presence of CO\(_2\), H\(_2\)S and higher hydrocarbons shifts the phase boundary to the right (stability zone is extending over lower pressure and higher temperature values).

FIRST IN-SITU DEPOSITS AND GLOBAL PERSPECTIVE

After a century of laboratory-limited experiments, gas hydrate research was finally extended to a broader perspective. In the 1930’s, first discovery of natural gas hydrates blocking the flow in Siberian gas pipes started a new era of gas hydrate investigations. Based on a practical need to reduce the risk of potential gas pipe blockage, new line of research on natural and synthetic inhibitors of gas hydrate grown has began (e.g. Wilcox et al., 1941). Extensive crystallography studies in the early 1940’s and 1950’s led to a discovery of clearly defined structure I and structure II hydrates (Clausen, 1951; Pauling and Marsh, 1952; Von Stackelberg, 1949).
However, first description of the most complex structure H gas hydrates was published decades after (MEHTA and SLOAN, 1993) and confirmed by drilling reports of Sassen (SASSEN and MACDONALD, 1994) on the Gulf of Mexico research cruise. Statistical thermodynamics which are commonly used in the present-day gas hydrate studies have been firstly used by Barrer and Stuart (BARRER and STUART, 1957) and van der Waals and Platteeuw (VAN DER WAALS and PLATTEEUW, 1959) to investigate gas hydrate properties, such as temperature, pressure and intermolecular potentials. In the 1960’s, first scientific investigations on hydrate kinetics grow have started, often related to the arising industry problems with freezing water content in gas pipes and wells. A promising perspective of using gas hydrate as potential energy resource was brought up by Soviet Union scientists in the mid- 1960’s as a result of prominent in-situ gas hydrate resources discovered within permafrost region of Siberia. This research direction had its important continuation in optimizing and further understanding of kinetically-driven formation dynamics of gas hydrate in natural porous media (e.g. MAKOGON, 1965), oil-containing systems and phase equilibrium. Soon after, Japanese researchers improved our understanding of natural gas hydrate-bearing reservoirs by performing extensive studies on the Okhotsk Sea and Nankai Trough regions (e.g. SATOH et al., 1996).

More common and successful off-shore campaigns investigating in-situ gas hydrate deposits by seismic imaging techniques resulted in several studies describing a seismic feature called a bottom simulating reflector (BSR) present at the locations were gas hydrate stability zone had been confirmed by thermodynamical calculations. Bottom simulating reflectors are commonly known as sharply-defined seismic reflection roughly parallel to the seafloor based on the impedance contrast between high-velocity free gas accumulations and low-velocity gas hydrate-bearing deposits. BSR depths are often interpreted as a base of the gas hydrate stability zone (see Figure II). However, gas hydrates are capable to form without underlying free gas layer and thus, being to some degree invisible to such geophysical methods. First comprehensive studies on the BSRs phenomena were presented in 1980 by Kvenvolden and McMenamin (KVENVOLDEN and
McMenamin, 1980) and followed in 1982 by Kvenvolden (Kvenvolden K. A., 1982) containing a list of regions with a confirmed BSR depths and ongoing studies (e.g. Bering Sea, Gulf of Mexico, Central America, Gulf of Oman, Blake Ridge off-shore South Carolina, and Western North Atlantic). A visible correlation of the BSR depth and free gas accumulations locked within marine sediments was already suggested therein and discussed in the context of potential free gas resource locating method.

Further investigation on bottom simulating reflectors and their application in gas hydrate research was conducted by several authors (e.g. Hynman R. D. and Spence G.D., 1992; Singh et al., 1993) emphasizing the importance of upward fluid expansion on the BSR.
depth (Hyndman R. D. and Davis E. E., 1992), and elastic properties of hydrate-bearing sediments (Chand and Minshull, 2003). Preceded by seismic investigations in 1997 which successfully located well-defined BSR depths, in-situ gas hydrate deposits were drilled and investigated in Canada (1998) and offshore Japan (1999). In parallel, technical problems related to gas and oil recovery located within gas hydrate stability regions (Alaska North Slope, North Sea, Siberia plateau, Gulf of Mexico) were constantly under discussion bringing more of scientific and public attention.

![Image](image-url)

Fig. III. The Gas Hydrate Stability Zone thickness in meters (Burwicz et al., 2011; see Chapter 1) calculated on 0.25° x 0.25° grid resolution based on global bottom water temperature, salinity and bathymetry dataset extracted from an Ocean General Circulation Model (OGCM) simulation run in the ORCA_R025 configuration (Barnier B., 2006), sediment thickness data by Divins D. L., 2003 and Laske G. and Masters G., 1997, and heat flow data by Hamza V. M. et al., 2008, assuming a constant thermal conductivity of sediments equal to 1.5 W/m/K.

Laboratory experiments on gas hydrate stability field, physical and chemical properties, growth inhibitors, and phase equilibriums were naturally followed by questions about global abundance and amounts of gas hydrates stored within marine and permafrost sediments. By applying well-known and confirmed stability diagrams into the wider context, global Gas Hydrate Stability Zone (GHSZ) was derived (see Figure III). Suggested by the stability calculations, deep sea and ocean exploration focused primarily on the regions along continental margins (e.g. Deep Sea Drilling Project-DSDP currently Ocean Drilling Program- ODP; see Figure IV). These scientific expeditions resulted in acquiring
important in-situ measured data on gas hydrate properties such as sonic velocities, thermal conductivities, calorimetric parameters, and dissociation energy.

**NEW TECHNOLOGIES – NUMERICAL MODELING**

In parallel with on-sea exploration, first computer programs focused on predicting gas hydrate properties and phase equilibrium were used (e.g. ASPEN™, HYPERCHEM™, and SIMSCI™). With an ongoing development of computational methods, more numerical models describing reactive gas hydrate formation and accumulation in marine sediments were presented (BAZA and KATO, 2004; DAVIE M. K. and BUFFETT B. A., 2001; DAVIE M. K. and BUFFETT B. A., 2003; KATO et al., 2000; LATYCHEV and EDWARDS, 2003; REMPEL A. and BUFFETT B. A., 1997). On a later stage, extensive studies on permeability evolution due to gas hydrates formation (NIMBLETT and RUPPEL, 2003; SEOL and KNEAKEY, 2011) and the influence of free gas layer underlying gas hydrate deposits (BHATNAGAR et al., 2007) were proposed.

A complexity of gas hydrate formation dynamics coupled with bio-geo-chemical processes (e.g. Anaerobic Oxidation of Methane (AOM), sulfate reduction via methane oxidation, alkalinity changes) were previously successfully incorporated into several numerical approaches (CHATTERJEE et al., 2011; EGEBERG and DICKENS, 1999; TORRES et al., 2002;
WALLMANN et al., 2006; WALLMANN K. et al., 2006). Additional accounting for carbonate precipitation and associated fluid flow were presented by LUFF R. and WALLMANN K., 2003 and LUFF R. et al., 2004. Comprehensive studies on the influence of modeling gas hydrate generation by kinetic rates of grow and dissolution vs. equilibrium thermodynamics was provided by KOWALSKY and MORIDIS, 2007. Numerical studies of gas hydrate-bearing systems under compaction were firstly presented by SUETNOVA E. I., 2007 and GARG S. K. et al., 2008. A year later, a numerical model resolving for methane bubble dissolution outside the stability field of gas hydrates has been proposed by REHDER et al., 2009.

First attempts to quantify and evaluate a total amount of hydrocarbons stored within gas hydrate deposits resulted in estimates ranging from 500 Gt C to 57,000 Gt C (MILKOV A. V., 2004; see detailed discussion in BURWICZ et al., 2011, Chapter 1 and WALLMANN et al., 2012, Appendix 2 of this study). Several authors presented numerical studies based on region-by-region data interpolation and assumed a presence of gas hydrates in the abyssal plains (KLAUDA J. B. and Sandler S. I., 2005) or applied a constant reactivity of organic matter within marine sediments which might have led to uncertain results (ARCHER et al., 2008; BUFFETT B. and ARCHER D., 2004; KVENVOLDEN K. A. and LORENSON T., 2001). Another numerical approach has been recently used by Marquardt (MARQUARDT et al., 2010) and reviewed by Piñero (PİNERO et al., 2013) which uses a mathematically-derived transfer function as a proxy for gas hydrate accumulations based on simple and easy-accessible input data (thickness of the GHSZ, organic carbon availability at the seafloor and rates of sedimentation). This approach has been successfully evaluated as a tool to predict a global amount of biogenic marine gas hydrate deposits (mostly associated with diffusion-dominated systems).

High, although debatable global estimates of a total amount of carbon stored within gas hydrate deposits had a natural consequence in the increasing number of publications considering 1) a potential sudden methane gas release from marine sediments and its influence on the climate change (e.g. “clathrates gun hypothesis” by KENNED J. P. et al., 2003 and contradicting conclusions by KVENVOLDEN K. A., 1998), and 2) importance of
such events in the history of the Earth (e.g. DICKENS, 2000). Specially two major catastrophic events from the past were investigated in the context of potential gas hydrate destabilization- Paleocene-Eocene Thermal Maximum (PETM; about 55Ma ago) modeled by BICE and MAROTZKE, 2002; DUNKLEY JONES et al., 2013; MACLENNAN and JONES, 2006; SECORD et al., 2010; WINGUTH et al., 2010; WINGUTH et al., 2012; ZEEBE, 2013 and Permian-Triassic extinction event (T-Pr; about 252 Ma ago) modeled by WINGUTH and MAIER-REIMER, 2005 with coupled oceanic-atmospheric model, HEYDARI and HASSANZADEH, 2003, and MAJOROWICZ et al., 2014.

![Slope instability](image1)
![Ocean acidification](image2)
![Global warming](image3)
![Mining hazards](image4)

Fig. V. Risks associated with gas hydrate vulnerability to the oceanic warming comprise but do not limit to continental slope instability and its potential failure, ocean acidification and bio-diversity reduction, impact on the global climate change enhancing the warming effect, subsurface deformation and seafloor infrastructure damage.

High vulnerability of specific gas hydrate provinces to a global temperature changes was postulated since 1990’s but only the last decade provided numerically-based attempts to understand the global climate sensitivity and response to the potential CH₄ emission from melting hydrate deposits (DUNKLEY JONES et al., 2010; RENSSSEN et al., 2004). Rapid dissolution of gas hydrates due to the global temperature increase (HUNTER et al., 2013; KWON et al., 2010; MASLIN et al., 2010; O’CONNOR et al., 2010; SULTAN et al., 2004) was considered as a potential cause of sudden continental slope failure (NIXON and GROZIC, 2007), subsurface deformation (KIMOTO et al., 2007). Regional shifts and shallowing of gas
hydrate stability zone have been reported for many gas hydrate provinces, e.g. Gulf of Mexico (Sassen et al., 2001), offshore Korea (Haacke et al., 2009), with special attention paid to the high altitude and sub-arctic regions, e.g. offshore Svalbard (Berndt et al., 2014; Marin-Moreno et al., 2013; Thatcher et al., 2013), Sea of Okhotsk (Kim et al., 2013), Arctic Ocean (Isaksen et al., 2011; McGuire et al., 2009; see BIAS ropch et al., 2011 [Appendix 2 of this study]), Norwegian margin and Storrega Slide (Mienert et al., 2005), and locations affected by strong bottom water temperature increase (Phrampus and Hornbach, 2012; Chapter 2 and Appendix 3 of this study).

With an increasing number of numerical approaches aiming for better understanding of gas hydrate-related processes, it is essential to distinguish the main factors controlling the models themselves and their limitations (see Wallmann et al., 2012 in Appendix 1 of this study). Many scientific publications based on numerical modeling were clearly showing an advantage of this method in understanding gas hydrate formation dynamics and predicting future climate changes. However, a high degree of complexity of natural gas hydrate deposits due to the presence of high-permeability faults, active venting structures, often associated with hydrates salt pillowing and tectonic activity has been a reason for relatively low number of numerical models resolving for fluid and gas migration in such diverse settings. For this purpose, a three-dimensional numerical model of one of the largest gas hydrate provinces- Green Canyon, Gulf of Mexico has been developed (see Chapter 3 of this study).
Accordingly, presence of high-permeability structures, salt emplacement, etc. within hydrate-bearing marine provinces emphasizes the role of numerical modeling in gas production perspectives (see Figure VI) and risk assessment in case of potential hydrate recovery. Development of numerical models began from early gas hydrate reservoir simulations (e.g. Sung et al., 2000; Mallik Site at the Mackenzie Delta by Moridis, 2004), gas hydrate de-pressurization models (e.g. Konno et al., 2010; Sun et al., 2005) towards gas production perspectives (e.g. Gamwo and Liu, 2010; Jang and Santamarina, 2011; Moridis et al., 2009) emphasizing the role of numerical modeling as a powerful tool in gas hydrate research providing complex global calculations, improving regional studies, and giving a perspective on the Earth’s past and future events.
OUTLINE OF THE THESIS

The main aim of the presented gas hydrate research is to use numerical modeling as a tool to analyze the complexity of gas hydrate formation and dissolution in heterogeneous marine sediments, global abundance, and vulnerability to the climate change. Chapters 1 – 3 of the following Thesis present first-author publications (published, and in preparation for submission), whereas Appendixes 1 – 4 present a selection of scientific work co-authored (published, accepted for publication, and in preparation for submission) in the course of PhD studies.

Chapter 1 of the following dissertation attempts to answer a primary question about global gas hydrate budget based on reliable numerical modeling approach and to narrow the gap between previous estimates which differ significantly by orders of magnitude. A new Finite Difference (FD) multi-1D numerical model quantifying the global gas hydrate accumulations as well as the free gas concentrations in the gas hydrate-free gas recycling zone (from the base of the GHSZ to 50 meters below) was built upon multi-disciplinary platform comprising geological, geophysical, and geochemical data with a high spatial accuracy. Moreover, a new parameterization of Holocene sedimentation rates and its first global application has been therein presented.

Chapter 2 consists of an application of a new Finite Element (FE) 1D multi-phase numerical model in order to study the regional influence of upward methane flux on gas hydrate formation and the potential co-existence between gas hydrate, free methane gas and pore fluids in porous marine media. As it was presented in the previous chapter, complexity and high computing needs required in global numerical approach do not allow for investigating gas hydrate dynamics in great detail and therefore, might lack some convenience in terms of direct model-to-measurement comparison. The new model presents a powerful tool resolving for major bio-chemical processes associated with gas hydrate formation (in-situ organic carbon degradation, methanogenesis, and sulfate reduction via methane oxidation) coupled with pore pressure, temperature and
Compaction solvers. This model has been adapted to study non-steady-state processes at the Blake Ridge site, offshore South Carolina.

Chapter 3 presents a state-of-the-art 3D numerical modeling of basin-scale gas hydrate reservoirs at the Green Canyon province, Gulf of Mexico. By virtue of high resolution seismic data available for the purpose of this study, it was possible to construct a detailed three-dimensional model of the investigated area which accounts for regional structural discontinuities (i.e. faults), evaporate accumulations (i.e. salt pillowing), and other high-permeability pathways influencing gas migration and, consequently, gas hydrate formation in their vicinities. The main goal of this study was to design a numerical model representing all regional features and their importance for gas hydrate formation from both biogenic and thermogenic methane as a result of maturing organic matter throughout the history of the basin.

Appendix 1 presented in the following dissertation contains a comprehensive theoretical study on predicting gas hydrate concentration in various marine settings and summarizes on the most important controlling parameters driving the formation and dissolution of gas hydrates on a global scale. Physical properties of sediments (mechanical and chemical compaction), CH₄ solubility in pore fluids, presence of additional fluid flow and gaseous methane ascent were investigated together with environmental factors such as microbial organic matter degradation, seafloor POC accumulation rates, and GHSZ thickness to derive a possibly the most naturalistic view on gas hydrate formation controls. Taking into account all above parameters, presented study concludes with minimum global gas hydrate inventory, global volume of marine sediments lying within the GHSZ, global POC accumulation rates derived for the present-day, and, finally, global rates of microbial CH₄ production.

Study presented in Appendix 2 was designed to predict the potential impact of gas hydrate destabilization in the Arctic region due to the anthropogenic global warming. A combination of climate modeling with regional gas hydrate formation potential and the
GHSZ thicknesses was used to evaluate the impact of rising bottom water temperatures on the shallowest gas hydrate accumulations stored underneath the Arctic Ocean. Despite the fact that the following study does not include microbial response to potentially melting gas hydrates and methane release to the ocean (e.g. *microbial filter* effect), it provides detailed information on high-latitude regions especially vulnerable to the changing climate and contributes to the discussion on greenhouse gas releases over the next century by arguing for a rather diminished effect of those.

A research problem of a global response of gas hydrate accumulations to the ongoing climate change is discussed in the Appendix 3. As it was initiated by previously published paper on regional gas hydrate vulnerability to rising bottom water temperatures (see Appendix 1), consecutive study has been undertaken pointing towards a crucial need of quantifying global methane release rates in the nearest future. High-resolution ocean circulation model was combined together with gas hydrate concentration predictions based on parameterized function presented within the framework of Appendix 2 outcome, additionally validating our previous approach and confirming its functionality. As a result, total fluxes of methane produced due to melting gas hydrate deposits within the next hundred years were computed and presented with a special attention paid to the regions mostly affected.

Study described in the Appendix 4 aims at quantifying global marine sediments available as a natural habitat for microorganisms and thus, deriving conclusions on the possible extent of life on Earth with a special focus on marine environments. Furthermore, a reactive continuum model was used in this study in order to estimate the distribution and abundance of organic matter in marine sediments throughout the Pleistocene. A global character of conducted study required a set of compatible input data collected on high-resolution spatial grid. Hindcast of global ocean circulation model which served a base for numerical modeling presented in previous publications (see Chapter 1, Appendix 1, Appendix 2, and Appendix 3 of this thesis) was used to evaluate the total volume of oceanic sediments lying within certain temperature ranges. This temperature distribution in
sedimentary column has a major effect on microorganism’s activity levels and thus, holds important information on present habitability parameters of marine strata, as well as on the paleo-climate.

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Introduction


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CHAPTER 1: 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

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ABSTRACT
This study provides new estimates for the global offshore methane hydrate inventory formed due to microbial CH4 production under Quaternary and Holocene boundary conditions. A multi-1D model for particular organic carbon (POC) degradation, gas hydrate formation and dissolution is presented. The novel reaction-transport model contains an open three-phase system of two solid compounds (organic carbon, gas hydrates), three dissolved species (methane, sulfates, inorganic carbon) and one gaseous phase (free methane). The model computes time-resolved concentration profiles for all compounds by accounting for chemical reactions as well as diffusive and advective transport processes. The reaction module builds upon a new kinetic model of POC degradation which considers a down-core decrease in reactivity of organic matter. Various chemical reactions such as organic carbon decay, anaerobic oxidation of methane, methanogenesis, and sulfate reduction are resolved using appropriate kinetic rate laws and
constants. Gas hydrates and free gas form if the concentration of dissolved methane exceeds the pressure, temperature, and salinity-dependent solubility limits of hydrates and/or free gas, with a rate given by kinetic parameters. Global input grids have been compiled from a variety of oceanographic, geological and geophysical data sets including a new parameterization of sedimentation rates in terms of water depth.

We find prominent gas hydrate provinces offshore Central America where sediments are rich in organic carbon and in the Arctic Ocean where low bottom water temperatures stabilize methane hydrates. The world’s total gas hydrate inventory is estimated at $0.82 \times 10^{13}$ m$^3$–$2.10 \times 10^{15}$ m$^3$ CH$_4$ (at STP conditions) or, equivalently, 4.18–995 Gt of methane carbon. The first value refers to present day conditions estimated using the relatively low Holocene sedimentation rates; the second value corresponds to a scenario of higher Quaternary sedimentation rates along continental margins.

Our results clearly show that in-situ POC degradation is at present not an efficient hydrate forming process. Significant hydrate deposits in marine settings are more likely to have formed at times of higher sedimentation during the Quaternary or as a consequence of upward fluid transport at continental margins.

1. **INTRODUCTION**

Gas hydrates are solid ice-like crystalline compounds in which hydrocarbon molecules are trapped within cages of host water molecules. Guest molecules include also higher hydrocarbons but methane is the most common one, which makes marine hydrates a potential energy resource and an important reservoir in the global carbon cycle.

In marine settings, gas hydrates are known to occur along passive and active continental margins where the physical conditions and organic carbon input favor their formation. In fact, hydrates are only stable at high pressure and low temperature conditions and a sharp phase boundary separates them from the free gas phase situated below. Hydrates are thus vulnerable to regional and global changes in sea level and temperature.

Sudden release of methane, a greenhouse gas with a global warming potential about 25 times higher than CO$_2$, may also be a trigger of climate change. A catastrophic methane
release as a result of marine hydrate dissociation is a hypothesis explaining a marked negative carbon isotopic excursion during the latest Paleocene (Kennett and Stott, 1991 and Dickens et al., 1995).

Melting of marine hydrates and subsequent venting of methane into the water column may, in fact, occur at present as a result of a warming seafloor in the Arctic (Shakhova and Semiletov, 2007 and Westbrook et al., 2009). Gas hydrates might also be a future energy source with the total volume of hydrocarbon gas locked within clathrate structures being potentially up to 10 times greater than the conventional gas reserves (0.436×1015 m³, USGS World Energy Assessment Team, 2000).

Quantifying the role of marine hydrates in the Earth System requires global estimates on their distribution and abundance. This has resulted in a rapidly increasing number of publications exploring the various aspects of their formation (Milkov, 2004). On a regional scale, numerical modeling is complementing a wealth of observational studies and progressively helps to understand hydrate formation and dissolution processes in important gas hydrate provinces, i.e. Hydrate Ridge, offshore Oregon (Luff and Wallmann, 2003, Torres et al., 2004, Liu and Flemings, 2006 and Garg et al., 2008). Global predictions rely on numerical modeling (Buffett and Archer, 2004, Klauda and Sandler, 2005 and Archer et al., 2008) and region-by-region extrapolation (i.e. adequate for passive and active margins) of the total amount of hydrate-bearing marine sediments and locally inferred fraction of hydrates (Kvenvolden and Lorenson, 2001 and Milkov, 2004). Recently published estimates on the global carbon inventory locked up in offshore hydrates vary over several orders of magnitude from 500 to 57,000 Gt C (Kvenvolden and Lorenson, 2001, Buffett and Archer, 2004, Milkov, 2004, Klauda and Sandler, 2005 and Archer et al., 2008). There is clearly an urgent need to better constrain these global estimates to evaluate both the resource potential and the contribution of hydrates to past and future climate change.

A common proxy to hydrate inventory is the Gas Hydrate Stability Zone (GHSZ) which is defined as a combination of physical parameters (pressure and temperature conditions), and, to a smaller degree, pore fluids salinity. While it does illustrate the volume of sediment
inside the stability zone it does not provide information on the actual hydrate saturation. The formation of hydrates is, in fact, mainly controlled by methane supply either through the direct degradation of organic matter within the GHSZ or through an upward flux of deeper biogenic and thermogenic methane. Such gas fluxes have been reported from active margins but unfortunately, global estimates of methane fluxes from deep sediments are still poorly constrained. Thus, Gas Hydrate Stability Zone thicknesses can be viewed as a proxy for potential hydrate deposits distribution but not necessarily for the real volume of hydrate-bearing sediments.

The aim of this study is to constrain the global inventory of methane hydrates in the seabed formed by the microbial degradation of organic matter within the GHSZ. For this purpose we explore the transport-reaction model that resolves for in-situ particular organic carbon (POC) degradation and hydrate formation and apply the model globally in a multi-1D mode. In contrast to previous attempts (Buffett and Archer, 2004, Archer and Buffett, 2005, Klauda and Sandler, 2005 and Archer et al., 2008), the new model considers the down-core decrease in reactivity of organic matter (Middelburg, 1989 and Wallmann et al., 2006). A validation of this approach was presented in the original paper by Wallmann et al. (2006) (Sea of Okhotsk and Blake Ridge) and by Marquardt et al. (2010) for a wide range of ODP sites (Costa Rica, Peru, Chile, California, Blake Ridge, and Namibia). We also introduce a new equation to calculate Holocene sedimentation rates as a function of water depth.

2. INPUT DATA

Global modeling requires global input data sets. We have compiled the necessary input data from a variety of different sources. To compute the global distribution of marine hydrate deposits all data sets are compiled on a $1^\circ\times1^\circ\times1^\circ$ resolution and presented in Electronic Annex (Figs. from EA-1 to EA-7).

Calculations of the GHSZ thicknesses are based on the global bathymetry (Fig. EA-1), salinity (Fig. EA-2), bottom water temperature (Fig. EA-3), and heat flow (Fig. EA-4) data. The first three data sets were extracted from an Ocean General Circulation Model.
(OGCM) simulation run in the ORCA_R025 configuration (Barnier, 2006). ORCA_R025 simulations were originally performed on a tri-polar mesh with a lateral resolution of 0.25°×0.25°. Vertical resolution was 6 and 250 m.

While temperature is a key parameter controlling hydrate stability, a global data set of geothermal gradients in marine sediments is unfortunately not available. We circumvent this problem by using available global heat flow data as a proxy to geothermal gradients. Sediment temperatures are assumed to be in steady-state and are computed from the global heat flow data provided by the International Heat Flow Commission (IHFC) (Hamza et al., 2008), bottom water temperatures extracted from the OGCM and a thermal conductivity $\kappa$ of 1.5 Wm$^{-1}$K$^{-1}$. This use of a constant thermal conductivity is, of course, a simplification. Grain conductivities of sedimentary rocks span a range of 1–6 Wm$^{-1}$K$^{-1}$ (Hantschel and Kauerauf, 2010) and the thermal conductivity of pore fluids is $\sim$0.6 Wm$^{-1}$K$^{-1}$ for a temperature range of 0–35 °C (Deming and Chapman, 1989). The assumed constant value of 1.5 Wm$^{-1}$K$^{-1}$ is based on the geometrical average of pore water and matrix conductivities for a shaly-sandstone lithology.

A modified Pitzer-approach from Tishchenko et al. (2005) was used to calculate the depth-dependent solubility of gas hydrate and methane gas phases from the temperature profile, pressure, and salinity data. The intersection of solubility curves defines the bottom of the GHSZ and phase boundary between gas hydrates and free methane gas. Pore fluid salinity was set up to the global ocean values, neglecting potential local fluctuations caused by hydrate formation or dissociation processes. At many deep-sea locations the thickness of the GHSZ exceeds the thickness of sediments deposited at the seafloor. For these cases, the vertical extent of the GHSZ was reduced considering the available sediment thickness data.

A combined set of global sediment thicknesses, mainly based on the global NOAA data (Divins, 2003) and arctic region data (Laske and Masters, 1997) with a maximum lateral resolution of 5′×5′5′×5′ was applied for this purpose (Fig. EA-5).

A key input parameter is the accumulation rate of particulate organic carbon (POC) in marine surface sediments. Both, POC concentrations in surface sediments and bulk sedimentation rates are needed to constrain this key parameter. The POC concentrations
in surface sediments were implemented in the model according to the data set from Seiter et al., 2004 and Romankevich et al., 2009 with a maximum lateral resolution of 1°×1°1°×1° (Fig. EA-6).

Unfortunately, sedimentation rates and burial velocities have not been measured and compiled for the global seafloor at suitable spatial resolution. Thus, water depth is often used as a proxy to estimate burial velocities (Middelburg, 1989). It is readily available for individual seafloor sites and for the global ocean. The burial velocity of Holocene surface sediments is reported for more than 500 stations in the compilations by Betts and Holland, 1991, Colman and Holland, 2000 and Seiter et al., 2004. These data clearly show that the burial velocity of Holocene surface sediments decreases with increasing water depth (Fig. 1).

![Burial velocity vs. water depth](image)

**Fig. 1.** Burial velocity of Holocene surface sediments. The data given by Betts and Holland, 1991; Colman and Holland, 2000 and Seiter et al., 2004a are shown as red dots, green triangles, and blue crosses, respectively. The solid line is defined by Eq. 1.

A logistic equation (Eq. (1)) is applied to define the relationship between burial velocity ($w$ in cm yr$^{-1}$) and water depth ($z$ in m):

$$w = \frac{w_1}{1 + \left(\frac{z}{z_1}\right)^{c_1}} + \frac{w_2}{1 + \left(\frac{z}{z_2}\right)^{c_2}}$$

(1)
The following set of parameter values was found to give the best fit to the three independent data sets shown in Fig. 1:

\[ w_1 = 0.117 \text{ cm yr}^{-1}, w_2 = 0.006 \text{ cm yr}^{-1}, z_1 = 200 \text{ m}, z_2 = 4000 \text{ m}, c_1 = 3, c_2 = 10. \]

Eq. (1) predicts that most of the sediment accumulation takes place on the continental shelves during the Holocene (see Table 1).

Table 1. Depth distribution of sedimentation rates at the Holocene seafloor. Seafloor areas are taken from Menard and Smith, 1966a. Mean burial velocities over the indicated depth interval are calculated by numerical integration of Eq. 1. They are converted into sediment accumulation rates considering the seafloor areas listed in the second column and applying a sediment factor of \( \xi = d_i (1 - \phi) = 0.5 \text{ g cm}^{-3} \).

<table>
<thead>
<tr>
<th>Water depth (m)</th>
<th>Seafloor area ( (10^2 \text{ m}^2) )</th>
<th>Mean burial velocity ( (\text{cm yr}^{-1}) )</th>
<th>Sediment accumulation rate ( (10^5 \text{ g yr}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 200</td>
<td>27.123</td>
<td>0.104</td>
<td>14.072</td>
</tr>
<tr>
<td>200 - 1000</td>
<td>16.012</td>
<td>0.0163</td>
<td>1.308</td>
</tr>
<tr>
<td>1000 - 2000</td>
<td>15.844</td>
<td>0.00635</td>
<td>0.503</td>
</tr>
<tr>
<td>2000 - 3000</td>
<td>30.762</td>
<td>0.00598</td>
<td>0.919</td>
</tr>
<tr>
<td>3000 - 4000</td>
<td>75.824</td>
<td>0.00463</td>
<td>1.754</td>
</tr>
<tr>
<td>4000 - 5000</td>
<td>114.725</td>
<td>0.00155</td>
<td>0.892</td>
</tr>
<tr>
<td>5000 - 6000</td>
<td>76.753</td>
<td>0.000278</td>
<td>0.107</td>
</tr>
<tr>
<td>6000 - 7000</td>
<td>4.461</td>
<td>5.50 x 10^5</td>
<td>1.23 x 10^3</td>
</tr>
<tr>
<td>7000 - 11000</td>
<td>0.529</td>
<td>5.67 x 10^6</td>
<td>1.50 x 10^5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>362.033</td>
<td></td>
<td>19.556</td>
</tr>
</tbody>
</table>

Soviet and Russian scientists compiled a large data set for modern sedimentation at the seafloor. Unfortunately, this data base is not available to the international scientific community. The mean sedimentation rates for different sediment types were, however, recently reported by Baturin (2007). The total amount of sediment being deposited at the seafloor as derived from that data set (18.84 x 1015 g yr⁻¹, Baturin, 2007) is consistent with the values calculated from Eq. (1) (19.56 x 1015 g yr⁻¹; see Table 1). The contribution of shelf and upper slope sediments (13.6 x 1015 g yr⁻¹, Baturin, 2007) compares well with our estimate (14.1 x 1018 g yr⁻¹, see Table 1). The validity of Eq. (1) may be further tested by considering independent data on the particle input to the global ocean compiled in Table 2. The global sediment accumulation rate derived from these data (19.62 x 1015 g yr⁻¹) is almost identical to the global rate derived from Eq. (1) (19.56 x 1015 g yr⁻¹; see Table 1). It
can thus be concluded that the overall rate and distribution of Holocene sediment accumulation is well represented by Eq. (1) (Fig. EA-7).

<table>
<thead>
<tr>
<th></th>
<th>Accumulation rate (10^{15} \text{g yr}^{-1})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riverine particles</td>
<td>14.0</td>
<td>Syvitski et al., 2005</td>
</tr>
<tr>
<td>Ice-rafted particles</td>
<td>2.9</td>
<td>Raiswell et al., 2006</td>
</tr>
<tr>
<td>Dust</td>
<td>0.45</td>
<td>Jickells et al., 2005</td>
</tr>
<tr>
<td>Shelf carbonate</td>
<td>1.0</td>
<td>Kleypas, 1997</td>
</tr>
<tr>
<td>Pelagic carbonate</td>
<td>1.0</td>
<td>Archer, 1996</td>
</tr>
<tr>
<td>Biogenic opal</td>
<td>0.27</td>
<td>Sarmiento and Gruber, 2006</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>19.62</strong></td>
<td></td>
</tr>
</tbody>
</table>

In many cases, the thickness of the GHSZ known from direct observations exceeds the depth of Holocene sediments by several orders of magnitude. Thus, mean sedimentation rates averaged over a period of several million years would be more appropriate for the prediction of hydrate accumulation than Holocene accumulation rates. During the Holocene, most riverine particles are deposited on the continental shelf because the shelf is not at isostatic equilibrium with the present sea level but is still affected by the much lower glacial sea level stand (Hay and Southam, 1977). The sea level was 120 m below its present value during the last glacial maximum (Rohling et al., 1998) reducing the water-covered shelf and marginal sea areas by approximately 50% (Menard and Smith, 1966, Peltier, 1994 and Ludwig et al., 1999). Under glacial conditions, the anomalous Holocene shelf accumulation rate may have been diminished by an order of magnitude (Hay, 1994) shifting the focus of sedimentation from the shelf to the continental rise and slope. Moreover, the transport of ice-rafted material and the deposition of eolian dust were strongly enhanced further increasing the accumulation rates at the margin seafloor (Lisitzin, 1996). Due to pressure conditions required for maintaining hydrate stability, gas hydrate accumulations occur only in margin sediments deposited at more than 300–350 m water depth on the continental slope and rise. The mean Quaternary sedimentation rate in this environment is certainly much higher than the Holocene value. The sediment accumulation at 200–3000 m water depth (Holocene value \(2.73 \times 10^{15} \text{g yr}^{-1}\); see Table 1)
would increase by a factor of up to 5 if most of the Holocene shelf sedimentation
\((14.1 \times 10^{15} \text{ g yr}^{-1}; \text{see Table 1})\) was shifted to larger water depth under glacial conditions as
proposed by Hay (1994). The hydrate accumulation model was thus run for two different
scenarios. In the first scenario, we applied Holocene sedimentation rates calculated via Eq.
(1). This run gives a minimum estimate of sediment and hydrate accumulation at the slope
and rise. In the second scenario we increased the sedimentation rate at the distance from
the continents of <500 km by moving deposited material from shallow water depth (0–200
m) areas to continental slopes while the sedimentation rates at (>500 km) distance were
maintained at the Holocene level defined by Eq. (1). This approach accounts for the
Quaternary maximum sedimentation rates within continental margins. Thus, the total
amount of sediments \((19.556 \times 10^{15} \text{ g yr}^{-1}; \text{see Table 1})\) remains the same over the global
ocean area.

3. MATHEMATICAL MODEL

3.1. INTRODUCTION

In order to constrain the global distribution and abundance of marine methane hydrates,
we have developed a 1D numerical model simulating gas hydrate formation and
dissolution processes in marine anoxic sediments and applied it globally in a multi-1D
mode. The reaction-transport model is based on kinetically controlled rates of microbial
POC degradation via sulfate reduction and methanogenesis. The system contains three
dissolved compounds (methane (CH\(_4\)), dissolved inorganic carbon (DIC), sulfate (SO\(_4^{2-}\))),
two solid compounds (gas hydrate (GH), particular organic carbon (POC)), and one
gaseous compound (free methane gas (FG)). The model predicts concentration profiles for
all chemical species and the total gas hydrate inventory of the considered sediment column.
Multi-1D modeling assumes a negligible effect of horizontal mass and energy exchange
which is a reasonable assumption in this kind of sedimentary systems. All sets of single
models were run until they reached steady-state conditions based on a steady amount of
methane within the entire sediment column (scenario without hydrate formation), steady
total mass of hydrates (hydrate and/or hydrate and free gas formation), or steady volume of methane gas (free gas formed alone).

To obtain a fine resolution of depth-dependent microbial, chemical, and kinetic reactions, each sediment column has been discretized with a centimeter scale numerical grid. The uppermost bioturbated part of sediment column was not considered in the model because of strongly variable gradients of chemical species concentrations.

3.2. Reference Frame

Ocean basins and continental margins experience continuous vertical motion due to sedimentation and isostatic compensation processes. This makes the choice of reference frame essential. We consider a reference frame which extends from the seafloor to the bottom of the GHSZ plus 50 m 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. The length of each sediment column is constant over time and is limited according to the global sediment thickness data. Therefore, the model column does not include the Free Gas Zone for those cases where the thickness of the GHSZ exceeds the sediment thickness. This fixed lower boundary results in the advective loss of system components through the bottom of the modeling domain.

Porosity, which decreases exponentially with depth, is calculated using Eq. (2) from Athy (1930) for the initial porosity \( \phi_0 \) and compaction length scale \( c_0 \).

\[
\phi(z) = \phi_0 \cdot \exp(c_0 \cdot z)
\]

where \( \phi \) is the porosity; \( \phi_0 \) is the initial porosity at the seafloor; \( c_0 \) is the compaction length scale (cm\(^{-1}\)); \( z \) is the depth (cm).
3.3. 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. (3)):

\[
-w_0 \frac{(1-\phi_0)}{(1-\phi)}
\]

(3)

where \( w \) is the burial velocity of solid species (cm yr\(^{-1}\)); \( z \) is the depth (cm); \( w_0 \) is the burial velocity at the upper boundary (cm yr\(^{-1}\)); \( \phi_0 \) is the initial porosity at the seafloor; \( \phi \) is the porosity.

Burial velocity applied at the top of each model domain (\( w_0 \)) is taken from Eq. (1). Sediment compaction results in pore fluid pressurization and expulsion of pore fluids carrying dissolved chemical species (Fig. 2). In high permeability systems all excess pressures are released by relative upward flow; significant excess pressures can build up in systems of low permeability. Permeability is often correlated to porosity and may further be affected by hydrate content. Garg et al. (2008) reported that the size of sediment pores may affect the process of gas hydrate formation. The lithology of the potential hydrate-bearing zone (i.e. coarse-grained sands) may result in preferential hydrate accumulation. According to Darcy’s law, high permeability allows for enhanced gas fluxes. However, a buffer effect caused by decreasing effective porosity due to formation of thick hydrate layers close to the bottom of the Gas Hydrate Stability Zone may block the advective free gas transport and support further hydrate accumulation within the lower part of GHSZ. These mechanisms are still poorly understood and were, thus, not considered in our model. Here we assume that permeability is always sufficiently high for pore fluids to be expelled by compaction. This allows us to use an analytical expression (Eq. (4)) for pore fluid flow (Hutchison, 1985):

\[
-v_e = \frac{-w_0 (1-\phi_0) \cdot \exp \left( z - \frac{B}{\lambda} \right)}{1-\phi_0 \cdot \exp \left( -\frac{B}{\lambda} \right)}
\]

(4)
where \( v \) is the burial velocity of solid species (cm yr\(^{-1}\)); \( z \) is the depth (cm); \( w_0 \) is the burial velocity at the upper boundary (cm yr\(^{-1}\)); \( \phi_0 \) is the initial porosity at the seafloor; \( \phi \) is the porosity; \( B \) is the basement depth (cm); \( \lambda = 1/c_0 \) is the characteristic depth (cm).

Fig. 2. An example of compaction-driven solid and fluid components movement within sediment column. Upward directed expulsion of fluids due to compaction processes provides a relative pore waters migration towards the seafloor, in relation to sediment grains (left panel). Progressing compaction results in depth-decreasing porosity (middle panel). Both solid and pore fluid velocities are directed downward in relation to the seafloor (right panel). Negative values of both velocities are the evidence of consequent downward movement of solid and fluid compounds. Gas phase included in the model is buried with sediment grains using the solid velocity.

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 (see Table 3). Note that this equation solves for fluid flow with respect to the seafloor and flow is therefore always directed downwards but of lower magnitude than the solid velocity. A potential gas phase included in the model is buried with sediment grains using the solid velocity.

Table 3. Complete list of symbols and parameters used in the model formulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B )</td>
<td>Basement depth</td>
<td>-</td>
<td>cm</td>
<td>description in text</td>
</tr>
<tr>
<td>( c_0 )</td>
<td>Compaction length scale</td>
<td>( 0.83 \times 10^5 )</td>
<td>cm(^{-1})</td>
<td>-</td>
</tr>
<tr>
<td>( n )</td>
<td>Number of grid points in the modeling domain</td>
<td>300</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( T_o )</td>
<td>Tortuosity</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
<td>Value</td>
<td>Notes</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
<td>---------------</td>
<td>------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
<td>year</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>z₀</td>
<td>Seafloor</td>
<td>cm</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>z</td>
<td>Depth</td>
<td>cm</td>
<td>-</td>
<td>-</td>
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<tr>
<td>λ</td>
<td>Characteristic depth</td>
<td>cm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>κ</td>
<td>Thermal conductivity</td>
<td>W m⁻¹ K⁻¹</td>
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<td>-</td>
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<tr>
<td>φ₀</td>
<td>Initial porosity</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>φ</td>
<td>Porosity</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>u</td>
<td>Velocity of dissolved species</td>
<td>cm year⁻¹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>w₀</td>
<td>Burial velocity of solid species</td>
<td>cm year⁻¹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>w₆₀</td>
<td>Burial velocity at the upper boundary</td>
<td>cm year⁻¹</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>Concentration of dissolved species</td>
<td>mM</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>Concentration of solid species</td>
<td>wt. %</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Dₘ</td>
<td>Molecular diffusion coefficient</td>
<td>cm² year⁻¹</td>
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<tr>
<td>Dₛ</td>
<td>Diffusion coefficient in sediments</td>
<td>cm² year⁻¹</td>
<td>-</td>
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</tr>
<tr>
<td>CH₄ ini</td>
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<td>mM</td>
<td>10⁻¹</td>
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<td>DIC ini</td>
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<td>mM</td>
<td>4</td>
<td>description in text</td>
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<td>SO₄ ini</td>
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<td>28.9</td>
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<tr>
<td>R(X)</td>
<td>Change in chemical species concentrations</td>
<td>-</td>
<td>see Table 6</td>
<td>s. Table 6</td>
</tr>
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<td>RPOC</td>
<td>Rate of POC degradation</td>
<td>wt. % year⁻¹</td>
<td>-</td>
<td>description in text</td>
</tr>
<tr>
<td>Rₐom</td>
<td>Rate of Anaerobic Oxidation of Methane</td>
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<td>-</td>
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<td>Rate of methanogenesis</td>
<td>mM year⁻¹</td>
<td>-</td>
<td>s. Table 4</td>
</tr>
<tr>
<td>Rₛᵣ</td>
<td>Rate of sulfate reduction</td>
<td>mM year⁻¹</td>
<td>-</td>
<td>s. Table 4</td>
</tr>
<tr>
<td>RGH</td>
<td>Rate of gas hydrate formation</td>
<td>wt. % year⁻¹</td>
<td>-</td>
<td>s. Table 5</td>
</tr>
<tr>
<td>RₐFG</td>
<td>Rate of free methane gas formation</td>
<td>wt. % year⁻¹</td>
<td>-</td>
<td>s. Table 5</td>
</tr>
<tr>
<td>RₜGH</td>
<td>Rate of gas hydrate dissolution</td>
<td>wt. % year⁻¹</td>
<td>-</td>
<td>s. Table 5</td>
</tr>
<tr>
<td>RₜFG</td>
<td>Rate of free methane gas dissolution</td>
<td>wt. % year⁻¹</td>
<td>-</td>
<td>s. Table 5</td>
</tr>
<tr>
<td>dₛ</td>
<td>Density of dry sediments</td>
<td>g cm⁻³</td>
<td>2.65</td>
<td>-</td>
</tr>
<tr>
<td>dGH</td>
<td>Gas hydrate density</td>
<td>g cm⁻³</td>
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<td>-</td>
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<tr>
<td>dFG</td>
<td>Free methane gas density</td>
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<td>-</td>
<td>description in text</td>
</tr>
<tr>
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<td>g mol⁻¹</td>
<td>12</td>
<td>-</td>
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<tr>
<td>MWGH</td>
<td>Molecular weight of gas hydrate</td>
<td>g mol⁻¹</td>
<td>124.13</td>
<td>-</td>
</tr>
<tr>
<td>MWfg</td>
<td>Molecular weight of free methane gas</td>
<td>g mol⁻¹</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>Vol</td>
<td>Molar volume of free methane gas</td>
<td>cm³ mol</td>
<td>-</td>
<td>description in text</td>
</tr>
<tr>
<td>CH₄ diss</td>
<td>Solubility of dissolved methane</td>
<td>mM</td>
<td>-</td>
<td>description in text</td>
</tr>
<tr>
<td>CH₄ free</td>
<td>Solubility of gaseous methane</td>
<td>mM</td>
<td>-</td>
<td>description in text</td>
</tr>
<tr>
<td>Kc</td>
<td>Monod inhibition constant of POC degradation</td>
<td>mM</td>
<td>47</td>
<td>description in text</td>
</tr>
<tr>
<td>a₀</td>
<td>Initial age of organic matter decomposition</td>
<td>year</td>
<td>-</td>
<td>description in text</td>
</tr>
<tr>
<td>kₛₐ</td>
<td>Age-dependent kinetic constant of POC degradation</td>
<td>year⁻¹</td>
<td>-</td>
<td>description in text</td>
</tr>
<tr>
<td>kₐom</td>
<td>Kinetic constant of methane oxidation</td>
<td>mM⁻¹ year⁻¹</td>
<td>10⁸</td>
<td>s. Table 4</td>
</tr>
<tr>
<td>Kₘ₂₇</td>
<td>Sulfate inhibition constant on methane</td>
<td>mM</td>
<td>1</td>
<td>s. Table 4</td>
</tr>
</tbody>
</table>
### 3.4. Governing Equations for Solid and Dissolved Compounds

Two major phases essential for gas hydrate formation were considered: liquid pore fluids containing dissolved chemical species (CH₄, CH₄, DIC and SO₄) and solids including incompressible sediment grains and particulate organic carbon. Free gas (formed due to hydrate recycling processes at the bottom of GHSZ or directly by POC degradation at great depths below the GHSZ) is attached to sediment grains and transported downward with solid phase velocity. Upward gas advection is thus neglected in the model since measurements in consolidated sediments indicate that gas migration occurs only if more than approximately 10% of the pore space is occupied by gas (Garg et al., 2008).

Transport of solid as well as dissolved compounds were solved as an advection process occurring via sediment burial into great depths with solid (ω) and fluid (v) velocities. Dissolved chemical species are able to diffuse through the entire sediment profile according to their molecular diffusion coefficients scaled by tortuosity (Dₜ). Source terms contain time and depth-dependent rates of various chemical reactions (organic carbon decay – \( R_{POC} \), anaerobic oxidation of methane – \( R_{AM} \), methanogenesis – \( R_{M} \), and sulfate reduction – \( R_{SO} \)). Advection and diffusion processes have been split and solved separately for each component.
Eq. (5) describes mass conservation of solid species. The first term on the right-hand side represents the advective transport of solid compounds, while the second term accounts for all chemical reactions (Table 4, Table 5 and Table 6):

\[
(1 - \phi) \frac{\partial G}{\partial t} = - \frac{\partial}{\partial z} \left( (1 - \phi) \cdot w \cdot G \right) + (1 - \phi) \cdot R \tag{5}
\]

where \( \phi \) is the porosity; \( G \) is the concentration of solid species (wt. %); \( t \) is the time (yr); \( w \) is the burial velocity of species (cm yr\(^{-1}\)); \( z \) is the depth (cm); \( R \) is the chemical reaction rates (wt. % yr\(^{-1}\)).

<table>
<thead>
<tr>
<th>Rate</th>
<th>Kinetic rate law</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anaerobic Oxidation of Methane (mmol · yr(^{-1}))</td>
<td>( R_{AOM} = k_{AOM} \cdot C(\text{SO}_4) \cdot C(\text{CH}_4) )</td>
</tr>
<tr>
<td>Methanogenesis (mmol · yr(^{-1}))</td>
<td>( R_{M} = 0.5 \cdot \frac{K_{\text{SO}<em>4}}{C(\text{SO}<em>4) + K</em>{\text{SO}<em>4}} \cdot R</em>{\text{POC}} \cdot r</em>{C} )</td>
</tr>
<tr>
<td>Sulfate reduction (mmol · yr(^{-1}))</td>
<td>( R_{SR} = 0.5 \cdot \frac{C(\text{SO}<em>4)}{C(\text{SO}<em>4) + K</em>{\text{SO}<em>4}} \cdot R</em>{\text{POC}} \cdot r</em>{C} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{AOM} ) (dm(^{3}) · mmol(^{-1}) · yr(^{-1}))</td>
<td>( 10^{-8} )</td>
</tr>
<tr>
<td>( K_{\text{SO}_4} ) (mM)</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conversion factor</th>
<th>Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( r_{C} = \frac{\phi \cdot MW_{C}}{\left(1 - \phi\right) \cdot d_{e} \cdot 10^{4}} )</td>
</tr>
<tr>
<td></td>
<td>where ( \phi ) = porosity ( MW_{C} ) = molecular weight of carbon (g · mol(^{-1})) ( d_{e} ) = density of dry sediments (g · cm(^{-3}))</td>
</tr>
</tbody>
</table>

Mass conservation of dissolved species is defined by Eq. (6) in which the first term on the right-hand side describes advective transport with the fluid velocity, the second one accounts for the molecular diffusion of dissolved species, and the last (source) term represents chemical reactions:

\[
\phi \cdot \frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left( \phi \cdot v \cdot C \right) + \frac{\partial}{\partial z} \left( \phi \cdot D_{S} \cdot \frac{\partial C}{\partial z} \right) + \phi \cdot R \tag{6}
\]
where \( \phi \) is the porosity; \( C \) is the concentration of dissolved species (mM); \( D_s \) is the diffusion coefficients (cm\(^2\) yr\(^{-1}\)); \( t \) is the time (yr); \( v \) is the burial velocity of dissolved species (cm yr\(^{-1}\)); \( z \) is the depth (cm); \( R \) chemical reaction rates (wt. % yr\(^{-1}\)).

Dissolved species concentrations are calculated in mmol dm\(^{-3}\) (mM) and subsequently converted into mol cm\(^{-3}\) to be consistent with depth (cm) and volume (cm\(^3\)) units. Conversion factors of chemical reactions and gas hydrate and free gas formation rates are presented in tables after the modeling rate expressions (Tables 4 and 6).

Molecular diffusion of dissolved species is controlled by changes in concentration gradients. Diffusion coefficients of dissolved chemical compounds in sediments are calculated as molecular diffusion coefficients \( (D_m) \) for constant temperature (2 °C) and salinity (35 PSU) according to the equations from Boudreau (1997) scaled by tortuosity \( (T_o) \) from Boudreau (1996) (Eq. (7)):

\[
T_o^2 = 1 - 2 \cdot \ln(\phi)
\]  

(7)

where \( T_o \) is the tortuosity; \( \phi \) is the porosity.

Diffusion coefficient of dissolved inorganic carbon was treated as a combination of HCO\(^3^-\) and CO\(_2\) (in 50:50 proportion) diffusivity which are the most wide-spread inorganic carbon carriers within marine anoxic sediments in close to neutral pH regimes.

3.5. Reactions

A key reaction is the degradation of organic matter (POC) which follows the kinetic approach developed by Wallmann et al. (2006) (Eq. (8)). This kinetic equation considers the decrease in organic matter reactivity with depth and age of sediments (Middelburg, 1989) and the inhibition of anaerobic degradation processes by the accumulation of dissolved metabolites in ambient pore fluids. Monod constant \( K_c \) describes the inhibition of organic matter decomposition by the concentration of CH\(_4\) and DIC. High values of \( K_c \) constant favor rapid POC decomposition and, consequently, gas hydrate formation:
\[ R_{POC} = \frac{K_c}{C(DIC) + C(CH_4) + K_c} \cdot k_x \cdot G(POC) \]  

(8)

where \( R_{POC} \) is the rate of POC degradation (wt. % yr\(^{-1}\)); \( K_c \) is the Monod inhibition constant (mM); \( k_x \) is the age-dependent kinetic constant (yr\(^{-1}\)); \( C \) is the concentration of dissolved species (mM).

A comparison of the new rate law with the classic Middelburg formulation showed that in mainly anoxic sediments with high concentrations of metabolites, Wallmann’s kinetic equation results in diminished POC degradation rates that are in good agreement with pore water data obtained at ODP site 997 (Blake Ridge) and seven stations at Sakhalin slope (Sea of Okhotsk) (Wallmann et al., 2006). Subsequently, the Wallmann formulation was applied to a wide range of geological settings represented by ODP sites 1041 (Costa Rica), 685 and 1230 (Peru), 1233 (Chile), 1014 (California), 995 (Blake Ridge), and 1084 (Namibia) (Marquardt et al., 2010). Required modeling parameters were taken directly from ODP reports and a good fit to the observed concentrations of dissolved metabolites accumulating in the pore fluids of the studied sediments was obtained applying a \( K_c \) value of 25–50 mM. Here, we used a relatively high value of 47 mM to allow for significant gas hydrate formation from in-situ POC degradation. Since microbial formation of methane remains only one of the multiple gas sources in marine sediments, our results should be considered as the minimum estimate of offshore gas hydrate deposits. The age-dependent kinetic constant \( k_x \) was computed following a simple formulation assuming a depth-decreasing reactivity of metabolites (Eq. (9); see Middelburg, 1989):

\[ k_x = 0.16 \cdot \left( a_0 + \frac{z}{w} \right)^{-0.95} \]  

(9)

where \( k_x \) is the age-dependent kinetic constant (yr\(^{-1}\)); \( a_0 \) is the initial age of organic matter decomposition (yr); \( z \) is the depth (cm); \( w \) is the burial velocity of solid species (cm yr\(^{-1}\)).
Chapter 1

The upper boundary of each modeling domain is situated 10 cm below the real sediment surface where the effects of bioturbation and bioirrigation processes become negligible. Thus, the initial age of POC degradation from Eq. (9) represents time needed to reach the undisturbed sediments.

POC is degraded via microbial sulfate reduction until the dissolved sulfate pool in ambient pore waters is depleted (see Table 4). Below the sulfate penetration depth, POC is microbiologically decomposed into methane and CO₂. Upward diffusing dissolved methane is consumed by anaerobic oxidation within the sulfate–methane transition zone. The rate of anaerobic oxidation of methane ($R_{AOM}$) depends on methane and sulfate concentrations in pore fluids and is additionally controlled by the kinetic constant $K_{AOM}$ (see Table 4).

4. GAS HYDRATE AND FREE GAS FORMATION

Gas hydrate formation occurs wherever the dissolved methane concentration within the Gas Hydrate Stability Zone exceeds the critical saturation (CH₄diss). Free methane gas is formed below the GHSZ when dissolved methane concentrations exceed the free gas solubility (CH₄free). Hydrate ($R_{GH}$) and free gas formation ($R_{FG}$) rates are controlled by kinetic constants $k_{GH}$ and $k_{FG}$ preventing over-saturations (see Table 5). Hydrate and free gas are dissolved in undersaturated pore fluids. Dissolution rates ($R_{DGH}$ and $R_{DFG}$) depend on saturation states with respect to hydrate and free gas and are mediated by corresponding kinetic constants (see Table 5). Dissolved methane is able to form either gas hydrates ($\text{CH}_4 \leftrightarrow \text{GH}$), free gas ($\text{CH}_4 \leftrightarrow \text{FG}$) or both at the same time, and vice versa. A modified Pitzer-approach from Tishchenko et al. (2005) is used to calculate the solubility curves of the mentioned phases for a wide range of temperature, pressure, and salinity values.
Table 5. Rates of the gas hydrate and free gas formation and dissolution

<table>
<thead>
<tr>
<th>Rate</th>
<th>Kinetic rate law</th>
</tr>
</thead>
<tbody>
<tr>
<td>if ( C(CH_4) \geq CH_4^{\text{diss}} ) ( R_{GH} ) (wt. % \cdot yr(^{-1}))</td>
<td>[ R_{GH} = k_{GH} \cdot \left( \frac{C(CH_4)}{CH_4^{\text{diss}}} - 1 \right) ]</td>
</tr>
<tr>
<td>if ( C(CH_4) &lt; CH_4^{\text{free}} ) ( R_{DGH} ) (wt. % \cdot yr(^{-1}))</td>
<td>[ R_{DGH} = k_{DGH} \cdot \left( 1 - \frac{C(CH_4)}{CH_4^{\text{free}}} \right) \cdot G(GH) ]</td>
</tr>
<tr>
<td>if ( C(CH_4) \geq CH_4^{\text{free}} ) ( R_{FG} ) (wt. % \cdot yr(^{-1}))</td>
<td>[ R_{FG} = k_{FG} \cdot \left( \frac{C(CH_4)}{CH_4^{\text{free}}} - 1 \right) ]</td>
</tr>
<tr>
<td>if ( C(CH_4) &lt; CH_4^{\text{free}} ) ( R_{DFG} ) (wt. % \cdot yr(^{-1}))</td>
<td>[ R_{DFG} = k_{DFG} \cdot \left( 1 - \frac{C(CH_4)}{CH_4^{\text{free}}} \right) \cdot G(FG) ]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{GH} ) (wt. % \cdot yr(^{-1}))</td>
<td>( 5 \cdot 10^{-3} )</td>
</tr>
<tr>
<td>( k_{DGH} ) (yr(^{-1}))</td>
<td>( 2 \cdot 10^{-2} )</td>
</tr>
<tr>
<td>( k_{FG} ) (wt. % \cdot yr(^{-1}))</td>
<td>( 10^{-3} )</td>
</tr>
<tr>
<td>( k_{DFG} ) (yr(^{-1}))</td>
<td>( 10^{-4} )</td>
</tr>
</tbody>
</table>

The rates of microbial and chemical reactions as well as rates of hydrate and free gas formation and dissolution processes were consequently updated after each time step according to the formulations listed in Table 6.

Table 6. Change in chemical species concentrations \( R(X) \) due to chemical reactions. Factor \( \xi \) used in the POC unit conversion has been described in Table 4

<table>
<thead>
<tr>
<th>Solid species (wt. %)</th>
<th>Rate expression (wt. % \cdot yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particular Organic Carbon POC</td>
<td>( R(POC) = -R_{POC} )</td>
</tr>
<tr>
<td>Gas hydrate GH</td>
<td>( R(GH) = R_{GH} - R_{DGH} )</td>
</tr>
<tr>
<td>Dissolved species (mM)</td>
<td>Rate expression (mM \cdot yr(^{-1}))</td>
</tr>
<tr>
<td>Methane ( CH_4 )</td>
<td>( R(CH_4) = R_M - R_{AOM} - (R_{GH} + R_{DGH})/r_{GH} - (R_{FG} + R_{DFG})/r_{FG} )</td>
</tr>
<tr>
<td>Dissolved Inorganic Carbon DIC</td>
<td>( R(DIC) = R_{POC}/r_c + R_{AOM} - R_M )</td>
</tr>
<tr>
<td>Sulfates ( SO_4 )</td>
<td>( R(SO_4) = -R_{SR} - R_{AOM} )</td>
</tr>
<tr>
<td>Gaseous species (wt. %)</td>
<td>Rate expression (wt. % \cdot yr(^{-1}))</td>
</tr>
<tr>
<td>Free methane gas ( FG )</td>
<td>( R(FG) = R_{FG} - R_{DFG} )</td>
</tr>
</tbody>
</table>

Conversion factor | Formulation |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_{GH} ) from (wt. %) into (mM)</td>
<td>( r_{GH} = \frac{\phi \cdot MW_{GH}}{(1 - \phi) \cdot d_s \cdot 10^4} ) &lt;br&gt;where</td>
</tr>
</tbody>
</table>
Gas hydrate and free gas formation rates were finally converted from wt. % into vol. % units by using the $r_{GH}^{vol}$ and $r_{FG}^{vol}$ factors (Eqs. (10) and (11)):

$$r_{GH}^{vol} = \frac{(1 - \phi) \cdot d_s}{\phi \cdot d_{GH}}$$ (10)

$$r_{FG}^{vol} = \frac{(1 - \phi) \cdot d_s}{\phi \cdot d_{FG}}$$ (11)

where $\phi$ is the porosity; $d_s$ is the density of dry sediments (g cm$^{-3}$); $d_{GH}$ is the density of gas hydrate (g cm$^{-3}$); $d_{FG}$ is the density of methane gas (g cm$^{-3}$).

Apart from gas hydrate density $d_{GH}$ which was set to a constant value of 0.916 g cm$^{-3}$ according to Wallmann et al. (2006), significant changes of temperature and pressure conditions due to increasing depth are important in free methane gas density $d_{FG}$ calculations. By using the Eq. (12) a depth-dependent free gas density profile was incorporated into our model:

$$d_{FG} = \frac{MW_{FG}}{Vol}$$ (12)

where $d_{FG}$ is the density of methane gas (g cm$^{-3}$); $MW_{FG}$ is the molecular weight of methane gas (g cm$^{-1}$); Vol is the molar volume of methane gas (cm$^3$ mol).

Calculations of pure methane gas molar volume (Vol) at various temperature, pressure, and fugacity coefficients were based on equations given in Tishchenko et al. (2005).
5. Numerical Procedure

As boundary conditions we assume constant concentrations of dissolved methane, dissolved inorganic carbon, and sulfate at the top of each modeled sediment column according to the mean concentrations observed at the bottom of the bioturbated zone (see Table 3). POC concentrations at the upper boundary of the model columns were set to the ambient values given by Seiter et al., 2004 and Romankevich et al., 2009. Burial velocities at zero depth \( w_0 \) were defined as a function of water depth applying Eq. (1). As discussed in a Section 3, in a second model run, \( w_0 \) values were enhanced by a factor of 5 along continental margins to estimate Quaternary burial velocities. Zero concentration gradients were applied at the lower boundary of the model column.

At modeling time zero sediment pore space was filled by pore fluids with salinity values consistent with the one at the sediment–water interface. The initial concentrations in the uppermost segment of the model column were defined according to the upper boundary conditions. Within the sediment column, the initial concentrations of POC, dissolved methane and DIC were set to zero while a simple exponential function was applied to define the down-core decrease in initial dissolved sulfate concentrations. Pressure regimes were calculated separately for each sediment bin as hydrostatic pressure values considering ambient water and sediment depths. Temperature profiles are set according to the bottom water temperature and heat flow data.

The governing diffusion–advection equations are solved using an operator-splitting technique. Diffusion is solved using a fully-implicit finite-differences method. Advection is solved by a Semi-Lagrangian scheme using linear interpolation functions. The update of all concentration profiles is sequential: during every time step, first the reaction rates are computed, next the transport parts of all equations are solved, and finally the diffusion parts. All chemical reactions are treated as source terms in the diffusion solver. The entire model was implemented in Matlab 7.7.0 (R2008b).
6. RESULTS AND DISCUSSION

6.1. GLOBAL GAS HYDRATE DISTRIBUTION

We have analyzed two scenarios of low and high sedimentation which represent minimum and maximum estimates of hydrate accumulation via microbial methane formation within the GHSZ. In the low sedimentation rate scenario we explored the dynamics of hydrate formation under Holocene boundary conditions. The total amount of methane carbon from hydrates is estimated to be ∼4.18 Gt. Gas hydrate deposits are distributed mostly in the Central America and Arctic region with concentrations not exceeding 150 kg C m⁻². Our results show that widespread hydrate formation based on in-situ POC degradation is very unlikely to occur due to low burial velocities of particulate organic matter. The amount of dissolved methane is usually too small to exceed the CH₄ solubility curve which is the critical step for hydrate precipitation. This model result clearly shows that hydrate formation is severely limited by low sedimentation rates at the continental slope and rise. Trapping of terrigenous particles in the shelf environment, thus, effectively inhibits hydrate formation via microbial POC degradation within the GHSZ under Holocene boundary conditions (Wallmann et al., 2006).

The Quaternary sedimentation conditions applied in the second scenario result in significant and wide-spread gas hydrate accumulations along active and passive continental margins (i.e. western and eastern coasts of North and South America). Hydrates are also formed in parts of the Indian Ocean, the Arctic Ocean, the Southern Ocean and the equatorial Pacific (see Fig. 3). Total amount of methane gas trapped within hydrate-bearing sediments in the high sedimentation scenario is estimated at 2.10×10¹⁵ m³ (expanded to atmospheric conditions) or, equivalently, 995 Gt of methane carbon. This value is in good agreement with predictions of 500–2500 Gt of carbon presented by Milkov (2004) based on field observations.
The highest gas hydrate concentrations (up to 830 kg C m$^{-2}$) are observed in regions of high organic carbon accumulation (Fig. EA-6), i.e. Central America, eastern coast of South America, Laptev Sea, and Arabian Sea and do not correlate in a simple way with GHSZ thicknesses (Fig. 4). For up to 0.5 % of the total number of hydrate-bearing modeling domains gas hydrate concentrations exceed 400 kg C m$^{-2}$ (i.e. Central America, Arctic, and Arabian Sea). Gas hydrates have been previously documented at various cold seeps (Schmidt et al., 2005) and ODP sites along the Central American margin (Hensen and Wallmann, 2005). Moderate hydrate concentrations (150–400 kg C m$^{-2}$) occur at ~8.5 % of total hydrate provinces (western and eastern coasts of North America, Arctic, Sea of Okhotsk, Antarctic, eastern coast of Australia, Africa continental margin, Indian Ocean, Central America, and eastern coast of Greenland). The remaining regions of hydrate accumulation feature low hydrate saturations (<150 kg C m$^{-2}$).
Fig. 4. Predicted thickness of the gas hydrate stability zone (GHSZ).

One of the first model-based estimates of the global methane hydrate inventory was presented by Buffett and Archer (2004). They used the rain rate of particulate organic carbon (POC) to the seabed as a major external driving force for the simulation of hydrate formation in marine sediments. The rain rate was calculated as a function of water depth and applied as an upper boundary condition for an early diagenesis model simulating the degradation of POC in the top meter of the sediment column (Archer et al., 2002). The POC burial rate at 1 m sediment depth calculated with this “muds” model was applied as an upper boundary condition for the simulation of methane turnover in the underlying sediment sequence. The later simulations consider the microbial degradation of POC via sulfate reduction and methanogenesis and the anaerobic oxidation of methane within the sulfate–methane transition zone (Davie and Buffett, 2001 and Davie and Buffett, 2003). POC was separated into an inert fraction and a labile fraction that was degraded over the top km of the sediment column following first order reaction kinetics (rate constant $3 \times 10^{-13} \text{ s}^{-1}$). The model also considers an externally imposed rate of upward fluid flow. It was calibrated using field data obtained at Blake Ridge (a passive margin site) and the Cascadia margin (active continental margin). The best fit to observations was obtained
assuming that the 25% of the total POC is labile and using upward fluid flow velocities of 0.23 mm yr$^{-1}$ (passive margin) to 0.4 mm yr$^{-1}$ (active margin). Applying these parameter values on a global grid and assuming a compensating downward fluid flow over 50% of the global seafloor area resulted in a total methane hydrate inventory of 3000 Gt C (Buffett and Archer, 2004). The hydrate inventory was to a large degree controlled by the velocity of upward fluid flow that was assumed to exceed the flow rate induced by sediment compaction by 20% (passive margins) to 60% (active margins). Without imposed fluid flow, the global hydrate inventory was reduced to 600 Gt C (Buffett and Archer, 2004). Subsequently, the authors discovered an extrapolation error in the calculation of POC rain rates as function of water depth (Archer et al., 2008). The model-based estimate of the global hydrate inventory was reduced from 3000 Gt C to approximately 700–900 Gt C after correction for this error (Archer et al., 2008).

Klauda and Sandler (2005) used a slightly modified version of the Davie and Buffett model (Davie and Buffett, 2001) to estimate the global marine hydrate inventory. The entire POC pool was assumed to be completely degradable with a reduced decay constant of only $1.5 \times 10^{-14}$ s$^{-1}$. In contrast to Buffett and Archer, 2004 and Archer et al., 2008, the upper boundary of the model domain was constrained by field data. POC concentrations measured in surface sediments and Holocene sedimentation rates averaged over the major ocean basins were applied to define the POC burial flux at the sediment surface (Klauda and Sandler, 2005). In contrast to the study of Buffett and Archer (2004) and the one presented in this paper, the numerical approach of Klauda and Sandler (2005) does not consider organic matter degradation via sulfate reduction processes. Thus, efficient methane production in the upper part of the sediment column is not inhibited by the presence of dissolved sulfate. The Klauda and Sandler (2005) model was run without imposing upward fluid flow. This global hydrate inventory of $\sim 57,000$ Gt C was calculated applying the 1D model to a global grid. This estimate considers only the hydrate formed by POC degradation within the GHSZ. It is almost two orders of magnitude higher than our estimate of the global hydrate inventory and the estimate presented by Archer et al. (2008). This large difference may be explained by the neglect of microbial sulfate reduction and
Chapter 1

AOM since the accumulation of methane in pore fluids and gas hydrates is strongly diminished by these processes. Moreover, Buffett and Archer, 2004 and Klauda and Sandler, 2005 applied the thermodynamic equilibrium model between gas hydrate, sea water, and methane gas phases presented by Zatsepina and Buffett (1998), whereas our model is based on the study presented by Tishchenko et al. (2005). The latter approach considers the measured CH₄ solubility in seawater and is in good agreement with other published data (Duan et al., 1992).

The commercial recovery potential of gas hydrate resources strongly depends on the type of clathrate accumulations. Stratigraphic-type of deposits (Milkov and Sassen, 2002) usually contain highly dispersed hydrocarbons of limited economic value. However, structural gas hydrate accumulations associated with high hydrocarbon fluxes from deep origin might have an economic potential as they are able to hold a large volume of methane gas concentrated in gas hydrates (Milkov and Sassen, 2002). Comparatively, the world’s conventional gas endowment which is estimated at 2.567 TBOE (Trillion Barrels of Oil Equivalent) equivalent to 436.4×10¹² m³ of natural gas (USGS World Energy Assessment Team, 2000), is at least a few times smaller than the global methane hydrate inventory calculated in our Quaternary simulation. It should, however, be noted that the simulation results and the global inventories presented in this study are only valid for finely dispersed gas hydrates (stratigraphic type of deposits).

Significant hydrocarbon fluxes from a deep origin are well-known to occur in many important gas hydrate provinces, i.e. the Gulf of Mexico or Hydrate Ridge (Torres et al., 2004 and Liu and Flemings, 2006). Gas hydrate deposits associated with active faults and craters of deep-water mud volcanoes usually present higher gas hydrate concentrations (30–50 % of the pore space is filled by hydrates according to Milkov and Sassen (2002)). Comparatively, stratigraphic types of accumulations located within passive margins are characterized by relatively low advective fluid fluxes and low hydrate concentrations (5–10 % of the pore space is filled by hydrates according to Xu and Ruppel (1999)).

The locations and abundance of deep methane sources are still under discussion and were not taken into account in our investigations. Fig. 5 presents the average pore-space filled by
gas hydrates for the high sedimentation scenario. The highest fractions of the total pore space occupied by hydrates (10–12 %) are characteristic of regions with relatively shallow water depths and high organic carbon content. Mean hydrate saturations calculated by our model approach do not exceed 2–4 % of the total pore space.

![Sediment pore space filled by hydrates](image.png)

Fig. 5. Predicted filling of pore space by gas hydrate in the high sedimentation scenario.

6.2. CONTROLS ON GAS HYDRATE FORMATION

Gas hydrates are able to precipitate in porous media situated within the Gas Hydrate Stability Zone (GHSZ) which is defined by ambient pressure, temperature, and salinity conditions. Gas hydrate and free gas solubility curves calculated by the thermodynamic model of Tishchenko et al. (2005) intersect at the lower boundary of the GHSZ. This vertical extent of the GHSZ is limited by sediment thickness for up to 38 % of the total world ocean surface. Thus, it can be suggested that a significant part of the global hydrate stability field in marine settings extends to the bottom of oceanic sediments. Free gas is thus not stable and present in many pelagic open ocean settings.

Gas Hydrate Stability Zones of significant thicknesses (600–800 m) are mainly situated in high-latitude regions (Arctic and Antarctic) due to low bottom water temperatures which maintain conditions required for hydrate formation. Extended GHSZs are also observed
along continental margins (>500 m) where thick sedimentary sequences are deposited. In these settings the extent of the GHSZ is not limited by sediment thickness such that free gas accumulates in sediments below the GHSZ.

Fig. 6 presents a relationship between thickness of GHSZ and depth-integrated hydrate concentration for the high sedimentation scenario. Presented data include all modeling domains where gas hydrates accumulate. For relatively low GHSZ thicknesses a delicate trend of increasing hydrate concentrations could be observed. However, moderate and large GHSZ thicknesses (>200–220 m) do not correlate in a simple way with the amount of hydrates. Under these conditions, simulated hydrate accumulations largely depend on the supply of methane via in-situ organic matter degradation.

Fig. 6. Relationship between gas hydrate stability zone (GHSZ) thickness and gas hydrate concentration for high sedimentation scenario. A correlation for relatively thin stability zones could be observed (see further description in text).

The availability of organic carbon at the seafloor is thought to be one of the most essential parameters limiting gas hydrate formation (Revelle, 1983, Kvenvolden, 1988 and Klauda and Sandler, 2005). The minimum concentration of TOC necessary to initiate and sustain hydrate precipitation was suggested to be larger than 1 wt. % (Kvenvolden, 1988), 0.5 wt. % (Revelle, 1983). We suggest that hydrate formation is not controlled by concentration of organic carbon but rather by the combination of TOC concentration and sedimentation rate. Fig. 7 presents the relationship between rates of sedimentation and organic matter
concentration for our high sedimentation scenario. All grid points where hydrates accumulate are included in this figure whereas grid points without hydrate accumulation are excluded. The minimum amount of TOC needed to form gas hydrates is around 0.3 wt. % for high sedimentation rates and relatively shallow water depths (~250 m). This threshold value increases with decreasing sedimentation rate and reaches a value of >1.0 wt. % at low sedimentation rates (~1 cm kyr⁻¹) characteristic for large water depths and open ocean settings. The TOC concentration threshold for hydrate formation is thus not a fixed value but a function of sedimentation rate.

![Graph](image)

Fig. 7. TOC concentration at the surface as a function of sedimentation rate shows the minimum amount of organic matter needed for gas hydrate formation in the high sedimentation scenario (see further description in text).

7. CONCLUSIONS

Using our approach the world’s total inventory of gas hydrates is estimated at 0.82×10¹³ m³–2.10×10¹³ m³ CH₄ (at STP conditions) or, equivalently, 4.18–995 Gt of methane carbon. The low estimate corresponds to the Holocene sedimentation scenario, while the high estimate refers to a scenario of higher Quaternary sedimentation at continental slope and rise settings. These estimates are significantly lower than previously reported values and are based on improved reaction kinetics of POC degradation in model calculations and a new compilation of global input data (see Figs. EA-1–EA-7).
Chapter 1

The new estimate of Holocene sedimentation rates presented in this contribution clearly shows that widespread gas hydrate formation is very unlikely to occur under Holocene boundary conditions. Holocene sedimentation is concentrated in shelf environments and is not high enough at continental slopes to form significant hydrates deposits. It appears likely that active upward transport of free methane gas and methane rich pore fluids from underlying sediment sequences is the main driving force for hydrate formation during the Holocene.

The high sedimentation scenario is likely to represent the present, steady-state hydrate budget formed in-situ by organic matter degradation. It assumes that hydrate formation occurs over the entire GHSZ, which includes sediments deposited not only during the Holocene but rather over a time span of several million years. Relatively high rates of sedimentation during the glacial periods of the Quaternary provided gas hydrate formation within continental margins thereby increasing the global budget of hydrates.

In-situ gas hydrate formation is directly limited by the amount of organic matter deposited at the sediment surface. Our studies show that not only the surface concentration of TOC controls hydrate formation but rather the supply rate. Analysis of all individual model runs has further shown that the thickness of the stability zone correlates only weakly with the amount of hydrate formed.

The present study illustrates how numerical modeling can help to synthesize and assimilate multiple data sets in order to make predictions on the global abundance of marine gas hydrates. Future work should aim at reducing the large span of such global hydrate estimates. For this it will be necessary to improve predictions on physical conditions at the seafloor, obtain converging estimates on methane solubility in seawater, and improve numerical reaction-transport models.

It should be noted that the hydrate accumulations presented in this study do not include hydrate deposits formed by the focused ascent of gas and fluids from deeper sedimentary strata. It is presently not possible to estimate the global amount of these additional hydrate deposits. Regional geophysical surveys and drilling information is needed to better constrain the abundance of these economically promising deposits.
ACKNOWLEDGMENTS

This paper has benefited from constructive reviews by Alexei Milkov and an anonymous reviewer. We appreciate the helpful comments of Associate Editor David Burdige which helped to improve the manuscript. We thank Arne Biastoch for providing the global bathymetry, bottom water temperature, and salinity data sets and Matthias Haeckel for discussions and helping us setting up the model.

APPENDIX A. SUPPLEMENTARY DATA

Fig. EA-1. Bathymetry data extracted from an Ocean General Circulation Model (OGCM) simulation run in the ORCA_R025 configuration (Barnier, 2006) (see further information in the main text).
Fig. EA-2. Salinity data extracted from an Ocean General Circulation Model (OGCM) simulation run in the ORCA_R025 configuration (Barnier, 2006) (see further information in the main text).

Fig. EA-3. Bottom water temperature data extracted from an Ocean General Circulation Model (OGCM) simulation run in the ORCA_R025 configuration (Barnier, 2006) (see further information in the main text).
Fig. EA-4. Heat flow data provided by the International Heat Flow Commission (IHFC) (Hamza et al., 2008a) (see further information in the main text).

Fig. EA-5. A combined set of global sediment thicknesses based on the NOAA data (Divins, 2003) and arctic region data (Laske and Masters, 1997) (see further information in the main text).
Fig. EA-6. POC concentrations in surface sediments according to the data from Seiter et al., 2004a and Romankevich et al., 2009a (see further information in the main text).

Fig. EA-7. Global sedimentation rate data obtained from a novel parameterization of Holocene sedimentation (Eq. 1; see further information in the main text).

REFERENCES


Chapter 1


CHAPTER 2: A NEW NUMERICAL SOLVER FOR A MULTIPHASE FLOW AT MARINE POROUS SEDIMENTS- NEW APPLICATION AND INSIGHTS ON GAS HYDRATE FORMATION AND FREE GAS CO-EXISTENCE FROM THE BLAKE RIDGE SITE

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ABSTRACT

Marine sediments of the Blake Ridge province, offshore South Carolina exhibit clearly defined geophysical indications for the presence of gas hydrates and the free gas phase. However, seismic indications for lower boundary of the gas hydrate stability zone (GHSZ) known as the Bottom Simulating Reflectors (BSRs) do not fully coincide with theoretically-derived GHSZ thicknesses. It was suggested that the present of mixed zone containing co-existing gas hydrate and free gas phases might explain the observed phenomena. By designing a new multi-phase Finite Element (FE) numerical model, we investigate the potential of gas hydrate formation from single and mixed methane sources (in-situ biogenic formation and deep methane flux). Adaptive mesh approach allows us to apply distinct compaction properties and sedimentation rates to each deposited layer.

Additionally, this study explores the conditions of methane supply via active fluid flow under which reported gas hydrate and free gas concentrations formed. We conclude that the CH4 mass flux of $1.6 \times 10^{11}$ kg s$^{-1}$ m$^{-2}$ (corresponding to $\sim$170 mM of CH4) is necessary to obtain observed gas hydrate concentrations and allows for mobile free gas phase being present with concentrations reaching up to $\sim$7.3 vol. %.
Keywords: gas hydrate, numerical modeling, reaction-transport modeling, Blake Ridge

INTRODUCTION

Gas hydrates (clathrates) are ice-like crystalline cage structures containing various greenhouse gases, such as methane or CO₂, which are locked within their spatial structure. The combination of relatively low temperature and high pressure conditions defines the Gas Hydrate Stability Zone (GHSZ) which is a proxy to the spatial abundance of gas hydrates in oceanic and permafrost regions. Thus, gas hydrate distribution in oceanic settings is mainly controlled by three factors: 1) low temperature regimes, 2) high pressure regimes, and 3) presence of biodegradable organic matter. Marine gas hydrate deposits were discovered mainly along continental margins (slope and rise) where water depths exceed 300 m and bottom water temperatures are low enough to sustain gas hydrate presence. Due to their composition, gas hydrates are vulnerable to temperature, pressure, and, to a smaller degree, salinity changes. Their potential impact on a climate change, slope stability, and global energy reserves has drawn considerable public and scientific attention over the last decades. However, there is still a lack of understanding of the processes dynamics associated with gas hydrate formation and decomposition. Important insights on the free gas migration through the GHSZ, gas hydrate crystallization in a heterogeneous media, and hazard assessment due to the slope instability are still required.

The amount of gas hydrates present on a global scale in marine sediments is still under debate (Boswell and Collett, 2011b; Milkov A. V., 2004). Several numerical models of a different complexity have been developed to estimate the potential amount of clathrates locked world-wide within marine sediments (Archer et al., 2009; Buffett B. and Archer D., 2004; Burwicz et al., 2011a; Dickens G. R., 2001; Klauda J. B. and Sandler S. I., 2005; Wallmann et al., 2012). Global estimates range from 500 Gt up to 75,000 Gt of methane carbon and show a variation of several orders of magnitude. In comparison, the world’s conventional gas endowment has been estimated at 2.567 TBOE (Trillion Barrels of Oil
Equivalent) = $0.436 \cdot 10^{15} \text{ m}^3$ of natural gas (USGS World Energy Assessment Team, 2000) which covers about 0.5 % - 40 % of the total methane gas volume potentially trapped in gas hydrates (from $1.06 \cdot 10^{15} \text{ m}^3 \text{ CH}_4$ up to $120.78 \cdot 10^{15} \text{ m}^3 \text{ CH}_4$ at STP condition). A major part of world’s total gas hydrate deposits becomes significantly vulnerable to increase in bottom water temperatures on long geological time-scale. However, it has been postulated that particular prominent gas hydrate provinces (e.g. Blake Ridge, Arctic Ocean, Gulf of Mexico) will suffer a noticeable reduction in gas hydrate stability zone thicknesses over the next century (Kretschmer et al., submitted) and therefore, become potentially important as methane gas release sites. Current climate changes may already trigger gas hydrate dissociation and cause observable methane releases around the world (Berndt et al., 2014; Biastoch et al., 2011; Bunz et al., 2012; Paull C. K. et al., 1996; Phrampus and Hornbach, 2012; Rajan et al., 2013; Rajan et al., 2012; Skarke A. et al., 2014; Westbrook G. K. et al., 2009). The presence of active venting structures on the seafloor has been observed in prominent hydrate-bearing regions (e.g. offshore Svalbard, Alaskan Beaufort Sea, Laptev Sea, offshore Spitsbergen, SW Barents Sea, and offshore South Carolina) that are primary vulnerable to a climate change. Seismic data confirm the co-existence of free methane in a gas phase being actively transported through sediment column lying within the Gas Hydrate Stability Zone (Bunz et al., 2012; Paull C. K. et al., 1996; Rajan et al., 2012). However, due to complexity of marine research in the Arctic regions, most of the data acquisition took place during the summer period which leaves the question of seasonality of such events open. Seasonal increase and decrease in methane release might suggest a vivid and immediate formation and dissolution of gas hydrate deposits within a time frame of weeks or months. Another important feature of hydrate-bearing sediments in terms of numerical modeling is their lithological heterogeneity (e.g. river delta fan environment) which implies a unique vertical and horizontal porosity and permeability profiles and thus, distribution of chemical species and organic matter necessary for hydrate formation. In the regions of a complex sedimentation history, it is required to take into account the influence of alternately deposited thin and thick sedimentary layers of different grain size and compaction properties.
Due to the complex and challenging matter of these processes, it is important to precisely validate the numerical approach on a well-studied gas hydrate province manifesting GHSZ thickness reduction due to currently undergoing significant bottom water temperature increase. Blake Ridge, offshore South Carolina has been widely investigated during the Ocean Drilling Project (ODP) Leg 164. Seismic profiles of two (995 and 997) out of three (955, 997, and 994) penetrated drilling sites, which form a transect across the Blake Ridge, exhibit clearly defined Bottom Simulating Reflector (BSR) which is a sub-parallel to the seafloor seismic signature marking the boundary of a high-amplitude seismic reflection (corresponding to the presence of a free gas) overlain by low-amplitude seismic reflection (also known as the ‘blanking effect’ after Shipley et al., 1979). The depth of a seismic BSR is often corresponding to the present or paleo-base of theoretical thermodynamic GHSZ which defines the sharp phase boundary between stability field of gas hydrate and free gas. However, in the case of a Blake Ridge hydrate province, relatively shallow position of BSRS at the 995 and 997 sites (~ 440 mbsf) might suggest a coexistence of free gas phase and gas hydrate deposits down to the bottom of the thermodynamic GHSZ (~ 520 mbsf) (Guerin G. et al., 1999; Paull C. K. and Matsumoto R., 2000; Paull C. K. et al., 1996). This transition zone shows no evidence for a major lithological or structural change that might give another explanation for this effect.

Microbial in-situ origin of gas hydrates stored within marine sediments of the Blake Ridge has been suggested by Borowski W. S. et al., 1997 and Paull C. K. and Matsumoto R., 2000 based on significantly depleted in δ13C pure methane gas analyses (Claypool G. E. and Kaplan I. R., 1974). However, previous modeling attempts (Davie M. K. and Buffett B. A., 2001, 2003a, b; Egeberg and Dickens, 1999; Garg S. K. et al., 2008; Wallmann K. et al., 2006; Xu W. and Ruppel C., 1999) based on numerical modeling approaches assuming a constant sedimentation rate and seafloor POC concentrations (besides Wallmann, 2006 which assumed a linear decrease in POC concentration for the last 0.8 Ma) over the entire history of the basin were not successful in confirming this hypothesis. As a result, modeled gas hydrate and free gas concentrations were, in many cases, far too little to support a hypothesis of their microbial in-situ origin. Therefore, several authors suggested the
importance of a deep-source upward methane flux in the formation of Blake Ridge gas hydrates (e.g. Garg S. K. et al., 2008; Wallmann K. et al., 2006). The rate of pore fluid flux within the GHSZ has been derived from halogen geochemical analysis (Egeberg and Dickens, 1999) and established at the level of 0.2 mm · year⁻¹. However, as it was suggested by Phrampus and Hornbach, 2012 and others, derivation of the pore fluid flux rates based on geochemical data is still debatable. By applying variable POC concentration at the seafloor, we have investigated herein: 1) the potential of the Blake Ridge gas hydrates formation from a single in-situ microbial source throughout the entire history of the basin as well as from the mixed source (microbial + deep-source methane flux), 2) gas hydrate and free gas formation dynamics including the potential phase co-existence, and 3) the impact of sediment deposition and compaction on fluid and gas flow regimes coupled with bio-chemical reactions occurring in the sediment column.

**MATHEMATICAL MODEL**

**INTRODUCTION**

The new numerical multi-phase model accounts for *in-situ* POC degradation that leads to gas hydrate and free gas formation and dissolution. The model contains four phases (solid porous matrix, pore fluids, gas hydrate, and gaseous methane (CH₄gas)) and four chemical species (organic carbon (POC), dissolved inorganic carbon (DICdiss), dissolved methane (CH₄diss), dissolved sulfates (SO₄diss)). Chemical reactions included in the model are resolving for the bio-chemical processes in anoxic marine sediments represented by: 1) POC degradation via sulfate reduction, 2) methanogenesis, and 3) anaerobic oxidation of methane (AOM). Sediment pore space can be occupied by three phases (pore fluids carrying chemical species, solid gas hydrates, and free methane gas) proportional to their saturations. Solid compound that is present in a pore space (gas hydrate) is stationary with respect to grains and follows the burial velocity of sediments. Gas hydrates in the model are assumed to represent structure I (pure methane hydrates). Formation of gas hydrate and free gas takes place whenever the concentration of dissolved in pore fluid methane exceeds the solubility limits (Tishchenko P. et al., 2005). Two possibilities of gas hydrate and free
gas formation have been investigated: i) under local thermodynamic equilibrium which neglects the kinetic effects of crystallization and ii) kinetically controlled gas hydrate and free gas formation and dissolution. The first assumption leads to a situation where only two phases can occupy the pore space at the same time (fluids and gas hydrates or fluids and free gas). However, as it has been already suggested, the presence of all three phases together at the same time takes place in natural hydrate systems (Bunz et al., 2012; Gorman et al., 2002; Torres M. E. et al., 2004). In the second scenario, kinetically controlled rates of gas hydrate and free gas formation has been incorporated into our model. Similar to the formation, gas hydrate dissolution and free gas condensation rates follow the kinetic approach previously described by Wallmann K. et al., 2006 and valid for the Blake Ridge Site, offshore South Carolina.

**GOVERNING EQUATIONS**

Water and methane components that are included in the model can occur in different phases: solid (gas hydrate), fluid (brine, dissolved methane), and gaseous (free methane). We assume that sediment pores are always fully saturated with fluid, gas, and gas hydrates ($S_f + S_g + S_h = 1$).

Sediment grains, gas hydrate and organic carbon (POC) are transported downward according to the burial velocity of the whole sediment column. Following Eq. 1 and 2 describe the mass balance formulation for solid sediment grains and gas hydrates, respectively:

\[
\frac{\partial ((1-\phi) \rho_s)}{\partial t} = -\nabla \cdot \left( (1-\phi) \rho_s \bar{V}_s \right) + Q_s
\]  

where $\phi$- porosity, $\rho_s$- density of sediment grains, $V_s$- burial velocity of solids, $Q_s$- source term accounting for in/situ POC degradation, and $t$- time.

\[
\frac{\partial (\phi S_h \rho_h)}{\partial t} = -\nabla \cdot \left( \phi S_h \rho_h \bar{V}_s \right) + Q_h
\]  

(2)
where $\phi$- porosity, $S_h$- hydrate saturation, $\rho_h$- density of hydrate, $V_s$- burial velocity of solids, $Q_{et}$- source term accounting for hydrate precipitation and dissolution, and $t$- time.

Mass conservation of fluid and gas phase is presented as Eq. 3 and Eq. 4, respectively.

$$\frac{\partial (\phi S_f \rho_f)}{\partial t} = -\nabla \cdot \left( \phi S_f \rho_f \mathbf{V}_f \right) + Q_f$$

(3)

where $\phi$- porosity, $S_f$- fluid phase saturation, $\rho_f$- density of fluid, $V_f$- fluid phase velocity, $Q_f$- source term accounting for bio-chemical reactions occurring in the fluid phase, and $t$- time.

$$\frac{\partial (\phi S_g \rho_g)}{\partial t} = -\nabla \cdot \left( \phi S_g \rho_g \mathbf{V}_g \right) + Q_g$$

(4)

where $\phi$- porosity, $S_g$- gas phase saturation, $\rho_g$- density of gas, $V_g$- gas phase velocity, $Q_g$- source term accounting for free gas formation and dissolution, and $t$- time.

Advection pore velocities were calculated for three phases ($V_s$- solids, $V_f$- pore fluids, and $V_g$- free gas). Gas hydrates are advected with a solid velocity $V_s$ according to the rate of sediment burial. Fluid ($V_f$) and gas ($V_g$) velocities were calculated according to the Darcy’ formulation and are shown in the Eq. 5 and Eq. 6, respectively:

Darcy’ velocity for fluids:

$$\mathbf{U}_f = \phi \frac{S_f}{S_f} \left( \mathbf{V}_f - \mathbf{V}_s \right) = -\frac{k^f}{\mu_f} \left( \nabla P - \rho_f g \right)$$

(5)

where $\phi$- porosity, $S_f$- saturation of fluid, $V_f$- pore velocity of fluids, $V_s$- burial velocity of solids, $k^f$- intrinsic permeability, $k^f_r$- relative permeability of fluid, $\mu_f$- viscosity of fluid phase, $dP$- pressure gradient, $\rho_f$- density of fluid phase, $g$- gravitational acceleration.
Chapter 2

Darcy’s velocity for gas:

\[
U_g = \phi S_g \left( \mathbf{V}_g - \mathbf{V}_s \right) = -\frac{k_{g}^{\phi}}{\mu_g} \left( \nabla P - \rho_g g \right)
\]  \hspace{1cm} (6)

where \( \phi \) - porosity, \( S_g \) - saturation of gas, \( \mathbf{V}_g \) - pore velocity of gas, \( \mathbf{V}_s \) - burial velocity of solids, \( k \) - intrinsic permeability, \( k_{g}^{\phi} \) - relative permeability of gas, \( \mu_g \) - viscosity of gas phase, \( \nabla P \) - pressure gradient, \( \rho_g \) - density of gas phase, \( g \) - gravitational acceleration.

The dynamic viscosity \( \mu_f \) (fluid phase) and \( \mu_g \) (gas phase) from Eq. 5 and Eq. 6 depend on temperature and pressure. Here, we use a constant average value of fluid and methane gas that is valid over the investigated pressure and temperature range (see Tab. 1).

Intrinsic permeability value can be derived from the Kozeny-Carman type relationship defined according to Eq. 7 (Hantschel T. and Kauerauf A., 2009). Parameters \( S \) and \( B \) included in the Equation represent scaling factors valid for various lithologies (see Tab. 1 for exact values used in the model). In case of gas hydrate precipitation process that occurs within the pore space of sediments, additional scaling of the intrinsic permeability is required. Thus, effective porosity and effective tortuosity should be introduced in the Eq. 7 as \( \phi_{\text{eff}} = \phi \cdot (1 - S_h) \) and \( T_{\text{o,eff}} = 1 - \log (\phi_{\text{eff}}) \).

\[
k = \frac{B \cdot \phi^3}{T_{\omega}^2 \cdot S^2}
\]  \hspace{1cm} (7)

where \( k \) - intrinsic permeability, \( B \) - geometrical factor, \( \phi \) - porosity, \( T_\omega \) - tortuosity, \( S \) - specific surface area.

In a case of a multiphase flow, the relative permeability of fluid \( (k_f^\phi) \) and methane gas \( (k_g^\phi) \) phases are defined as follows (Parker et al., 1987):
\[ k_r^f = \left( \frac{S_f - S_{df}}{1 - S_{df}} \right)^{\gamma_f} \cdot \left( 1 - \left( \frac{S_f - S_{df}}{1 - S_{df}} \right)^{\gamma_f} \right)^m \]  
\[ k_r^g = \left( 1 - \text{Min} \left[ \frac{S_f - S_{df}}{1 - S_{df} - S_{rg}}, 1 \right] \right)^2 \cdot \left( 1 - \text{Min} \left[ \frac{S_f - S_{df}}{1 - S_{df} - S_{rg}}, 1 \right] \right) \]

where \( k_r^f \) - relative permeability of fluid, \( S_f \) - saturation of fluid, \( S_{df} \) - residual saturation of fluid, \( m \) - sediment factor.

\[ k_r^g = \left( 1 - \text{Min} \left[ \frac{S_f - S_{df}}{1 - S_{df} - S_{rg}}, 1 \right] \right)^2 \cdot \left( 1 - \text{Min} \left[ \frac{S_f - S_{df}}{1 - S_{df} - S_{rg}}, 1 \right] \right) \]

where \( k_r^g \) - relative permeability of gas, \( S_f \) - saturation of fluid, \( S_{df} \) - residual saturation of fluid, \( S_{rg} \) - residual saturation of gas.

The sediment factor \( m \) (Eq. 8 and 9) varies with lithology and represents the most suitable value for a given sediment type (see Tab. 1). The residual fluid \( S_{df} \) and residual gas \( S_{rg} \) saturations are describing the immobile fraction of each phase that can be present in the pore space without having an impact on the relative permeability of this phase (see Tab. 1). The minimum condition \( \text{Min} \) is introduced to maintain the relative gas permeability \( k_r^g \) at zero for gas saturations below the residual value \( S_{rg} \). The exact amount of gas that represents the residual immobile fraction is still under discussion. \( S_{rg} \) is believed to have very small values during drainage processes (from 0 to 0.02). Thus, only a small fraction of the upward migrating gas is trapped when gas ascends into previously water filled pore space. However, the value of \( S_{rg} \) increases during wetting (imbibition) processes when gas is displaced by water. The hysteresis that occurs during alternating drainage as well as the wetting cycles are not considered in the model since our focus is essentially limited to drainage processes. We found it convenient to use \( S_{rg} = 0.05 \) - 0.1 to describe the gas flow reported from naturally occurring gas hydrate provinces (see Tab. 1).
### Tab. 1. Physical parameters used in numerical simulations (see further description in text)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>Gravitational acceleration</td>
<td>g</td>
<td>9.81 m·s²</td>
<td></td>
</tr>
<tr>
<td>Density of sediment grains</td>
<td>ρ_s</td>
<td>2650 kg·m⁻³</td>
<td></td>
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<tr>
<td>Density of gas hydrate</td>
<td>ρ_h</td>
<td>913 kg·m⁻³</td>
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<td>Intrinsic permeability</td>
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<td>Geometrical factor</td>
<td>B</td>
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<td>Specific surface area</td>
<td>S</td>
<td>10⁻² m²/m³</td>
<td>Hantschel T. and Kauerauf A., 2009</td>
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<td>Relative permeability of fluid</td>
<td>k_i</td>
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<td>Relative permeability of gas</td>
<td>k_j</td>
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<td></td>
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<td>Dynamic viscosity of fluid</td>
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<td>Xu and Germanovich, 2006</td>
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<tr>
<td>Dynamic viscosity of gas</td>
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<td>Sediment factor</td>
<td>m</td>
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<td>Residual water saturation</td>
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<td>Residual gas saturation</td>
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<td>This study</td>
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</tr>
</tbody>
</table>

The pore pressure has been calculated according to the following Eq. 10 where i denotes fluid, free gas and hydrate phases and j stands for fluid and gas phase only:

$$
\sum_i \left[ \phi S_i \frac{D\rho_i}{Dt} \right] = \sum_j \left[ \nabla \cdot \left( \frac{kk_j}{\mu_j} \rho_j \left( V_P + \rho_j g \right) \right) \right] - \sum_i \left[ \frac{1}{1 - \phi} \frac{D\phi}{Dt} + \frac{\phi \rho_i S_i}{\rho_i} \frac{D\rho_i}{Dt} \right]
$$

(10)

where φ - porosity, S - saturation of a given phase, ρ - density of a given phase, k - intrinsic permeability, k_j - relative permeability of a given phase, μ - viscosity of a given phase, g-gravitational acceleration, V_s - burial velocity of solids, t- time, and D- material (substantial) derivative defined as:
\[
\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{V}_s \cdot \nabla
\]  

(11)

where \( \frac{D}{Dt} \) is the material (substantial) derivative, \( t \) is time, and \( \mathbf{V}_s \) is the burial velocity of solids.

Material derivative (Eq. 11) is commonly used to describe the rate of change of physical property (e.g., density in Eq. 10) in the presence of time-dependent velocity field. The choice of the reference frame used in the model implies that all the material derivatives turn into the normal derivatives due to the fact that the motion of sediment grains (\( \mathbf{V}_s \) from Eq. 11) is compensated by the adjustment of the reference frame. Therefore, the secondary term on the RHS of the Eq. 11 drops out (see detailed description in the following reference frame section).

The LHS of the Equation 10 accounts for a density change of fluid, gas, and hydrate phase with time. The first term on the RHS accounts for mobility of a fluid and gas phases due to the pressure change and gravitational flow and does not apply for gas hydrates. The second term on the RHS describes changes in porosity with time due to a change of mass of a given component that occupies the pore space (e.g., due to advection or diffusion processes or phase transitions such as gas hydrate crystallization and dissolution). Derivation of the Equation 10 will lead to the assumption that the transport of stationary with respect to the grains phase (gas hydrate) is equal zero and the reference frame is not attached to the seafloor but adapts to the uppermost contour of modeling column (see Fig. 1 and detailed description in the following reference frame section). During a derivation of the pressure equation (Eq. 10), compressibility factors for fluid, gas, and gas hydrate phases are introduced (\( \beta_f, \beta_g, \) and \( \beta_h \), respectively). Note that the compressibility factor \( \beta \) for a hydrate phase is relatively small in comparison to the similar parameter for fluid and gas phases due to the stiffness of a hydrate crystal structure (see Tab. 1 for exact values).

Methane compound in the modeling system can exist in three different phases—dissolved in pore fluids, trapped within a hydrate structure, or as a free gas filling the pore space of sediments. All three phases are advected independently according to their own pore
velocities (fluid and gas phase) and burial velocity of sediments (gas hydrates). On top of the advective transport, methane dissolved in pore fluids is also migrating in the system due to the process of diffusion similar to the other dissolved chemical components included in the model (SO₄ and DIC). The following Eq. 12 shows the general mass balance equation for chemical species dissolved in pore fluids that exist in the system, however, each of the transport processes has been solved independently by the operator splitting method:

\[
\frac{\partial (\phi S_f C)}{\partial t} = \nabla \cdot (\phi S_f D \nabla C) - \nabla \cdot (\phi S_f C \nabla \vec{v}_{\text{f}}) + Q_f
\]  

(12)

where \( D \) - derivative, \( \phi \) - porosity, \( V_f \) - pore velocity of fluids, \( S_f \) - fluid saturation, \( C \) - concentration of chemical species dissolved in pore fluids, \( D \) - diffusion coefficient, \( Q_f \) - source term accounting for bio-chemical reactions occurring in the fluid phase, and \( t \) - time.

The rate of molecular diffusion in marine sediments depends on temperature and salinity conditions. Molecular diffusion coefficients \( (D_m) \) of chemical species dissolved in pore fluids (CH₄, SO₄, and DIC) are calculated according to formulations from Boudreau B. P., 1997. The effect of tortuosity has been considered by applying the Archie’s law and calculating the diffusion coefficients in sediments \( (D_s) \). Diffusive transport of DIC is calculated as a mixture (1:1) of two major DIC species: HCO₃ and CO₂ that are widely present at the anoxic, near-neutral pH conditions.

The source term \( Q_f \) in the above mass balance equation accounts for all additional chemical species supply as a result of bio-chemical reaction rates, such as AOM, sulfate reduction, and methanogenesis. Further description of these processes can be found in the following section 2.3.
**Source Terms – Bio-Chemical Reactions**

Influence of the POC decay on gas hydrate formation has been widely discussed by Wallmann et al., 2012 and remains a crucial parameter in gas hydrate modeling. A large amount of globally predicted gas hydrate accumulations was formed due to anaerobic decay of a deeply buried organic matter (Burwicz et al., 2011; Wallmann et al., 2012). The rate and efficiency of this degradation greatly influences the amount of gas hydrate formed within the GHSZ. However, only a relatively small fraction of the POC deposited at the seafloor is transported to a certain depth below the bioturbated surface layer of sediments. According to Flogel et al., 2011, about 10% of the POC rain fraction is buried below 10 cm sediment depth at continental margins while only about 1% of POC passes by the bioturbated zone of the first 10 cm of sediments in pelagic deep-ocean environments which partially explains the lack of gas hydrate deposits in the latter case.

In our model, the rate of organic carbon degradation follows the approach from Middelburg J. J., 1989 modified by Wallmann K. et al., 2006 which assumes a depth- and age-decreasing reactivity of POC according to the following Eq. 13:

\[
R_{POC} = \frac{K_c}{C(DIC) + C(CH_4) + K_c} \cdot k_z \cdot G(POC) \tag{13}
\]

where \( R_{POC} \) - rate of organic carbon degradation, \( C(DIC) \) - concentration of dissolved inorganic carbon, \( C(CH_4) \) - concentration of dissolved methane, \( G(POC) \) - concentration of solid POC fraction, \( K_c \) - Monod inhibition constant, \( k_z \) age-dependent kinetic constant.

The age-dependent kinetic constant \( k_z \) is calculated according to the following expression (Middelburg J. J., 1989):

\[
k_z = 0.16 \cdot \left( a_0 + \frac{z}{V_s} \right)^{-0.95} \tag{14}
\]
where $a_0$, the initial age of organic matter decay (entering the methanogenic zone), $V_z$, burial velocity of solids, and $z$, depth.

Furthermore, methanogenesis is inhibited in the presence of sulfate such that methane generation occurs only after dissolved sulfate has been depleted by microbial sulfate reduction and AOM (Wallmann et al. 2006). The resulting rates of methane generation and oxidation are applied as source term Q in the mass balance equation for methane (Eq. 11) to quantify the supply of CH$_4$ into the system as a result of above microbial reactions. The full compilation of modeling parameters considering POC degradation and AOM processes at the Blake Ridge Site 997 is presented in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial age of organic matter decomposition</td>
<td>$a_0$</td>
<td>$5 \times 10^6$ years</td>
<td>Wallmann K. et al., 2006</td>
</tr>
<tr>
<td>Monod inhibition constant of organic matter degradation by DIC and CH$_4$</td>
<td>$K_N$</td>
<td>40 mM</td>
<td>Wallmann K. et al., 2006</td>
</tr>
<tr>
<td>Monod inhibition constant of CH$_4$ formation by SO$_4$</td>
<td>$K_{SO4}$</td>
<td>1 mM</td>
<td>Wallmann K. et al., 2006</td>
</tr>
<tr>
<td>Kinetic constant for AOM</td>
<td>$k_{AOM}$</td>
<td>1 cm$^3$·year$^{-1}$·mmol$^{-1}$</td>
<td>Wallmann K. et al., 2006</td>
</tr>
<tr>
<td>Sulfate concentration at the upper model boundary</td>
<td>$C_{SO4}$</td>
<td>28 mM</td>
<td>Paull C. K. et al., 1996</td>
</tr>
<tr>
<td>Methane concentration at the upper boundary</td>
<td>$C_{CH4}$</td>
<td>$10^{-4}$mM</td>
<td>Wallmann K. et al., 2006</td>
</tr>
<tr>
<td>Dissolved Inorganic Carbon (DIC) concentration at the upper boundary</td>
<td>$C_{DIC}$</td>
<td>4 mM</td>
<td>Wallmann K. et al., 2006</td>
</tr>
</tbody>
</table>

Density of a pore fluid occupying the pore space of sediments depends on temperature, pressure, presence of salt and dissolved methane. To calculate the density of pore fluids including salt (brine), we have used a numerical toolbox for Matlab codes that was developed by IOC et al., 2010 and McDougall et al., 2012. Additional scaling of the salinity input data from practical salinity units (PSU) into absolute salinity (SA) was required. Density of a H$_2$O-NaCl-CH$_4$ mixture was calculated from the equation-of-state derived by Duan Z. et al., 1992.
Methane gas density, methane gas solubility and gas hydrate solubility are calculated as time-dependent variables according to the equations from Tishchenko P. et al., 2005 and Duan Z. et al., 1992 which include the effect of salinity.

**Temperature**

The initial temperature conditions assume a constant heat flux at the bottom of a modeling domain \((z_{max}(t))\) and fixed temperature value at the sea-surface \((z=0)\). Temperature distribution for this multi-phase system has been calculated according to following Eq. 15:

\[
\left( \rho C_p \right)_{bulk} \frac{\partial T}{\partial t} = - \left( \rho C_p \right)_{bulk} \mathbf{V}_s \cdot \nabla T - \rho_f C_{pf} \mathbf{U}_f \cdot \nabla T - \rho_g C_{pg} \mathbf{U}_g \cdot \nabla T + \nabla \cdot \left( \nabla \lambda_{bulk} T \right) + Q
\]

(15)

where \(T\)- temperature, \((\rho C_p)_{bulk}\)- volumetric heat capacity, \(V_s\)- burial solid velocity, \(U_r\)- Darcy’ fluid velocity, \(U_g\)- Darcy’ gas velocity, \(C_{pf}\)- heat capacity of fluid phase, \(C_{pg}\)- heat capacity of gas phase, \(\rho_f\)- density of fluid phase, \(\rho_g\)- density of gas phase, \(\lambda_{bulk}\)- bulk thermal conductivity, \(Q\)- latent heat from melting hydrates, and \(t\)- time.

Bulk volumetric heat capacity accounts for all phases present in the model according to their saturations which contribute to the total energy balance:

\[
\left( \rho C_p \right)_{bulk} = (1-\phi) \rho_s C_{ps} + \phi S_f \rho_f C_{pf} + \phi S_g \rho_g C_{pg} + \phi S_h \rho_h C_{ph}
\]

(16)

where \((\rho C_p)_{bulk}\)- volumetric heat capacity, \(\phi\)- porosity, \(\rho_s\)- density of solid phase, \(\rho_f\)- density of fluid phase, \(\rho_g\)- density of gas phase, \(\rho_h\)- density of hydrate phase, \(S_f\)- saturation of fluid phase, \(S_g\)- saturation of gas phase, \(S_h\)- saturation of hydrate phase, \(C_{pf}\)- heat capacity of fluid phase, \(C_{pg}\)- heat capacity of gas phase, \(C_{ph}\)- heat capacity of hydrate phase.

According to Deming and Chapman, 1989, bulk thermal conductivity can be expressed as:
\[ \lambda_{\text{bulk}} = \lambda_s^{(1-\phi)} \lambda_f \phi \]  

(17)

where \( \lambda_{\text{bulk}} \) - bulk thermal conductivity, \( \lambda_s \) - thermal conductivity of solid phase, \( \lambda_f \) - thermal conductivity of fluid phase, and \( \phi \) - porosity.

However, in the four-phase system, we have to include another two terms accounting for hydrate and free gas components (Waite et al., 2007):

\[ \lambda_{\text{bulk}} = \lambda_s^{(1-\phi)} \lambda_f \phi S_f \phi^s \phi S_h \phi S_h \]  

(18)

where \( \lambda_{\text{bulk}} \) - bulk thermal conductivity, \( \lambda_s \) - thermal conductivity of solid phase, \( \lambda_f \) - thermal conductivity of fluid phase, \( \lambda_g \) - thermal conductivity of gas phase, \( \lambda_h \) - thermal conductivity of hydrate phase, and \( \phi \) - porosity.

According to Waite et al., 2007, in porous (>30 %) sediments filled in by at least 10% hydrates, their contribution to the bulk thermal conductivity increases significantly. We found the number of 0.65 W · m\(^{-1}\) · K\(^{-1}\) accounting for the thermal conductivity of gas hydrate convenient and used this constant value in our simulations. Latent heat from gas hydrate dissociation (term Q in Eq. 14) has a constant value of 450 kJ kg\(^{-1}\) (equivalent to 53.8 kJ mol\(^{-1}\)) as it was previously reported by Garg S. K. et al., 2008.

**NUMERICAL MODEL**

**REFERENCE FRAME**

In case of modeling the history of sedimentary basins undergoing processes of new sedimentary material deposition and consequent compaction, it is necessary to resolve for modeling domain which size increases with time according to the rates of sedimentation. One way is to prescribe a reference frame with fixed coordinates, adding a new grid point at each time step which, in total, increases the overall thickness of modeling column. The alternative which was chosen here is to use an adaptive mesh which re-adjusts to the
known reference point in depth (i.e. the seafloor) and consequently extends to a greater depth as the sedimentary material deposition continues with time. There are several advantages of this solution amongst which the most important are the clarity and intuitive localization of the reference point ($z_0$ coordinate at the seafloor) and the ability of using distinct compaction laws (initial porosity at the deposition time and compaction length scale) separately for each sedimentary layer which has a great implication for modeling heterogeneous media with non-uniform lithologies.

A schematic visualization of the reference concept used in the modeling is shown in Fig. 1. Initially, our modeling domain extends from the seafloor ($z_0$) to the bottom of a given, relatively small, sediment depth ($z_{\text{max}}$) and is described by a stationary coordinate system. Pore space is assumed to be fully saturated with compressible fluids of a given properties (Tab. 1) that are in equilibrium under the weight of a water column and the weight of overburden sediments.

![Diagram](image)

Fig. 1. Schematic illustration of the reference frame concept used in the model. Starting from the left: step 0 represents the initial state of modeled sedimentary column extending from the seafloor ($z_0$) to the maximum sediment depth ($z_{\text{max}}$) with an initial porosity curve (red line) ranging from high seafloor porosity value ($\phi_{(z_0)}$) up to low maximum sediment depth value ($\phi_{(z_{\text{max}})}$) containing an initial number of nodes in the $z$-direction. In the step 1, additional sedimentary layer represented by the node #7 has been deposited on top of the existing column. Top of the new layer has been marked by the $z_{\text{new dep}}$ symbol and porosity of the new layer
remains constant with depth. Step 2 depicts a compaction process of all deposited layers according to their lithological properties (in the drawing assumed to be homogeneous for simplicity) and a new porosity curve (violet line) as a result of this process. Finally, step 3 shows a vertical adjustment of the reference frame (plain translation) to match the upper boundary of sedimentary column with the seafloor coordinates \( z_0 \) and a new porosity curve (violet line). Note that porosity curves, including initial (seafloor) porosity values are only symbolic and do not represent the real compaction properties of the Blake Ridge sediments.

At the beginning of each time step, a new sedimentary layer is deposited at the top of the modeling domain (see step 1 in Fig. 1) and the whole sedimentary package undergoes the process of compaction (see step 2 in Fig. 1) which therefore modifies the spatial location of the upper boundary and following sedimentary layer contours. As a result of this reference frame adjustment (see step 3 in Fig. 1), the new upper boundary of the modeling column matches with the seafloor level \( z_{0, \text{new}} \) in the Fig. 1 and the entire sediment package extends downwards to a greater depth \( z_{\text{max, new}} \) in Fig. 1. The thickness of newly deposited layer is determined by multiplying the sedimentation rate and the time-step.

The model contains uncompressible sediment grains of a given constant density (Tab. 1) and various lithological properties. According to a given resolution, all sediment layers included in the model compact separately due to their own compaction scheme which allows us to construct a precise model of porosity and permeability evolution within the time frame of each modeling scenario (Eq. 19).

\[
\phi(z) = \phi(0) \cdot \exp(c_0 \cdot z)
\]  

where \( \phi(0) \) - porosity change with depth, \( \phi(0) \) - initial porosity on top of a sediment layer, \( z \) - depth, and \( c_0 \) - the compaction length scale of a given lithology.

It has been reported that the effect of compaction in marine sediments has a great influence on chemical species distribution within pore fluids (Wallmann et al., 2012) and thus, gas hydrate and free gas formation. To capture the potential impact of sediment heterogeneity, it is essential to implement a compaction approach that accounts for distinct lithological properties, i.e. various pore space sizes. Here, we assume that the expulsion of
pore fluids, as a result of compacting sediments, is the major process responsible for the distribution of dissolved chemical species and their residence time in a pore space. In general, methane supply to the GHSZ can occur via three distinct processes: in-situ CH₄ formation within stability zone, dissolved methane transportation within fluids migrating from great depths, or by an upward methane bubble ascend. In a simple case of in-situ methane generation, no flux boundary conditions are prescribed at the bottom of modeling column. Base of the sediment column acts like a finite basement depth and remains non-porous, thus, no additional flow occurs. Fluids mobilized in a compaction process tend to move upwards with respect to the sediment grains. However, due to the deposition of new sedimentary layers and burial velocity of grains, expelled pore fluids never reach the seafloor surface. In the case of prescribed upward flux of pore fluids that cross the lower boundary of modeling domain and enter the system, two further scenarios of fluid migration are possible: 1) the rate of fluid in-flux is high enough to diminish the effect of burial solid velocity and result in a seafloor venting, or 2) fluid velocity directed upwards with respect to the sediment grains has been enhanced by the flux but remains directed downwards with respect to the seafloor and thus, no venting occurs.

Several geological settings situated at the continental margins show an evidence for pore fluids seeping through the seafloor due to the local over-pressure conditions. As it was concluded by Wallmann et al., 2012, slope failure, tectonic stress, and active salt diapirism processes are mainly responsible for the fluid escape from the sediment to the water column and thus, should be considered, to some degree, in modeling of gas hydrate-bearing provinces.

**INITIAL CONDITIONS**

Sulfate concentration profile at the beginning of each model run decreases exponentially with depth. Initial concentration of POC (wt. %) at the top of sediment column is set up separately for each simulation scenario. Finally, salinity of pore fluids is assumed to be constant along the whole modeling domain and represents the seafloor value of investigated site (for further description of the site see Chapter 4). To initialize the P-T
conditions, we have calculated a hydrostatic pressure curve that accounts for changes in fluid density due to salinity and CH₄ concentrations and a steady-state geotherm based on the local heat flow and seafloor temperature measurements.

**Solution Algorithm**

Each computational step starts with a deposition of a new sedimentary layer according to the sedimentation rate and the time-step. The process of compaction follows the deposition and comprises the adjustment of modeling contours (top of each layer) to a new reference frame attached to the sedimentary grains. According to the new porosity values, pore pressure is calculated on every grid node of modeling column. The entire pressure equation has been solved in the Finite Elements (FE) scheme with phase properties calculated by the up-wind numerical approach. Darcy velocity calculations for fluid and gas phase are based on the outcome of the pressure solver and relative permeability computation. At this stage of modeling procedure, Courant number is calculated which limits the time-step in case of a Darcy flow exceeding the volume of one modeling cell. If the time-step needs to be reduced, solution algorithm starts from the beginning which implies that the pore pressure is computed again with accordingly decreased $dt$. Temperature solver calculates the temperature profile for entire sedimentary column including the influence from presence of each possible phase (solid, fluid, gas, and gas hydrate). Accordingly to the temperature profile, sediment diffusion coefficient for dissolved in pore fluids chemical species are updated. The processes of advection and diffusion were split and solved separately for each phase component using a Finite Volumes (FV) numerical approach. The last part of numerical procedure contains computation of all bio-chemical reaction occurring in the system, including gas hydrate formation and dissociation and phase transitions. Equation-of-state (EOS) for brine-gas-gas hydrate system is applied at the end to account for new saturations, densities and volume changes of each phase. The model has been entirely implemented in Matlab v.2012/v.2014.
**Blake Ridge Site 997 Description**

**Geological Setting**

The Blake Ridge, as one of the biggest gas hydrate province worldwide, is also one of the best studied. It is situated offshore the southeastern US coast (offshore South Carolina) as a stable Neogene and Quaternary sediment drift deposit. The Blake Ridge Site has strong seismic indications for the presence of gas hydrates that has been confirmed by the Ocean Drilling Program (ODP) Leg 164 in 1995 with a drilling Sites 994, 995, and 997 that form a transect line across the Blake Ridge province (Fig. 2). The shape of sediment waves along the Blake Ridge southern flanks is mostly determined by the presence of the Gulf Stream that mixes with the Western Boundary Undercurrent (WBUC) at moderate bottom water depths (Bryan, 1970). Since this area is strongly influenced by the Gulf Stream which is a major oceanic current affecting the climate on the Northern Hemisphere, it has become particularly vulnerable to climate change. Large quantities of methane gas locked within Blake Ridge sediments contribute to the discussion on submarine slope failure scenario and other natural hazards that might take place once the hydrate reservoir becomes unstable (Flemings et al., 2003; Hornbach et al., 2004; Phrampus and Hornbach, 2012). Sediments at the Blake Ridge are rather homogenous and contain mostly clays, claystones, and fine-grained mudstones (Paull C. K. et al., 1996) that were deposited at relatively high sedimentation rates (Ikeda A. et al., 2000). Collected drill sites data are not showing major changes in sediment composition, grain size or structural unconformities (Paull C. K. et al., 1996).
CO-EXISTENCE OF GAS HYDRATES AND FREE GAS AT SITE 995 AND 997

Two of the Blake Ridge Sites (995 and 997) show a clear seismic evidence for sharply defined BSRs on a depth of ~440 mbsf (Paull C. K. et al., 1996). However, a difference between these two Sites can be observed at higher depths (440 – 530 mbsf) where the dipole waveform amplitudes have relatively high values for the Site 977 and low values for the Site 995 which gives a clear indication about distinct elastic properties of the sediments in these two locations (Paull C. K. et al., 1996). Core from the Site 995 has been studied in details to give a qualitative interpretation of gas hydrate and free gas concentrations as well as the possible mixing zone of these two phases (Guerin G. et al., 1999). As it was reported, presence of gas hydrates was indicated for the depth interval between ~ 200 mbsf – 440 mbsf by the core thermal measurements, chemical analysis, and sediment samples recovered using Pressure Core Sampler (PCS) (Dickens et al., 1997; Paull C. K. et al., 1996). The effect of thermal blanking has been also observed over this section (Paull C. K. et al., 1996). Moreover, high gradients of seismic velocities $V_p$ and $V_s$ suggest propagating consolidation of sediments due to hydrate crystallization. From a depth of ~ 440 mbsf up to ~ 520 mbsf strong decrease of $V_p$ can be observed which is a good indicator of a free gas
presence over this section. However, it has been reported by Guerin G. et al., 1999 that parallel to the $V_p$ decrease, no drop in $V_p/V_s$ has been observed. It has been interpreted as non-standard situation for normal, partially gas-saturated sediments which suggests a different mechanical behavior of this unit. Furthermore, the authors discuss a possibility of enhanced gas hydrate dissociation over this interval to explain the differences in sediment consolidation decreasing with depth. The deepest analyzed section (> ~520 mbsf) is characterized by significant decrease in $V_p/V_s$ ratio which suggests the presence of free gas phase that partially saturates sediments without a clear indication for gas hydrates.

In contrary to the direct observations, thermal and chemical analysis of the core from Site 995 did not indicate gas hydrate presence deeper than ~ 440 mbsf. However, extend of thermodynamic GHSZ (based on theoretical steady-state calculations) is deeper and ranges ~ 540 mbsf. Several authors gave hypothetic explanations for this GHSZ thickness discrepancy. Hovland et al., 1997 and Ruppel, 1997 suggested a development of strong capillary forces arising in the fine-grained sediments that move the BSR upper in vertical direction. As a consequence of newly developed capillary forces, preferential gas hydrate dissociation occurs in smaller sediment pores which would allow free methane gas and gas hydrates co-exist in bigger sediment pores. Hornbach et al., 2004 suggested that free methane is able to build an interconnected network and migrates upwards along the developed faults.

Some similarities in gas hydrate and free gas distribution between Site 995 and Site 997 have been observed. Gas hydrates were present at the Site 997 at depths from ~180 to ~240 mbsf and from ~380 to ~450 mbsf (Dickens et al., 1997; Paull C. K. et al., 1996) and were usually appearing as nodules and veins (Paull C. K. and Matsumoto R., 2000). Concentration of hydrates estimated upon ODP drillings is relatively low and reaches ~4 % - 7 % (Paull C. K. et al., 1996, Egeberg and Dickens, 1999) and the rate of an external upward fluid flow at 0.2 mm · year⁻¹ (Egeberg and Dickens, 1999) based on measured Br/Ι ions ratio. Thickness of the thermodynamic GHSZ extends to ~ 500 mbsf and does not entirely match the depth of interpreted BSR (~450 mbsf). A hypothesis of gas hydrate and free gas co-existence in the overlapping interval (450 mbsf – 500 mbsf) might be applicable.
to this Site with some additional comments: as it was reported by Guerin G. et al., 1999, only a thin 40 m-thick interval below 450 mbsf has some indications for free gas presence. Monopole waveforms of the deeper part of this section remain not attenuated. One explanation given by the authors suggest the presence of significant gas hydrate concentrations below ~ 500 mbsf that maintain the stiffness of sediment structure and free gas concentrations not sufficient to visibly attenuate the waveforms. Based on our modeling runs with a non-steady-state geotherm and dynamically resolved compaction, we investigate the potential co-existence of gas hydrate and free gas over the discussed depth intervals to explain the discrepancy between observed BSR depth and thermodynamic GHSZ calculations.

**Site 997 Characterization**

Blake Ridge Site 997 is characterized by relatively low fluid advection rates and homogenous sediment composition with a clay fraction of 60% - 70% and limited changes in a grain size over the entire depth profile (Paull C. K. et al., 1996). Present-day, average organic carbon content in these sediments oscillates around 0.5 wt. % - 1 wt. % (Paull C. K. and Matsumoto R., 2000) or up to 1.6 wt. % (Borowski W. S. et al., 1997; Paull C. K. et al., 1996) which represents the typical range of values for oceanic margins that are enriched in organic matter in comparison to the deep-sea sediments. Rapid burial of organic matter might additionally explain the high preservation of POC in Blake Ridge region. Organic matter supply did not vary significantly over time for any of the sampled Sites 994, 996, and 997 as it was reported by Paull C. K. et al., 2000, and the source of sedimentary organic matter has been described as mainly marine. Isotopically lighter terrestrial POC might be additionally transported into the system from the neighborhood. Isotopic composition of low molecular-weight hydrocarbons (methane and ethane) suggest the microbial origin ($\delta^{13}$C$_{CH_4}$ values more negative than -61‰). According to the relationship between $\delta^{13}$C$_{CH_4}$ and $\deltaD_{CH_4}$ values, the production of methane occurred via CO$_2$ reduction at all Leg 164 Sites (Paull C. K. et al., 2000) and the pools of CH$_4$ and CO$_2$ were decoupled from each other which implies an existence of an open carbon system during diagenetic processes. As
it was suggested by the authors, majority of the \( \text{CH}_4 \) and \( \text{CO}_2 \) flux was added to the system from the sediments lying underneath and it was rather not locally produced. The best fit to the data was obtained for a scenario assuming a depth- decreasing reactivity of metabolites which confirms the right choice of our POC degradation term.

As it was postulated by Borowski W. S. et al., 1997, anaerobic oxidation of methane is the main process responsible for sulfate depletion in marine sediments of Blake Ridge province. This conclusion stands upon the contestation of sulfate concentration gradient linearity with depth. The boundaries of sulfate presence zone range from the seafloor to \(~20 \text{ mbsf} \) or \(~23 \text{ mbsf} \) and are mainly controlled rather by the flux of methane from underlying sediments than organic matter supply from the top (Borowski W. S. et al., 1997). Calculations of methane flux based on the sulfate concentration profile suggest a noticeable lateral variation of methane concentration in sediment column which might be an implication for heterogeneous gas hydrate distribution underneath.

Gas hydrate deposits at the Blake Ridge province are mainly represented by structure I hydrates with 94 % cage occupancy and volumetric ratio of gas to water ~204 which corresponds to the hydration number of \( n = 6.1 \) assuming that \( n \) varies with depth (calculated for in-situ pressure conditions at the Blake Ridge). Table 3 contains the general characteristics of Site 997 that were previously established from drilling reports, seismic data interpretations, and other sources.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water depth</td>
<td>2781 m</td>
<td>Borowski W. S. et al., 1997; Paull C. K. et al., 1996</td>
</tr>
<tr>
<td>Bottom water temperature</td>
<td>2 °C</td>
<td>Borowski W. S. et al., 1997; Paull C. K. et al., 1996</td>
</tr>
<tr>
<td>Geothermal gradient</td>
<td>0.035 °C \cdot m(^{-1})</td>
<td>Borowski W. S. et al., 1997; Paull C. K. et al., 1996</td>
</tr>
<tr>
<td>Salinity</td>
<td>32 PSU (value from Site 995)</td>
<td>Paull C. K. et al., 1996</td>
</tr>
<tr>
<td>Gas composition</td>
<td>99 % ( \text{CH}_4 ), 1 % ( \text{CO}_2 )</td>
<td>Paull C. K. et al., 2000</td>
</tr>
<tr>
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<td>Curve fitting parameter</td>
</tr>
<tr>
<td>Compaction length scale</td>
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<td>Curve fitting parameter</td>
</tr>
<tr>
<td>Organic carbon available at the seafloor</td>
<td>1.6 wt. %</td>
<td>Borowski W. S. et al., 1997; Paull C. K. et al., 1996</td>
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</tbody>
</table>

63
To understand a depositional history of Blake Ridge province, detailed study on nannofossils and sedimentary particles has been performed by Ikeda A. et al., 2000. According to the authors, productivity regimes at the Blake Ridge Site 997 can be divided into five distinct stages: low- productivity stage 1 from 6.6 Ma to 6 Ma, high- productivity stage 2 from 6 Ma to 4.8 Ma, low- productivity stage 3 from 4.8 Ma to 3.6 Ma, fluctuating productivity stage 4 from 3.6 Ma to 0.8 Ma, and the final low- productivity stage 5 from 0.8 Ma to present. This data imply a down- core increase in sedimentation rates (see Tab. 4) which has been used as an input data set for our modeling runs.

<table>
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<tr>
<th>Epoch</th>
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<td>0 – 18</td>
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<td></td>
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<td>2.76 – 3.62</td>
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<td></td>
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<td></td>
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**PREVIOUS NUMERICAL MODELING APPROACHES OF THE BLAKE RIDGE SITE 997**

Previous modeling attempts to investigate the dynamics of gas hydrate formation at Blake Ridge Site 997 have been conducted by several authors (Davie M. K. and Buffett B. A., 2001, 2003a, b; Garg S. K. et al., 2008; Wallmann K. et al., 2006; Xu W. and Ruppel C., 1999). Xu W. and Ruppel C., 1999 investigated the potential of gas hydrate crystallization and distribution for diffusive- and advective- dominated systems using a steady- state analytical model. According to Xu W. and Ruppel C., 1999, high enough methane mass flux at the bottom of GHSZ which exceeds a critical value of about 3·10⁻¹¹ kg s⁻¹ m⁻² is required for the observed base of gas hydrate accumulations to coincide with the
theoretical GHSZ. However, these calculations assumed no effect of sedimentation which implies a constant upward fluid flux of a given interstitial velocity equal to 0. A quasi-steady state has been achieved after 10 Myr simulation time. They have concluded that the surface POC fraction of 1.5 wt. % that has been reported for the Blake Ridge site yields to an average hydrate fraction of about 2 vol. % and does not fully explain observed gas hydrate concentrations (4 – 7 vol. % after Paull C. K. et al., 1996). Thus, significant methane supply from underlying sediments is required to match numerical modeling with field observations. Davie M. K. and Buffett B. A., 2003a and Davie M. K. and Buffett B. A., 2003b were investigating the dynamics of gas hydrate formation in terms of 1) constant upward fluid velocity of about 0.26 mm year\(^{-1}\) and 2) in-situ bio-methane source with 50 % conversion of the available organic carbon and fluid flow restricted to 0.08 mm year\(^{-1}\). This numerical approach did not contain bacterial sulfate reduction zone. First scenario yields to the results of 3 vol. % of gas hydrates and 2 vol. % of free gas occupying the pore space, whereas the second one leads to 5 vol. % and 3 vol. % of gas hydrates and free gas, respectively. Integrating AOM reaction into the model (Davie M. K. and Buffett B. A., 2003b) showed that a good fit of modeled sulfate curves occurs for first scenario assuming a high upward flux of the fluid phase. Although it has been concluded that the anaerobic oxidation of methane is the dominant reaction leading to sulfate depletion at the Blake Ridge site, it was rather difficult to fit the modeling data with the observations of both chloride and sulfate concentration curves. Wallmann K. et al., 2006 conducted a complex study on gas hydrate dynamics at the Blake Ridge site incorporating the entire biogeochemical data sets of dissolved bromide, ammonium, iodide, sulfate, total nitrogen and organic carbon available at the seafloor. Moreover, this modeling approach contained a novel reaction rate for in-situ biogenic methane formation that links the concentration of degradable organic carbon to the concentration of dissolved methane and inorganic carbon via Monod inhibition rates and age- dependent kinetics. POC concentration at the seafloor has been kept constant (1.6 wt. %) for the first period of 5 Myr and then, subsequently, lowered into 0.65 wt. % for the last 0.7 Myr. The best fit to the field data could be observed for the interstitial fluid velocities of 0.12 mm year\(^{-1}\) calculated at the sediment surface. It
has been concluded that relatively low hydrate concentrations of about 0.6 vol. % are caused by a combination of in-situ POC degradation and low upward fluid flux that is not sufficient to supply enough methane necessary for creating one order of magnitude higher hydrate concentrations observed at that Site. Presence of gas bubbles ascending from the deep origin has been proposed as an explanation for higher hydrate concentrations reported from the field. Garg S. K. et al., 2008 presented a series of modeling scenarios for a Blake Ridge Site including in-situ methane generation, prescribed flux of dissolved methane through a lower boundary (fluid mass of $9 \cdot 10^9$ kg s$^{-1}$ m$^{-2}$), and a mixed methane source (in-situ generation plus 40% of previous fluid mass flux). It has been concluded that in-situ methane generation alone does not explain gas hydrate concentrations observed in the Blake Ridge and, moreover, an upward fluid flux applied in the second scenario corresponds to the seafloor fluid velocities of about 0.28 mm year$^{-1}$ which remains too high in comparison to the deduced interstitial fluid velocities presented by Egeberg and Dickens, 1999. However, the third modeling scenario assuming mixed methane source stays in good agreement with reported seafloor velocities and the average gas hydrate concentrations obtained in this case are about 5 vol. %. Free gas concentrations do not exceed 4 vol. % and remain immobile which implies no hydrate recycling at the base of GHSZ.

**MODELING SCENARIONS FOR THE BLAKE RIDGE SITE**

As it was indicated before, we evaluate here the potential of gas hydrate formation from a single in-situ methane source as well as possible impact of the upward transport of dissolved in pore fluid methane from great depth on the formation of gas hydrate at the Blake Ridge site. We have performed several numerical modeling scenarios which assume various sedimentation rates and sources of methane formed either in-situ or entering the GHSZ through the lower modeling boundary. First modeling scenario assumes that the only source of methane is the in-situ organic matter degradation with a constant organic carbon supply of 1.6 wt. % for the entire modeling period of 10 Myr. Sedimentation rate is constant and equal to 22 cm $\cdot$ kyr$^{-1}$. Gas hydrate and free gas formation occur under local
thermodynamic equilibrium and no kinetic grow and dissolution rates are introduced. At the beginning of the simulation, modeling domain contains initially only 1 m of sediments and is prescribed by two numerical mesh nodes. The resolution of modeling domain increases with subsequent sedimentation and deposition of new contours at the top of modeling column. One mesh node is added according to the each single time step (time step $dt$ is about $10^3 - 10^4$ year) which results in sediment layer thicknesses of about 1 – 23 cm ($dt$ of $10^3$ year) or 10 – 235 cm ($dt$ of $10^4$ year). In the second modeling scenario, sedimentation rate varies according to the data from Ikeda A. et al., 2000 (see Tab. 4). Remaining modeling parameters stay the same as in the Scenario 1, including a constant POC supply at the upper boundary of the model equal to 1.6 wt. %. Additionally, two specific cases with diminished (by a factor of 0.5) and enhanced (by a factor of 2) diffusion of chemical species within pore waters were analyzed here (Scenario 2a and Scenario 2b, respectively). Scaling of chemical species diffusion coefficients (CH$_4$, DIC, SO$_4$) were applied to the previously calculated values after Boudreau B. P., 1997. Third modeling scenario is based on the variable sedimentation rates from Ikeda A. et al., 2000 (see Tab. 4). Moreover, seafloor POC concentrations implemented as the upper boundary condition in the model have been modified to fit the measured and reported POC concentrations after the organic matter decomposition. Fourth modeling scenario assumes a mixed source of methane that enters the model via biogenic CH$_4$ production and an upward fluid mass flux that contains dissolved methane. The mass of fluid entering the system through the lower boundary is assumed to be constant over modeling period of time (10 Myr) and equal to $5.9 \cdot 10^{-9}$ kg s$^{-1}$ m$^{-2}$ which corresponds to an upward fluid velocity at the seafloor equal to $6.29 \cdot 10^{-12}$ mm s$^{-1}$ and stays in a very good agreement with the reported data (Egeberg and Dickens, 1999). Mass of dissolved in pore fluids methane that enters the sediment column through the lower boundary is equal to $1.6 \cdot 10^{-11}$ kg s$^{-1}$ m$^{-2}$ which corresponds roughly to the concentration of 170 mM. However, the rate of methane input into the system depends on the entering velocity at the lower boundary of modeling domain. As the pore fluid velocity tends to increase with time, the amount of dissolved methane being transported through the bottom decreases. In the final fifth modeling scenario, we have combined the
approach from scenario 3 and scenario 4 to evaluate the influence of precisely resolved POC input rates coupled with additional methane flux on gas hydrate and free gas formation. This scenario was expected to bring the best fit to the measured and observed gas hydrate and free gas concentrations at the investigated site.

RESULTS AND DISCUSSION

First modeling scenario represents the situation where in-situ POC degradation remains the only source of methane entering the GHSZ and causing gas hydrate formation. This simulation predicts maximum gas hydrate saturations of 0.75 vol. % at about 390 mbsf and free gas concentrations of 0.61 vol. % (see Fig. 3) which poorly corresponds to the reported amounts (4 – 7 vol. % of gas hydrates and 1 - 2 vol. % of gas). Methane diffusion occurring at the base of the GHSZ leads to a gas hydrate recycling process observed for this scenario. Net seafloor fluid velocity is about \(-1.23 \cdot 10^{-12} \text{ m} \cdot \text{s}^{-1}\) (\(-0.039 \text{ cm} \cdot \text{year}^{-1}\)) at the end of computational time (detailed information can be found in the Table 5) which means that no seafloor venting occurs. This seafloor velocity does not confirm suggestions of Egeberg and Dickens, 1999 who evaluated seafloor fluid velocity to be about 0.02 cm \cdot year^{-1} (6.31 \cdot 10^{-12} \text{ mm} \cdot \text{s}^{-1}) based on bromide-iodide pore water measurements. However, as it was previously suggested by Wallmann K. et al., 2006, this estimate should be considered as relatively high due to pore water burial and halogens production from in-situ organic matter degradation that were not included in the study of Egeberg and Dickens, 1999. Results from this modeling scenario correlate well with ones obtained by Wallmann K. et al., 2006 who used a constant rate of sedimentation throughout the modeling time frame. Likewise in Wallmann K. et al., 2006, dissolved sulfate profile obtained in the modeling Scenario 1 fully correlates with the data.
Fig. 3. Scenario 1 modeling results (constant sedimentation rate over time). This simulation was performed with no flux boundary conditions and thus, in-situ POC degradation was the only source of methane in sediments. Upper panel, starting from left: pressure, temperature, porosity, and methane concentration profiles modeled for Blake Ridge Site 997. Methane concentration (blue line) is plot together with gas hydrate solubility limit (red line) and free gas solubility limit (black line). Lower panel, starting from left: dissolved SO$_4$ concentration (blue line), dissolved inorganic carbon, POC concentration (blue line), and gas hydrate (blue line)/ free gas (green line) saturations. Porosity measurements data points (black dots), SO$_4$ data points (purple circles) and POC data points (purple circles) were adapted from Paull C. K. et al., 1996.

In the second scenario, the influence of changing sedimentation rates to the dynamics of gas hydrate formation was investigated. Gas hydrate deposits are mainly focused at the depth of 390 mbsf (see Fig. 4) with maximum concentration very similar to the one obtained at the first modeling scenario and equal to 0.68 vol. % (gas hydrate recycling at the base of the GHSZ was observed). Maximum free gas concentrations are equal to 0.4 vol. % and remain immobile. Thus, the influence of changing sedimentation regimes on the amount of gas hydrate formed throughout the basin history seems to be of a minor importance.
Fig. 4. Scenario 2 modeling results (variable sedimentation rate over time). This simulation was performed with no flux boundary conditions and thus, in-situ POC degradation was the only source of methane in sediments. Upper panel, starting from left: pressure, temperature, porosity, and methane concentration profiles modeled for Blake Ridge Site 997. Methane concentration (blue line) is plot together with gas hydrate solubility limit (red line) and free gas solubility limit (black line). Lower panel, starting from left: dissolved SO$_4$ concentration (blue line), dissolved inorganic carbon, POC concentration (blue line), and gas hydrate (blue line)/ free gas (green line) saturations. Porosity measurements data points (black dots), SO$_4$ data points (purple circles) and POC data points (purple circles) were adapted from Paul C. K. et al., 1996.

Keeping all modeling parameters constant, additional runs were performed to evaluate the influence of diminished (see Fig. 5) as well as enhanced (see Fig. 6) chemical diffusion of CH$_4$, DIC, and SO$_4$ species on gas hydrate formation potential (Scenario 2a and Scenario 2b, respectively). Lower rates of diffusion result in about 30% higher crystallization rates of gas hydrates and about 50% faster formation of free gas due to longer residence times of dissolved in pore fluids methane within the GHSZ and close to its base. On the other hand, enhanced diffusion coefficients caused faster removal of methane and, in case of no additional pore fluid flux from great depths, its constant downward transportation. In this case, both gas hydrate and free gas formation was slowed down by a factor of ten.
Fig. 5. Scenario 2a modeling results (variable sedimentation rate over time). Diffusion coefficients for dissolved chemical species (CH₄, DIC, SO₄) reduced by a factor of 2. Upper panel, starting from left: pressure, temperature, porosity, and methane concentration profiles modeled for Blake Ridge Site 997. Methane concentration (blue line) is plot together with gas hydrate solubility limit (red line) and free gas solubility limit (black line). Lower panel, starting from left: dissolved SO₄ concentration (blue line), dissolved inorganic carbon, POC concentration (blue line), and gas hydrate (blue line)/free gas (green line) saturations. Porosity measurements data points (black dots), SO₄ data points (purple circles) and POC data points (purple circles) were adapted from Paull C. K. et al., 1996.

Based on the modeling parameters of the second scenario, GHSZ base depth changes over simulation time (10 Ma) were calculated and presented in Fig. 7 to discuss discrepancy between observed BSR levels and theoretical GHSZ base. It has been reported that the depth of BSR for the Blake Ridge Site 997 clearly indicated on the seismic profiles is situated ~ 450 mbsf. Above this depth, seismic blanking effect has been observed which indicates the presence of free gas phase underneath. On the other hand, some theoretical GHSZ calculations show that the present base of hydrate stability lies about 50 m deeper (Garg S. K. et al., 2008; Xu W. and Ruppel C., 1999). This situation is very similar to the observation from the Blake Ridge Site 995 where BSR (~ 440 mbsf) do not match the depth of theoretical GHSZ in an even more evident way (base of the GHSZ is ~ 520 mbsf).
Moreover, the transition between BSR and GHSZ depths has strong indication for coexistence of methane gas and partially dissolving gas hydrates (Guerin G. et al., 1999).

![Graphs showing pressure, temperature, porosity, and methane concentration profiles](image)

Fig. 6. Scenario 2b modeling results (variable sedimentation rate over time). Diffusion coefficients for dissolved chemical species (CH₄, DIC, SO₄) enhanced by a factor of 2. Upper panel, starting from left: pressure, temperature, porosity, and methane concentration profiles modeled for Blake Ridge Site 997. Methane concentration (blue line) is plot together with gas hydrate solubility limit (red line) and free gas solubility limit (black line). Lower panel, starting from left: dissolved SO₄ concentration (blue line), dissolved inorganic carbon, POC concentration (blue line), and gas hydrate (blue line)/ free gas (green line) saturations. Porosity measurements data points (black dots), SO₄ data points (purple circles) and POC data points (purple circles) were adapted from Paull C. K. et al., 1996.

Previous authors (Xu W. and Ruppel C., 1999) investigated this problem using an analytical steady-state model to find a limiting rate of the upward methane flux necessary for matching the occurrence zone of gas hydrates together with the top of previously reported free gas zone. As it was concluded, a critical flux of methane entering the model through the lower boundary was estimated at $3 \cdot 10^{-11} \text{ kg} \cdot s^{-1} \cdot m^2$. The following approach neglected, however, the effect of sedimentation and assumed a constantly present flux of methane resulting in seafloor pore fluid velocity of 0.03 cm · year$^{-1}$. 

72
We have observed that in the case of single microbial methane source and no additional flux present in the system, changes in depth of the GHSZ base (see Fig. 7) are rather limited after the first 5.4 Ma of simulation time and that the final depth thermodynamic gas hydrate stability field oscillates around 450 mbsf (5.4 Ma – 6.3 Ma) or 440 mbsf (8.9 Ma – 10 Ma) which corresponds very well with reported BSR data. Periods between 6.3 Ma – 8.9 Ma are characterized by slight fluctuations of the GHSZ base which, however, do not exceed 10 meters at most. There are at least several reasons for observed fluctuations in the depth of the GHSZ lower boundary: 1) multi-phase system is in the out-of-equilibrium state and undergoes dynamic changes incl. phase transitions (gas hydrate-free gas-dissolved methane, specially at the gas hydrate recycle zone), 2) gas hydrate crystallization and free gas migration are mainly controlled by the kinetic factors which allow for the presence of all three phases in the system at the same time, and/or 3) structural uniformities are disturbed which leads to local free gas migration along ice-cover pore throats and channel-like structures. In the scope of this study, we have investigated the first possible explanation assuming a non-steady-state temperature profile which has been confirmed as a valid hypothesis in case of the Blake Ridge Site 997.

Fig. 7. Scenario 2 (no flux boundary conditions, variable sedimentation rate over time). Change in the GHSZ thickness over simulation time (10 Ma).
Third modeling scenario assuming time-changing sedimentation rate has been improved by applying a variable amounts of POC at the upper boundary of sedimentary column according to the well POC data. As a result, maximum gas hydrate concentrations were observed in two zones: at the depth of about 220 mbsf (roughly 2.4 vol. %) and at the depth of 390 mbsf (roughly 2 vol. %) which corresponds to reported gas hydrate occurrence zones by Paul K. C. and Matsumoto R., 2000 (see Fig. 7). Noticeable free gas concentrations could be observed, firstly, in the relatively thick but shallow sediment interval underneath the base of GHSZ (~440 – 600 mbsf) with concentrations of about 0.6 vol. % and, secondly, around 680 mbsf with concentrations of about 0.6 vol. %. Net pore fluid velocity at the upper boundary (seafloor) equal to \(-1.72 \cdot 10^{12} \text{ m} \cdot \text{s}^{-1}\) \((-0.55 \text{ cm} \cdot \text{year}^{-1})\) poorly correlates with conclusions derived by Egeberg and Dickens, 1999 suggesting an upward direction of pore fluid transport. On the other hand, sulfate concentration profile matches very well with reported data.

Fig. 8. Scenario 3 modeling results (variable sedimentation rate over time and POC fitting). Upper panel, starting from left: pressure, temperature, porosity, and methane concentration profiles modeled for Blake Ridge Site 997. Methane concentration (blue line) is plot together with gas hydrate solubility limit (red line) and free gas solubility limit (black line). Lower panel, starting from left: dissolved \(\text{SO}_4\) concentration (blue
line), dissolved inorganic carbon, POC concentration (blue line), and gas hydrate (blue line)/free gas (green line) saturations. Porosity measurements data points (black dots), SO$_4$ data points (purple circles) and POC data points (purple circles) were adapted from Paull C. K. et al., 1996.

In the fourth modeling scenario, methane required for gas hydrate formation was transported to the GHSZ from two distinct sources: in-situ POC degradation and an upward flux from great depths (see Table 5 for detailed values). The rate of the flux was designed to fit the suggested pore fluid seafloor velocities (Egeberg and Dickens, 1999) of $6.29 \cdot 10^{12}$ mm $\cdot$ s$^{-1}$ (0.02 cm $\cdot$ year$^{-1}$). As a result, maximum gas hydrate concentrations obtained within this scenario were about 4.4 vol. % at the depth of 440 mbsf (close to the base of GHSZ) suggesting an ongoing process of gas hydrate recycling. Maximum free gas concentrations of about 2 vol. % were found at the GHSZ base (related to the previously described process of gas hydrate-free gas phase transitions) and at the lower boundary of modeling domain (~850 mbsf) with concentrations of ~2.5 vol. % (see Fig. 9). Observed free gas concentrations are most likely immobile and do not migrate upward towards the GHSZ. As a result of imposed pore fluid flux from great depths and consequent seafloor venting, sulfate concentration profile does not match the observations. These finding of gas hydrate and free gas formation from a mixed methane source are very similar to the observations of Davie M. K. and Buffett B. A., 2003a; Davie and Buffett, 2001 and Davie M. K. and Buffett B. A., 2003b which obtained gas hydrate concentrations of 5 to 7 vol. % and free gas concentrations of 3 to 5 vol. % close to bottom of modeling domain (about 850 mbsf). However, seafloor velocity of pore fluids equal to 0.008 cm $\cdot$ year$^{-1}$ derived in cited studies does not match with a value presented here of 0.02 cm $\cdot$ year$^{-1}$ according to Egeberg and Dickens, 1999. This mismatch is somehow not influencing our final results due to the fact of using different POC degradation approaches. Whereas here, we use a rather complex reaction solver accounting for in-situ organic matter decomposition, methanogenesis, sulfate reduction and AOM processes, Davie M. K. and Buffett B. A., 2001 assumed a constant degradable POC fraction and did not account for methane oxidation by microbes. Further investigation presented in the later publications (e.g. Davie M. K. and Buffett B. A., 2003b) which incorporated methane-sulfate reaction zone into modeling.
approach, found it rather difficult to match observed SO$_4$ concentrations due to the presence of relatively high upward flux of pore fluids (similar effect has been also noticed in this study). Likewise, another modeling scenario presented by the same authors assuming a single methane source (upward flux of pore fluids and dissolved methane) and resulting in gas hydrate concentrations of about 3 vol. % did not match with measured sulfate concentrations due to a rather high pore fluid flux (0.026 cm · year$^{-1}$). Interestingly, maximum free gas concentrations obtained by authors (2 – 3 vol. %) were found at the base of the GHSZ suggesting an ongoing process of gas hydrate recycling.

![Diagram](image)

Fig. 9. Scenario 4 modeling results (variable sedimentation rate over time). Additional dissolved methane flux through the lower boundary matches with reported seafloor pore fluid velocities (Egeberg and Dickens, 1999). Upper panel, starting from left: pressure, temperature, porosity, and methane concentration profiles modeled for Blake Ridge Site 997. Methane concentration (blue line) is plotted together with gas hydrate solubility limit (red line) and free gas solubility limit (black line). Lower panel, starting from left: dissolved SO$_4$ concentration (blue line), dissolved inorganic carbon, POC concentration (blue line), and gas hydrate (blue line)/ free gas (green line) saturations. Porosity measurements data points (black dots), SO$_4$ data points (purple circles) and POC data points (purple circles) were adapted from Paul C. K. et al., 1996.

Results from the fifth modeling scenario show maximum gas hydrate concentrations of about 4 vol. % close to the base of GHSZ (~440 mbsf) and about 3 vol. % at the depth of
~220 mbsf (see Fig. 10). Maximum free gas concentrations can be found at the depth of ~850 mbsf (lower boundary of modeling domain) with concentrations of around 7 vol. % as well as at the depth of ~680 mbsf with corresponding concentrations of around 2.5 vol. %. It is important to notice that free gas concentrations above 5 – 10 vol. % are most likely becoming mobile and capable of being transported upwards through porous sedimentary column due to their phase buoyancy. This process might have a significant impact on 1) gas hydrate formation, especially close to the base of GHSZ, and 2) potential co-existence of gas hydrate and methane gas phase within GHSZ as locally decreased permeability (due to gas hydrate formation) traps relatively little amounts of gas (few percent) at the limit of their mobility. This effect would be clearly visible at the depths just above the GHSZ base which coincides with observations of Paull C. K. et al., 1996 and Paull C. K. and Matsumoto R., 2000.

Fig. 10. Scenario 5 modeling results (variable sedimentation rate over time and POC fitting). Additional dissolved methane flux through the lower boundary matches with reported seafloor pore fluid velocities (Egeberg and Dickens, 1999). Upper panel, starting from left: pressure, temperature, porosity, and methane concentration profiles modeled for Blake Ridge Site 997. Methane concentration (blue line) is plot together with gas hydrate solubility limit (red line) and free gas solubility limit (black line). Lower panel, starting from left: dissolved SO$_4$ concentration (blue line), dissolved inorganic carbon, POC concentration (blue line), and gas hydrate and free gas in vol. %
gas hydrate (blue line)/ free gas (green line) saturations. Porosity measurements data points (black dots), SO\textsubscript{4} data points (purple circles) and POC data points (purple circles) were adapted from Paull C. K. et al., 1996.

Tab. 5. Comparison of modeling parameters for five different scenarios including a short summary of the crucial input parameters and results

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<th>Scenario 2</th>
<th>Scenario 3</th>
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<td>In-situ POC decay</td>
<td>In-situ POC decay</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<table>
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<tr>
<td>Max. hydrate saturation (vol. %)</td>
<td>0.75</td>
<td>0.88</td>
<td>0.68</td>
</tr>
<tr>
<td>Max. free gas saturation (vol. %)</td>
<td>0.61 (immobile)</td>
<td>0.60 (immobile)</td>
<td>0.40 (immobile)</td>
</tr>
</tbody>
</table>

Low-productivity period reported by Ikeda A. et al., 2000 which refers to the decrease in organic matter formation at the last stage of Blake Ridge basin evolution for the last 0.8 Ma, has been incorporated in modeling scenarios 3 (see Fig. 8) and scenario 5 (see Fig. 10) with different results. Third scenario assumes only in-situ POC decomposition as the main
source of methane supply. The rates of CH₄ formation under these conditions are relatively low and result in limited gas hydrate and immobile free gas concentrations (up to 2.37 vol. % and 0.64 vol. %, respectively). Methane formed via biogenic reactions is immediately dissolved in pore fluids and transported further in the process of advection and diffusion. Due to relatively low rates of sedimentation reported for the investigated Blake Ridge site, it is very uncommon to observe large portions of methane being advected upwards and entering the zone of anaerobic methane oxidation (AOM) situated at the upper 20-23 meters of sediment column. Thus, the AOM process responsible for methane depletion at these shallow depths is characterized by comparatively low reaction rates in the modeling scenario 1, 2, and 3. In comparison, Scenarios 4 and 5 assume an active influx of brine carrying dissolved methane through the lower boundary of modeling domain which results in enhanced fluid outflow at the top of sedimentary column and more vivid transport of all dissolved in pore fluids chemical species. This additional mass of methane (1.6·10¹¹ kg s⁻¹ m⁻²) entering the system from underneath is strongly affecting the rates of AOM reactions in the upper section of sediments and thus, has to be considered as rather seasonal feature of the system.

**CONCLUSIONS**

To summarize, the investigation of complex processes associated with gas hydrate and free gas formation and further co-existence at the Blake Ridge province has shown that gas hydrate concentrations reported from the Blake Ridge Site 997 are in the best fit with the modeling scenario 4 in terms of gas hydrate concentration (maximum concentration of about 4.4 vol. %) which assumes a mixed source of methane entering the system from in-situ POC degradation and deep methane flux from underlying sediments with a value of ~170 mM (corresponds to the mass of methane flux of 1.6·10¹¹ kg s⁻¹ m⁻²). However, slightly lower gas hydrate concentrations (up to 3.8 vol. %) observed in modeling scenario 5 together with free gas concentrations up to 7.25 vol. % (most likely becoming mobile) seem to fit better the local features of the investigated site e.g. due to unfolding second gas hydrate maximum at the depth of about 220 mbsf which matches the observations.
Presence of mobile gas phase rapidly migrating upwards and towards the GHSZ might give an explanation of postulated co-existence of all three methane phases (dissolved, gaseous and gas hydrate) in the pore space lying already within the GHSZ Guerin G. et al., 1999. In case of a vivid gas bubble ascend, some part of methane might not be entirely consumed in a process of gas hydrate formation and continues to rise throughout GHSZ up to sulfate-methane transition zone and/or ultimately, the seafloor. Thus, it is worth noticing that in the case of potential presence of two distinct phases (gas hydrate and free gas) within the sediment pore space, a critical (residual) gas saturation is the limiting factor responsible for free gas mobility in sediments, strongly influencing gas hydrate formation potential. Based on the reported values of gas hydrate and free gas concentrations as well as derived seafloor fluid velocities we have concluded that only a mixed source of methane can explain the features of investigated site. However, constant flux of methane would lead to a complete removal of sulfate-methane transition zone which does not take place. Considering only in-situ biogenic methane formation (which seems to be confirmed by isotope analysis as the primary CH$_4$ source) and variable organic matter input we able to fully fit all the remaining geochemical profiles including the AOM zone depth and, to a fair degree, gas hydrate concentrations and free gas concentrations.

REFERENCES


CHAPTER 3: NEW GAS HYDRATE AND FREE GAS ESTIMATES FROM GREEN CANYON SITE, GULF OF MEXICO, BASED ON BASIN-SCALE MULTIPHASE MODELING

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ABSTRACT

The Green Canyon area located in the Northern part of the Gulf of Mexico is known for petroleum field discoveries which locations are often related to the presence of allochthonous salt structures. The evolution of large salt structures dominantly controls the location and the moment of formation of supra- and subsalt hydrocarbon reservoirs. Petroleum migration pathways in the region are strongly influenced by the extensive formation and time evolution of salt canopies, welds and sheets. This multi-level salt system (known as the Louann Salt formation) deposited mostly within Callovian age (upper Middle Jurassic) and mobilized during late Miocene up to Pliocene-Pleistocene times controls the extension and direction of petroleum components migration over the entire history of the basin which, in return, has a major impact on potential thermogenic gas transportation into the gas hydrate stability field (GHSZ). In the context of gas hydrate formation, presence of extensive salt deposits tends to bend gas migration pathways from vertical (typical for the Gulf of Mexico region) towards rather horizontal and dispersed.
However, amalgamation of two or more salt structures often results in re-focusing of the flow towards the local topographic subsalt heights. Together with the formation of local sediment discontinuity structures such as faults developing at the rims and tops of rootless salt deposits related to further stages of allochthonous salt mobilization, new high-permeability migration pathways develop and act as direct connection for the thermogenic gas to the GHSZ.

Our study presents the 3D modeling solution quantifying and exploring the gas hydrate accumulation potential in the marine environment experiencing salt tectonics such as the Green Canyon, Gulf of Mexico. This modeling study evaluates the potential of bio- and thermogenic gas hydrate formation within Pliocene-Pleistocene reservoir layers based on full basin re-construction which accounts for depositional and transient thermal history of the basin, source rock maturation, petroleum generation, expulsion and migration, salt tectonics and associated faults development. Based on a numerical study calibrated with the existing field data, we present a new distribution pattern of gas hydrates attributed to both microbial and thermogenic origin.

We present here an explanation for a formation mechanism of large gas hydrate amounts (> 80 vol. %) wide-spread at the base of the stability zone as a result of the gas hydrate-free gas recycling process enhanced by very high Neogene sedimentation rates in the region. We suggest that the rapid development of secondary intra-salt mini-basins situated on top of the allochthonous salt deposits and following sediment subsidence caused a consequent dislocation of the GHSZ lower boundary and led to efficient gas hydrate dissociation process followed by a free gas re-charge into the GHSZ.

**Keywords:** methane, gas hydrate, basin modeling, salt tectonism, Gulf of Mexico, Louann Salt
Chapter 3

INTRODUCTION

GEOLOGICAL SETTING AND BASIN EVOLUTION

The Green Canyon area is located in the Northern part of the Gulf of Mexico, at the edge of the Mississippi frontal fold belt (MFFB) directed NE-SW (see Fig. 1), at water depths of about 2,000 meters. The name of the province recalls to the important paleo-channel-levee complex of sandy sediments deposited towards the deep abyssal plain of the central Gulf. Prominent buried paleo-channel systems in the region can be clearly identified on seismic images (Boswell et al., 2012a; Boswell et al., 2012b; Chand and Minshull, 2003; Diegel et al., 2001; Hutchinson et al., 2011; Salvador, 1991; Shedd et al., 2012) due to large portions of siliciclastic material delivered from the NW direction towards deeper parts of the basin over Pleistocene. The modeling domain chosen for this study is situated at the edge of allochthonous salt front which represents some of the last stages of salt tectonic re-mobilization in the region and covers about 32 by 14 km region (see Fig. 1). The influence of evaporate deposits in the region on the subsalt petroleum components migration was broadly discussed by many authors (McBride et al., 1998a; McBride et al., 1998b; Weimer et al., 1998).

The evolution of the Northern part of the Gulf of Mexico Basin starts by a Late Triassic-Early Jurassic event of North American and African-South American plate separation as a result of crustal stretching and thinning processes. Basin subsidence during the Mesozoic era was especially large in the central part of the basin; however, the Northern part of the Gulf experienced the largest sedimentary load over the Cenozoic. The total amount of sediments deposited within the Northern part of the basin is difficult to estimate due to the lack of precise geophysical data and regional reconstructions. It is suggested that at least a 10-15 km thick package of Upper Triassic to Holocene sediments was deposited along the life-span of the basin (Salvador, 1991). For the purpose of this study, depth of the basement has been set to a depth of 14,500 meters below the sea-level which stays within the consensus range of values.

87
Gas hydrate and free gas presence was confirmed by geophysical data but limited to sediment depth most likely correlating with the base of the Gas Hydrate Stability Zone (around 500 - 600 meters). There are three wells drilled within the modeling area as a result of the Joint Industry Project (JIP) Leg II campaign (see notations of well GC955-I, GC955-Q, and GC955-H on Fig. 1) which provided important information about character of the Pleistocene sediments and their potential to act as gas hydrate reservoirs (Guerin et al., 2009; Lee and Collett, 2012; Zhang et al., 2011). A detailed analysis of the drilling site location before the JIP Leg II campaign (Hutchinson et al., 2009) revealed abundant faulting structures in the surrounding of salt deposits heights and their direct vicinity which confirms existence of potential high-permeability pathways for thermogenic gas migration necessary to transport sufficient amounts of methane into the GHSZ. Direct
observations of sediments obtained during the drilling process confirmed presence of both, fracture- and pore-filling gas hydrate accumulations for at least two out of three wells.

**Stratigraphy**

The oldest synrift Upper Triassic-Lower Jurassic material deposited in the Northern part of the Gulf of Mexico Basin contains mostly siliclastics of non-marine origin. During the Callovian age (upper Middle Jurassic) thick accumulations of evaporates started to form throughout almost the entire basin. This unique in size large Louann Salt deposits dominated the geometry of the basin controlled only by previously existing large-scale structures such as basement fault blocks related to the earliest stage of basin rifting. Following the change from dry to shallow marine environment, carbonate deposits started to form from the Late Jurassic to Early Cretaceous period. Deeper part of the basin experienced shale and pelagic carbonate ooze depositions. A clearly defined Middle Cretaceous unconformity (sequence boundary) level marks the time when siliclastic sediments start to dominate in lithology. Shales and silts were the most abundant formations at the end of the Cretaceous period. In response to the Sevier orogeny (more Western compressional event) and parallel in time Laramide orogeny (more Eastern compressional event) responsible for forming several mountain ranges in North America and Mexico, large portions of siliclastic material started to deposit at the local depocenters of the Northern Gulf. These thick sandy Pleistocene accumulations are of the primary importance for channel levee systems and deepwater fans serving a base for petroleum and gas hydrate reservoirs. Fig. 2 presents a simplified litho-stratigraphic column of the Northern Gulf of Mexico (modified after Piggott and Pulham, 1993) indicating stratigraphic locations of the source rocks used in this study and horizons identified by the interpretation of the seismic data.
Fig. 2. Litho-stratigraphy of the Northern Gulf of Mexico (modified after Piggott and Pulham, 1993) presenting the most important litho-stratigraphic units, locations of three source rocks used in the study, and hydrocarbon reservoir rocks. Moreover, location of stratigraphic horizons clearly identified during seismic interpretation is marked (grey stars).
SALT TECTONICS AND RELATED FAULTING SYSTEMS

Due to distinct thermal (high thermal conductivity) and sealing properties of salt deposits, their importance in hydrocarbon maturation and migration processes is large. Sedimentary strata underlying thick salt deposits are exposed to anomalously low temperatures which results in a slowdown of organic matter maturation and change in geochemical composition of surrounding pore fluids (Reitz et al., 2007). On the other hand, perfect sealing properties of evaporates re-direct the flow of hydrocarbon components and strongly influence their migration pathways. For the purpose of this study it was essential to combine a right timing of the Louann salt deposition, re-mobilization events, and thickness variations within the space boundaries of the modeled 3D domain.

Several geological salt-related structures of primary importance can be identified within the studied region; a large-scale topographic contrast caused by the presence of the MFFB along the NE-SW transect refers as well to the Jurassic Louann salt movement front progressing in the SE direction during several re-mobilization events in the history of the Northern Gulf of Mexico and defines the furthermost extent of salt towards the deep abyssal plain. A topographic high called the Green Knoll salt dome located in the SE part of the region (see Fig. 1) represents salt-cored anticline formed due to most recent tectonically-based re-mobilization of salt. Schematic illustration presented in Fig. 3 shows simplified present-day NW-SE transect across Northern Gulf of Mexico (modified after Prather, 2003, based on published data from Diegel et al., 2001) with abundant salt-withdrawal intraslope mini-basins, which currently dominate sub-surface geometry the Northern Gulf of Mexico. Complex networks of high permeable pathways (most likely faults) associated with salt structures are commonly observed in the region (Boswell et al., 2012a; Diegel et al., 2001; Prather, 2003). There are characterized by a) shallow-rooted faulting structures developing directly above the rising salt diapirs, and b) deeply-rooted faulting structures associated with progressive and large-scale salt mobilization in the SE direction. These two distinguished types of structural disconformities are schematically presented in Fig. 3 and described as shallow-rooted fault structures (green shading) and deeply-rooted fault structures (violet shading).
Impermeable salt deposits form a physical barrier for vertical fluid and gas migration and thus, remain an important part of the regional petroleum system. It is commonly observed that migration pathways of pore fluids and free gas tend to deflect more horizontally directly underneath salt accumulations and continue migrating along the base of the salt layer until they reach a local topographic high or structural unconformity, e.g. tectonic fault. Potentially large amounts of gas accumulated under impermeable salt layer are usually not sufficient to fracture the overlying evaporates due to local overpressures and form a local reservoir.
Commonly, faults related to salt remobilization events in the area are generally steep and do not deviate laterally fluid and gas migration pathways but rather focus the flow. In case of gas migration through the faulting structures, buoyancy seems to be the driving factor enhanced by local gas overpressure zones leading to sediment fracturing.

**Presence of Gas Hydrates**

Gas hydrates occurrence in the Green Canyon region has been postulated in the past decades and based on the presence of porous sandy layers close to the base of the GHSZ as well as high permeable pathways which might provide efficient migration properties for gas and methane-rich fluids. Presence of gas hydrate deposits (both pore space- and fracture-filling) has been confirmed at the Green Canyon (Boswell et al., 2012a; Boswell et al., 2012b; Hutchinson et al., 2009; Lee and Collett, 2012; Zhang et al., 2011) area by seismic data analysis (abundant high-amplitude geophysical responses, continuous and discontinuous BSRs after Shedd et al., 2012), geochemistry and direct drilling campaigns (JIP Leg II resulting in GC955-H, GC-955-I, and GC955-Q drill sites with locations shown on Fig. 1). The JIP campaign was conducted in order to validate the hypothesis of prominent gas hydrate accumulations close to the base of the GHSZ which might be acting as a physical barrier for further upward free gas migration. Two of the three wells (GC955-H and GC-955-I) reached the depths of about 550 mbsf and 650 mbsf, respectively whereas the GC955-Q penetrated shallower depths of Pleistocene sediments up to about 450 mbsf. Accordingly, two first wells managed to penetrate and collect the data at the inferred base of the gas hydrate stability zone at a depth of about 400 to 500 mbsf. As it was reported after conducting the JIP drilling campaign (Boswell et al., 2012b; Guerin et al., 2009; Lee and Collett, 2012; Zhang et al., 2012), sediment drilled by the GC955-I well were mostly highly water-saturated with minor indications for a direct gas hydrate presence. Data obtained during the drilling of the GC955-H well gave a clear suggestion for thick gas hydrate-filled fractures present within mud sediments at the depth of about 152 to 305 meters below the seafloor with average gas hydrate concentrations of about 20 vol. %. Furthermore, three distinct gas hydrate-bearing zones were identified within sandy
sediments at the depth of 400 to 500 mbsf with some average gas hydrate saturation reaching about 60 - 80 vol. %. An indication for the free gas presence in the underlying sediments was also made along the data analyze procedure. The third GC955-Q drilled well exposed prominent gas hydrate accumulations at the depth of 430 up to 457 mbsf, most likely turning into free gas deposits in greater depths. However, the drilling procedure was stopped at this moment due to a high risk of gas migration through the well. In general, four main logging units were commonly defined based on LWD drill data (Guerin et al., 2009): unit 1 characterized by smooth transition in lithology from marine interbedded clays (near the seafloor zone) into sand (base of the unit at the depth of about 280 mbsf for wells GC955-I and GC955-Q and 225 mbsf for well GC955-H), unit 2 exposing sandy paleo-levee systems extending up to the depths of about 360 – 405 mbsf, unit 3 of similar to the unit 2 lithology but apparent evidence for high gas hydrate saturations based on resistivity values particularly for drill holes GC955-H and GC955-I up to the depth of about 480 mbsf, and unit 4 reached only by the GC955-H and GC955-I wells marking change in lithology into clay-rich sediments with some indication for either free gas or gas hydrate presence. Litho-stratigraphic levels at which gas hydrate occurrence has been prominently exposed is dominated by sandy paleo-levee systems of Pleistocene age. Location of the primary gas hydrate reservoir rocks can be found on the Fig. 2 presenting the overview of local stratigraphic levels present in the region.

Geochemical and carbon isotope studies conducted in the Green Canyon block suggest a mixed- biogenic and thermogenic origin of methane within the GHSZ (Lorenson T. D. et al., 2008; Sassen et al., 2003). However, seafloor gas venting sites and high-flux seeps often present in the region do not always reveal a significant contribution of the bacterial component and suggest a deep methane source feeding such structures. Bacterial methane source not only limited to the shallower Pleistocene sedimentary layers but extending deep into subsurface of the Green Canyon block has been postulated (Sassen et al., 2003) and related to a high-temperature microbial activity in relatively old sediments. Moreover, due to a complex burial history of the basin, it is probable that multiple episodes of gas recharge in reservoirs took place and therefore, basin-scale interpretation of the gas origin remains
very difficult. In the following study, we aim at quantifying the amount of gas hydrates formed within the Green Canyon domain via both microbial in-situ methane generation and thermogenic organic matter decomposition at great depth, as well as analyzing the proportions between both sources in a series of test runs assuming various Pleistocene TOC content and primary Tithonian source rock productivity.

**PETROLEUM GEOLOGY OF THE REGION**

**SOURCE ROCK LOCATIONS AND CHARACTERIZATION**

Northern Gulf of Mexico region has been reported as a full petroleum system in a sense of containing all required elements and mechanisms supporting source rock presence and its maturation, hydrocarbon generation, efficient hydrocarbon migration pathways and potential reservoir formations (Nunn and Sassen, 1986). Due to the lack of deep drilling data, the presence of the source rocks in this region was indicated by geochemical, biomarker and whole-rock analysis performed onshore Louisiana for the same stratigraphic layers being exposed and drilled in the vicinity of the Gulf in the context of the Deep Sea Drilling Project (DSDP).

There are three source rocks of different productivities indicated to be present within the modeling domain of the Green Canyon, situated on three different stratigraphic levels: secondary Late Jurassic-Oxfordian source rock, primary Late Jurassic-Tithonian source rock and secondary Middle Cretaceous-MCU source rock called after the mid-Cenomanian unconformity stratigraphic level (Cole et al., 2001; Nunn and Sassen, 1986; Piggott and Pulham, 1993; Sassen, 1990). Although the secondary Oxfordian and MCU source rocks are thought to contribute to the petroleum formation in the Northern Gulf of Mexico, the primary Tithonian source seems to be the major hydrocarbon origin.

These source rocks contain mainly type II kerogen with rare exceptions of type II-S (enriched in sulfur) and gas-generating type III kerogen (Sassen et al., 1993). Initial TOC and HI values for the Northern Gulf of Mexico source rocks are difficult to establish. Complex burial history and presence of allochthonous salt layers influence thermal maturation and thus, productivity peaks for each source rock both in space and in time.
This fact results in overlapping productivity stages of particular source rock levels which, furthermore, influenced by wide-spread salt tectonics modifies the gas migration potential into gas hydrate reservoir sands of Pleistocene age. However, migration pathways from all hydrocarbon-generation layers seem to be similar and shared amongst the three source rocks present (Cole et al., 2000). For a course of this study, we assume following source rock parameters listed in the Table 1 based on previous publications (stratigraphic location of the source rocks can be found as well in Fig. 2):

Tab. 1 Source rock properties used in the modeling study

<table>
<thead>
<tr>
<th>Source rock</th>
<th>Importance</th>
<th>Lithology</th>
<th>TOC</th>
<th>HI</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tithonian</td>
<td>primary</td>
<td>marls/carbonates</td>
<td>4 wt. % - 6 wt. %</td>
<td>550 – 700 mg HC/ g TOC</td>
<td>80 – 200 m</td>
</tr>
<tr>
<td>Oxfordian</td>
<td>secondary</td>
<td>marls/carbonates</td>
<td>about 3 wt. %</td>
<td>450 – 550 mg HC/ g TOC</td>
<td>about 50 m</td>
</tr>
<tr>
<td>MCU</td>
<td>secondary</td>
<td>shales to marls</td>
<td>2 wt. % - 3 wt. %</td>
<td>200 – 500 mg HC/ g TOC</td>
<td>30 – 50 m</td>
</tr>
</tbody>
</table>

Biogenic methane generation suggested previously as potentially prominent CH$_4$ source in the shallowest Pleistocene sediments of the Green Canyon region (Kennicutt et al., 1986; Lorenson T. D. et al., 2008; Rice, 1980) has been modeled using the Middelburg formulation (Middelburg J. J., 1989) incorporated into the software biodegradation module assuming 1 wt. % TOC content and HI = 100 mg HC/ g TOC (see Gas hydrate formation from biodegradation module paragraph in the following Simulation section for details).

**MODELING APPROACH**

**INTRODUCTION**

This 3D modeling study has been developed and simulated within the frame of the PetroMod$^\text{TM}$ software package v. 2014.1 by Schlumberger. The basin analysis approach in the PetroMod$^\text{TM}$ software package is based upon the back-stripping method which uses the present-day geometry of the basin to recon-construct initial layer thicknesses and densities together with the age of deposition to give a reliable proxy for the initial state of the basin. This method assumes a solid matrix conservation of mass and allows for tracking back in
time the evolution of particular geological facies and lithologies present in the region of interest. According to the well data and other accessible sources of data correlation, it is possible to modify the input of physical properties of each modeled sedimentary layer (e.g. initial seafloor porosity, compaction length scale used in the Athy’s law formulation (Athy L. F., 1930), density, permeability, and sealing properties), as well as their thermal properties (e.g. thermal conductivity, heat capacity, and radiogenic heat), and specific gas hydrate-related features (e.g. methane diffusion in pore fluids, gas hydrate formation and dissolution, presence of in-situ organic matter and its decomposition into methane). Reconstruction of sedimentation rates applied during depositional events was based on the original thickness of the deposited layer and its age derived from seismic interpretations. No significant events of erosion were reported for the geological history of the Green Canyon region and thus, such events were not considered in the presented study.

Boundary conditions including heat flow, temperature and paleo-bathymetry were assigned to the model (see further description in the following boundary conditions section) together with implementation of the additional high-permeability pathways present in the region and interpreted as faults (see further description in the faults section), and allochthonous salt layer (see further description in the salt tectonics section). Source rocks present in the model were characterized by assigned TOC and HI values as well as hydrocarbon generation kinetics which define the time evolution of oil and gas production.

**INPUT PARAMETERS**

**SURFACE MAPS AND AGE ASSIGNMENT**

The 3D model contains 61 2D (XY-direction) depth horizons covering strata from the Lower Jurassic basement to the present seabed. 28 of these horizons were interpreted directly from the 2D and 3D seismic data. Due to the lack of seismic images of the deepest part of the basin, basement horizon was assumed to have a depth of 14,500 meters below the sea-level. Remaining 32 horizons result from layer splitting performed on the uppermost thick Pleistocene and Upper Miocene (subsalt) package to increase the vertical resolution of the model (Z-direction) in order to achieve a better control on potential gas
hydrate formation in the reservoir layers, and subsalt gas migration, respectively. Splitting of the horizons was assuming a uniform thickness distribution. Special attention was paid to avoid depth overlapping (crossing) of the horizons and if necessary, manual correction on the seismic interpretation was applied.

As a result, 60 sedimentary layers were defined as distinct sediment packages between 2D depth horizons. Age of the deposition of each sedimentary package was derived from stratigraphic sequence of the Green Canyon region. Where necessary, some age assumption needed to be done due to the lack of precise data in literature. This problem applied to the oldest and deepest sedimentary layers (mostly of the Jurassic age). Age units clearly identified in the model comprise Lower, Middle and Upper Jurassic sediments, Middle Cretaceous unconformity, Upper Cretaceous sediments, Wilcox unit strata, Intra Eocene sediments, several lithologically distinct layers of the Oligocene and Miocene age, allochthonous salt layer (unknown exact age of invading the modeling domain), thin Pliocene and thick Pleistocene sediment packages.

Finally, a uniform XY-direction resolution was applied to all interpreted depth maps and, consequently, to sedimentary layers defined between the upper and lower horizon of each section. As a result, we obtained a 3D model of 128x128 grid point resolution in the XY-direction which refers to about 257 m by 106 m in X- and Y- direction, respectively, shown in the Fig. 4.
LITHOLOGY, FACIES DEFINITIONS AND SEDIMENT PROPERTIES

Lithology of each sedimentary layer defined in the model was derived from either Northern Gulf of Mexico stratigraphy publications (Piggott and Pulham, 1993) and Green Canyon reports (Guerin et al., 2009; Hutchinson et al., 2009; Lee and Collett, 2012), indications from drilling campaigns performed in the Green Canyon region and its vicinity (applicable only foe the upper most layers) or, if necessary, deduced from other published sources on the Gulf of Mexico (e.g. big-scale cross-sections). In general, main stratigraphic levels present in the Northern Gulf of Mexico have been clearly indicated during seismic interpretation of the achieved 3D/2D seismic data and served a base for more detailed reconstruction of all horizons and assigned deposition ages. In case of unknown lithology or its rather general description in literature (e.g. Mesozoic syn- and post-rift siliclastics, post-middle Cretaceous unconformity shales and silts etc.), standard physical properties of indicated lithology were taken from the inbuilt software library.

Whenever possible, compaction properties of the youngest Pleistocene sediments such as initial seafloor porosity and compaction length scale were derived by direct correlation to the well data and published porosity profiles of three Green Canyon wells drilled during
the JIP Leg II campaign (Guerin et al., 2009). Fig. 5 presents porosity data points for three Green Canyon drill sites (GC955-I, GC955-Q, and GC955-H) and the preliminary modeling outcome (solid curve) extracted from the 3D modeling domain at the well location. Moreover, distinct logging units 1 – 4 defined after Guerin et al., 2009 and exposing important lithological changes in the sedimentary column (see presence of gas hydrates paragraph) were marked with yellow, brown, blue, and orange shading, respectively according to their positive or negative identification at each well.

No lateral variation of porosity within each sedimentary layer is assumed in the model which allows us to apply a similar compaction properties exhibited at three examined drilling sites to the respective layers stretched out along the entire modeling domain. This assumption and the resolution of the model induces a slight depth misfit between high-porosity interval exposed at the drill well GC955-H at the depth of about 420 to 520 mbsf and an analogue zone from the well GC955-I extending from 350 to 450 mbsf is visible (see Fig. 5). However, it was not feasible to introduce a horizontal heterogeneity in lithology for the entire model based on data from a single GC955-I drill well misfit, accounting for a fact that the single high-permeability zone which does not overlap with other high-permeability strata is even thinner than a vertical model resolution. Moreover, the primary gas hydrate-filled logging unit 3 (shown with blue shading in Fig. 5) does not fully correlate with the entire upper part of the high-porosity zone (350 – 370 mbsf) in the case of drill well GC955-I which suggest rather local character of these changes.

The correlation of preliminary modeling results with measured data obtained during the JIP Leg II drilling campaign (e.g. porosity) was further used to re-calibrate the numerical model before performing the high-resolution runs.
Fig. 5. Porosity data from drill wells GC955-H (in red), GC955-Q (in green), and GC-955-I (in blue) plotted together with preliminary porosity calculations performed for each well (solid black lines) in the uppermost Pleistocene layer. Yellow, brown, blue, and orange shadings mark the position of logging units 1, 2, 3, and 4, respectively defined after Guerin et al., 2009.

SALT TECTONICS

The kinematics of salt layer evolution present within the modeling domain is described by constructing additional paleo-thickness maps implying the change of salt volume, location, and thickness during the process of dome development and salt floating-like migration. Change in salt layer thickness incorporates processes of layer stretching and thinning to achieve a present-day geometry at the end of simulation. Since the local lithology within modeling domain does not vary spatially and does not contain major shale formation directly underneath the salt which might result in additional ‘doming’ of this formation, it is possible to assume a homogeneous (linear) mechanism of salt domes growth along the entire study area. Although precise analysis of salt re-mobilization events exist for the Northern Gulf of Mexico, it is not justified to include this additional complexity into the relatively small modeling domain presented herein.
Salt layer is assumed to have perfect sealing properties and therefore no flow of neither fluid nor gas phase can occur within. Thermal properties of salt layer, such as extremely high thermal conductivity which might influence the spatial extend of the gas hydrate stability zone, were applied according to the values from the inbuilt software library.

**Faults**

Structural discontinuities present in the region were identified during seismic interpretation (see Fig. 3) and grouped into two main categories presented in Fig. 6: deeply-rooted faulting structures associated with multiple salt re-mobilization events and shallow-rooted faulting structures representing sediment response to underlying salt dome rising and layer deformation, usually recognized as a complex of normal faults associated with high probability of active fluid flow (McConnell et al., 2010). Due to the lack of precise data, we assume here that all faults remain open until the present time and no closing or re-opening of permeability occurs. Group 1 of deeply-rooted faults has an assigned constant permeability of 1 log (mD) whereas the group 2 faults permeability has a value of 2 log (mD). An important parameter describing the ability of petroleum/gas phase to invade the enhanced fault permeability already occupied with the fluid (water) is the capillary entry pressure (CEP). Temperature and pressure-dependent interfacial tensions between the already existing phase (pore fluid) and invading phase (oil, gas) are commonly used from reference databases based on lithologies (pore throat radius) and phase properties (e.g. density). Since it is beyond the scope of this study to evaluate in details capillary entry pressures for each fault present in the model, CEPs for both groups of faults are defined as a constant value of 0.01 MPa which represent an average value for a present lithology and geological setting (Hantschel and Kauerauf, 2009).
Fig. 6. Location of faulting structures interpreted within the modeling domain from seismic data. Horizons representing the top of the salt (upper horizon) and the basement (lower horizon) are shown. Group 1 of faults (left side of the legend) represents deeply-rooted structures associated with large-scale re-mobilization of salt occurring primarily at the edge of the modeling domain. Group 2 of faults represent shallow structures developing at the top of salt dome and acting as a high-permeability pathway for focused gas migration (gas phase collected at the local topographic high underneath the salt layer) which further enters the GHSZ. Note that symbols used in the legend do not represent a type of faulting present.

**Boundary Conditions**

According to the model of McKenzie, 1978, amounts and rates at which the basement heat flow affects the sedimentary basin mainly depend on the rift-extensional events (basin formation) and following subsidence due to lithosphere contraction and cooling. Based on the structural evolution of the Gulf of Mexico basin presented by Sawyer et al., 1991, we have assumed a syn-rifting phase occurring from 210 Ma to 170 Ma with high heat flow values (locally up to about 91 mW/m² at 170 Ma when the Pangea break up and following separation of North and South America occurred) followed by a post-rifting phase until present when the heat flow reaches a modern value of about 40 mW/m² (Nagihara et al., 1992).
Fig. 7. Paleo-water depth (upper panel) and paleo-heat flow (lower panel) trends used in the modeling study. Water depth data were implemented after Alegret and Thomas, 2005; Davis, 2011; Miller et al., 2005; Salvador, 1991; Schroeder et al., 1995; Simms et al., 2009; Wright et al., 2005, whereas heat flow trend shown here represents only an average trend of values taken from the precise 2D maps calculated from the McKenzie crustal rifting model (Jarvis and McKenzie, 1980; McKenzie, 1978) and assigned separately to each modeled event (e.g. layer deposition) in the history of the basin. Modeling times for which 2D heat flow maps were extracted (see Fig. 8) are marked with a grey star.

Basin subsidence in time and crustal parameters were used to calculate beta stretching factors and create 2D surface maps of paleo-heat flow at every event predicted in the modeling history. These beta values calculated from the 2D McKenzie crustal model (Jarvis and McKenzie, 1980; McKenzie, 1978) were compared with good results to data from Sawyer et al., 1991 adequate for the region and confirmed modeled here paleo-heat flow trends. Fig. 7 presents paleo-water depth trend and a simplified (averaged in 1D) heat flow trend used in the study. A set of four 2D heat flow maps showing its exact surface distribution at modeling times: 200 Ma, 170 Ma, 85 Ma, and 0 Ma are presented in Fig. 8. Moreover, radiogenic heat sources from the sedimentary column were incorporated into the model based on the average lithology of deposited layers. Bottom water temperature value used as an upper boundary condition over the entire modeling period was constant and equals 2°C. The relatively large time-steps used in the calculations implies that seafloor-water interface temperature changes due to the recent global climate change can
be ignored. Hence, the presented model cannot be used to draw conclusions on gas hydrate deposits perturbations from ocean bottom temperature increase.

Fig. 8. A set of 2D heat flow maps calculated from the McKenzie crustal rifting model (Jarvis and McKenzie, 1980; McKenzie, 1978) for a - 210 Ma ago (beginning of the rifting phase), b - 170 Ma ago (end of the rifting phase), c - 85 Ma ago (exponential decay of the heat flow), and d - 0 Ma ago (present-day heat flow) according to the points in time marked in Fig. 7 (grey stars). Note that the color scale of each map has different minimum and maximum values.

Sea level changes in the history of the Northern Gulf of Mexico, mostly driven by plate tectonics, reached up to hundreds of meters until it achieved a relatively stagnant period after the initial 10 Ma of evolution. However, the influence of these changes in the context of gas hydrate formation in the history of the basin remains limited. On the other hand, present-day gas hydrate resources might experience a reduction in the GHSZ due to rising bottom water temperatures (Kretschmer et al., 2015) but analyzing the fate of gas hydrate deposits under global warming conditions is beyond the scope of this study. Paleo-water depth trend used in the modeling study resulted from a compilation of data from various sources of a different time resolution starting from 165 Ma up to the present-day (Alegret and Thomas, 2005; Davis, 2011; Miller et al., 2005; Salvador, 1991; Schroeder et al., 1995; Simms et al., 2009; Wright et al., 2005) based on paleo-basin re-construction, oxygen isotope data, as well interglacial and glacial shoreline locations (see Fig. 7). Due to a large amount of data giving precise sea level change trends during Quaternary but sparse and
rare remarks on e.g. Jurassic or Cretaceous periods, some interpolations, especially for the older (>60 Ma) systems, had to be made. Moreover, it was also not possible within the frame of presented numerical study and time-step limitations to resolve for a short-scale (tens of thousands of years) sea level changes observed in the glacial-interglacial periods.

SIMULATION

Final simulations run as well as preliminary test runs were performed on 8-CPU workstation in a parallel-run mode. Simulations contained a total of 93 separate events. Maximum time-step of each event (e.g. sedimentary layer deposition) could not exceed 10 Ma. In case of such, total thickness of initially computed sedimentary layer would be automatically split into thinner packages fulfilling the time-step requirements. For the purpose of this study, basin sides were assumed to be open for the entire modeling time allowing a non-limited migration (outflow) of the pore space-filling components.

MIGRATION METHOD

Modeling of a multi-phase flow in a basin-scale numerical domain containing both low-permeability (e.g. uniform fine-grain lithology) and high-permeability pathways (e.g. faults) is challenging. Fluid, oil, and gas flow in the low-permeability regions is often computed according to the Darcy’s law when the flow velocity of the phase remains rather slow. On the other hand, numerical stability of such solution strongly depends on keeping relatively small time-steps which automatically limits the overall computational time. To avoid high inefficiency of this method in case of high-permeability regions experiencing large fluid flow rates, a flowpath analysis method is introduced which is based only on the geometric property of the domain and an indication for a flow direction (honoring the assumption of primarily vertical and upward migration). On the further step of the flowpath analysis, quantitative determinations on the amount of e.g. gas phase being transported towards the local topographic high are made. This assumption allows for relatively fast and accurate modeling of e.g. high-buoyancy or petroleum phases and components migration on geological time-scales.
Due to high complexity of the 3D modeling domain presented in this study containing both low- and high-permeability regions, we have decided to use a Hybrid method of migration introduced by Hantschel et al., 2000 and incorporated into the PetroMod™ software package. The main advantage of this method is an ability to recognize both kinds of domain with distinct migration efficiency and perform a decomposition of modeling domain prior to the simulation run. In this case, regions recognized as high-permeability structures are faults and reservoirs with permeability threshold value of 30 % (2.01 log (mD)). It should be noted here that in a large portion of the basin representing the low permeability domain, a Darcy’s migration formulation was used to compute the pore fluid and gas migration. In case of moderate resolution runs, this formulation would tend to slightly overestimate in-cell methane concentrations and thus, gas hydrate formation.

**GAS HYDRATE FORMATION FROM BIODEGRADATION MODULE**

Shallow gas found within Pleistocene layers of the Green Canyon region is mainly attributed to the biogenic in-situ formation (Lorenson et al., 2008; Sassen et al., 2003) due to high Cenozoic rates of sedimentation and large TOC input (Hutchinson et al., 2011). However, reaction rates (i.e. methanogenesis, anaerobic methane oxidation, and sulfate reduction) in the shallow subsurface are highly variable and lead to abundant but locally focused methane gas seepages and seafloor venting sites. These minor scale phenomena could not be incorporated into the presented basin-scale simulation. Nevertheless, we have introduced an in-situ biogenic gas formation possibility in the sedimentary layers above salt with a constant TOC value of 1 wt. % and constant HI of 100 mg HC/ g TOC which is in accordance to DSDP data from site 96 (Kennicutt et al., 1985; Kennicutt et al., 1986) an average value acceptable for such marine setting (Frye, 2008). Biogenic methane formed according to the Middelburg’s formulation (Middelburg J. J., 1989) was furthermore allowed to diffuse in pore fluids and form gas hydrates within the GHSZ according to the local equilibrium conditions.
**HYDROCARBON GENERATION KINETICS**

Three source rocks located on different stratigraphic levels are present in the model: Tithonian (Upper Jurassic) source rock of a primary importance for hydrocarbon generation in the region, Oxfordian (Upper Jurassic) source rock and MCU (Middle Cretaceous) source rocks, both of secondary importance. Table 2 contains modeling parameters describing source rock productivities and modeling assumptions used in the study.

<table>
<thead>
<tr>
<th>Source rock</th>
<th>Tithonian (Upper Jurassic)</th>
<th>Oxfordian (Upper Jurassic)</th>
<th>MCU (Middle Cretaceous)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Importance</td>
<td>primary</td>
<td>secondary</td>
<td>secondary</td>
</tr>
<tr>
<td>TOC content</td>
<td>6 wt. %</td>
<td>3 wt. %</td>
<td>3 wt. %</td>
</tr>
<tr>
<td>HI</td>
<td>640 mg HC/ g TOC</td>
<td>550 mg HC/ g TOC</td>
<td>500 mg HC/ g TOC</td>
</tr>
<tr>
<td>Thickness</td>
<td>200 m</td>
<td>50 m</td>
<td>50 m</td>
</tr>
<tr>
<td>Secondary cracking</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>HC generation kinetics based on</td>
<td>Type II kerogen (Burnham, 1989)</td>
<td>Type II kerogen (Burnham, 1989)</td>
<td>Type II kerogen (Burnham, 1989)</td>
</tr>
</tbody>
</table>

**RESULTS**

**BURIAL HISTORY**

Burial history of the basin extracted nearby JIP Leg II drill wells is shown in the Fig. 9. The upper plot presents sediment deposition within the entire modeling time (210 Ma to present) whereas the lower plot focuses on the most recent Neogene sedimentation (23 Ma to present) to emphasize Plio-Pleistocene depositional periods characterized by very large amounts of clastic material delivered to the Green Canyon area mainly from the NW direction. Due to high sedimentation rates and changes in lithology within Miocene unit, significant overpressures were recognized and consistent with reported data (Piggott and Pulham, 1993). These overpressures result in an enhanced hydrocarbon migration potential within the deeper part of sedimentary column and probable development of local fractures acting as high-permeable conduits transporting petroleum components directly into the intra-salt mini-basins. Moreover, high sedimentation rates which are common for this part of the Gulf of Mexico affect the thermal history of the basin. New sedimentary
particles freshly deposited in large portions at the top of the basin consume a portion of lithospheric heat to thermally equilibrate with already accumulated and partially compacted underlying sediments. On the other hand, coarse clastic material deposited at high rate contains relatively high concentrations of radiogenic elements which lead to an increase in the overall heat balance. A process of radiogenic decay has been included in the presented modeling study based on average presence of uranium, thorium, and potassium for each lithological facies recognized in the region.

Fig. 9. Burial history plot (upper pane: 210 Ma – present, lower pane: 23 – present) extracted from the JIP Leg II drill site location showing the most important sediment packages deposited in the history of the basin. Lower pane represents a close-up on the most recent burial history emphasizing the presence of high sedimentation rates starting in late Miocene up to the present-day.
SOURCE ROCKS PRODUCTIVITIES AND HYDROCARBON GENERATION

Upper Jurassic and mid-Cretaceous organic-rich deposits considered in the modeling study are fully mature and productive (see Fig. 10). Hydrocarbon generation at the primary Tithonian source rock started about 80 Ma ago (oil) and 75 Ma (thermogenic methane) and reached its productivity peak about 35 Ma with a petroleum mass generation of about 5,800 Mt for oil and 1,200 Mt for thermogenic methane component. This finding stays in good agreement with previous estimates of total petroleum components generated in the productivity peak (Cathles L. M., 2004; Cole et al., 2001). The peak of Tithonian source rock productivity seems to last until the present-day. Second Upper Jurassic source rock of the Oxfordian age remains in a productivity stage since about 110 Ma with a productivity peak of about 4,700 Mt of oil and 1,000 Mt of thermogenic gas at about 40 Ma ago. Most likely, Oxfordian source rock experience the post-productivity peak phase in the present-day. Mid-Cretaceous MCU source rock which is the youngest one present in the study seems to be productive since about 30 Ma ago (oil) and 28 Ma (thermogenic gas) with productivity peak at 5 Ma.

Fig. 10. Oil and thermogenic methane generation from Tithonian (upper and left), Oxfordian (upper and right), and MCU (lower) source rocks showed as total generated oil, accumulated in the source oil, total generated gas, and accumulated in the source gas curves.
However, overlapping productivity stages and migration pathways for all three source rocks make precise analysis of the hydrocarbon origin somewhat difficult. As it was previously suggested (Cole et al., 2000; Cole et al., 2001), petroleum systems of the Northern Gulf of Mexico seem to represent a highly mixed systems which makes the connection between particular source rock and reservoir accumulation difficult to establish. Relatively significant changes in the thermal history of the basin caused by high sedimentation rates modified heat distribution and source rock maturation potentials. Thermogenic component present in gas venting sites and gas seeps broadly observed at the Gulf of Mexico seafloor cannot therefore be attributed to a single deep hydrocarbon source. Sediments younger than Miocene present in the region are commonly thought to be thermally immature and thus, not productive (Nunn and Sassen, 1986; Piggott and Pulham, 1993). However, in-situ microbial production of methane occurs in the Pleistocene layers and significantly contributes to the overall gas hydrate concentration.

Tab. 3 Modeling results on source rock productivities, oil and thermogenic methane generation

<table>
<thead>
<tr>
<th>Source rock</th>
<th>Tithonian (Upper Jurassic)</th>
<th>Oxfordian (Upper Jurassic)</th>
<th>MCU (Middle Cretaceous)</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HC generation by primary cracking:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oil</td>
<td>7,787 Mt incl.</td>
<td>6,688 Mt incl.</td>
<td>2,034 Mt incl.</td>
<td>16,509 Mt incl.</td>
</tr>
<tr>
<td>thermogenic methane</td>
<td>5,680 Mt</td>
<td>4,773 Mt</td>
<td>1,429 Mt</td>
<td>11,882 Mt</td>
</tr>
<tr>
<td></td>
<td>1,055 Mt</td>
<td>886 Mt</td>
<td>266 Mt</td>
<td>2,207 Mt</td>
</tr>
<tr>
<td><strong>HC generation by secondary cracking:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oil</td>
<td>83 Mt incl.</td>
<td>21 Mt incl.</td>
<td>401 Mt incl.</td>
<td>505 Mt incl.</td>
</tr>
<tr>
<td>thermogenic methane</td>
<td>0 Mt</td>
<td>0 Mt</td>
<td>0 Mt</td>
<td>0 Mt</td>
</tr>
<tr>
<td></td>
<td>6 Mt</td>
<td>21 Mt</td>
<td>19 Mt</td>
<td>46 Mt</td>
</tr>
<tr>
<td><strong>Accumulation in the source:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oil</td>
<td>33 Mt incl.</td>
<td>54 Mt incl.</td>
<td>71 Mt incl.</td>
<td>158 Mt incl.</td>
</tr>
<tr>
<td>thermogenic methane</td>
<td>4 Mt</td>
<td>1 Mt</td>
<td>50 Mt</td>
<td>55 Mt</td>
</tr>
<tr>
<td></td>
<td>28 Mt</td>
<td>48 Mt</td>
<td>19 Mt</td>
<td>95 Mt</td>
</tr>
<tr>
<td><strong>Expulsion from the source:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oil</td>
<td>7,748 Mt incl.</td>
<td>6,614 Mt incl.</td>
<td>1,962 Mt incl.</td>
<td>16,324 Mt incl.</td>
</tr>
<tr>
<td>thermogenic methane</td>
<td>5,665 Mt</td>
<td>4,730 Mt</td>
<td>1,378 Mt</td>
<td>11,773 Mt</td>
</tr>
<tr>
<td></td>
<td>1,032 Mt</td>
<td>859 Mt</td>
<td>248 Mt</td>
<td>2,139 Mt</td>
</tr>
<tr>
<td><strong>TOTAL generation of petroleum components in the source rocks</strong></td>
<td><strong>18,135 Mt</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL expulsion of petroleum components from the source rocks</strong></td>
<td><strong>16,632 Mt</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

111
PREDICTED GAS HYDRATE ACCUMULATIONS

Total (biogenic + thermogenic) gas hydrate distribution within the 3D modeling domain and a map view of gas hydrates attributed only to a thermogenic origin are presented in Fig. 11. Due to the upward migration of gas component and high thermal maturity of in-situ organic matter, sedimentary layers close to the base of the gas hydrate stability zone are primarily saturated in methane and thus, gas hydrate formation occurs mostly at that depth. A majority of prominent and wide-spread gas hydrate accumulations is located at the local depressions developed between the salt rims (see Fig. 11) and contains mostly biogenic methane. According to our simulations, a vivid biogenic methane production resulting in abundant gas hydrate deposits at local depressions started about 2.8 Ma ago. However, at the beginning of biogenic gas hydrate formation within these areas, gas hydrate concentrations remained relatively small (about 10-15 vol. %) in comparison to the present-day ones and progressively increased up to >80 vol. %. We explain this behavior by very high Neogene sedimentation rates which caused a rapid subsidence of the basin and, consequently, translation of the lower GHSZ boundary upwards and towards the seafloor. As a result of newly deposited thick sediment packages on top of local depressions, relatively deep secondary intra-salt mini-basins developed. Gas hydrate deposits located at the base of the GHSZ were subsequently buried deeper and moved outside the stability field which caused their dissolution and the free gas formation which, in return, started to migrate upward and re-entered the stability zone causing a significant increase in gas hydrate saturation at that depth. Time scales of methane gas migration with respect to the burial velocities of sediments are much faster and thus, an instantaneous re-charge of gas hydrate deposits at the base of the GHSZ occurred. We attribute this process of gas hydrate-free gas re-cycling at the base of stability field due to an extreme Neogene sediment load to be the major cause of wide-spread gas hydrate deposits in the local topographic lows.

Taking into account high gas hydrate saturations (> 80 vol. %) commonly present in this low-topographic areas (see Fig. 11), a consequent reduction in sediment porosity and permeability is observed in the present-day state which effectively blocks the pore fluid
flow and additional methane supply from underlying layers and allows local overpressure to evolve due to the presence of a free gas phase. Presence of free gas directly underneath abundant gas hydrate accumulations located at the GHSZ base and consequent decrease in methane fraction dissolved in shallower pore fluids was postulated and confirmed by the JIP Leg II cruise reports (Guerin et al., 2009; Hutchinson et al., 2009; McConnell et al., 2010) and remains consistent with our findings.

Migration efficiency of biogenic shallow methane gas responsible for majority of gas hydrate deposits in the investigated area seems to be much higher than the efficiency of its thermogenic equivalent as it was previously suggested (Frye, 2008; Sassen et al., 2003). A timing of salt invasion coupled with thermogenic petroleum components expulsion from the source rock and their further upward migration plays a significant role in the fact that gas hydrate of pure thermogenic origin are rare in our modeling outcome. Based on performed numerical simulations we have concluded that the majority of thermogenic gas expelled from the source rock and transported upwards towards the basin top reaches the upper boundary and vents out before sufficient sediment load traps it within reservoir formation or the GHSZ.

A role of faults in gas migration towards the GHSZ seems to be large. Due to high gas hydrate concentrations at the base of the GHSZ, local high-permeability pathways piercing through its lower boundary are necessary to transport methane component directly to shallower layers. This mechanism is visible especially in the region of the three JIP drill sites were shallow-rooted fault structures were recognized in a seismic images and implemented into the numerical model. Gas hydrate concentrations attributed to the present of regional faults and unconformities are relatively high (above 50 vol. %) and often exist in a form of local vents extending from the GHSZ base up to the seafloor. It should be noticed here that the effects of anaerobic oxidation of methane (AOM) is not recognized in the model and therefore gas hydrate concentrations in the uppermost sedimentary layers (up to about 50 meters) are overestimated. The AOM process is reported to have a major impact on pore fluid methane concentrations due to a presence of dissolved in pore fluids sulfates (Knittel et al., 2003; Treude et al., 2003). It is commonly
thought that about 50% of the total dissolved methane can be depleted due to bicarbonate compound formation and authigenic carbonates precipitation (Biastoch et al., 2011). However, these chemical reactions occur only in the dissolved state and do not affect the free gas methane phase which can be continuously transported within the AOM zone and, eventually, vented out through the seafloor. Additionally, kinetics rates of gas hydrate formation are usually much slower than transport velocities of the gas phase which allows it to co-exist with gas hydrates within the GHSZ and furthermore escapes to the ocean.

Fig. 11. Total gas hydrates distribution within Pleistocene sediments of the Green Canyon province (3D view) presented together with isolated gas hydrate accumulations of thermogenic methane origin (upper map view). Very low gas hydrates concentrations (< 3 vol. %) commonly observed within uppermost Pleistocene layers were not shown on this figure to keep the clarity of the picture. Salt layer visible in the 3D view is
marked with solid red color, whereas the basement horizons defining the bottom boundary of modeling domain is shown with solid blue. Interpreted faulting structures have been shown here to emphasize the 3D interplay between fault position and gas hydrate accumulations within the GHSZ.

Low concentrations of gas hydrates within the uppermost Pleistocene layers (first 300 - 500 meters) of about 1 – 3 vol. % (not shown in Fig. 11) are mainly caused by two factors: high gas hydrate concentrations at the base of the GHSZ blocking methane migration, and insufficient in-situ methane production due to relatively short time of organic matter residence. A detailed location of any non-zero gas hydrate concentrations with respect to the well location (GC955-H, GC955-I, and GC955-Q) is shown as a 2D cross-section in Fig. 12. Advance carbon isotope study on the methane origin from the Green Canyon area was performed by Sassen et al., 2003 who concluded that the bulk of methane venting out from the seafloor contains both microbial and thermogenic components, however, without almost any contributions from the modern carbon sources.

![Fig. 12. Total gas hydrates distribution within uppermost Pleistocene sediments of the Green Canyon province plotted for each JIP Leg II well. A bathymetric contour map showing the location of the well GC955-H, GC955-I, and GC955-Q is presented on the lower left side. Plotting scale for gas hydrate concentrations is limited to 10 vol. % to emphasize low hydrate concentrations due to local biogenic methane levels. Continuous horizon with high (here > 10 vol. %, in reality about 80 – 100 vol. %) is clearly visible for each well and corresponds to the base of gas hydrate stability zone.](image-url)
A deep fossil origin of methane in the Green Canyon supports a hypothesis of insufficient modern organic matter biodegradation that takes place in the uppermost Pleistocene layers. Unfortunately, a complex burial history of the Northern Gulf of Mexico and multiple periods of salt re-mobilization resulted in consequent re-charge of reservoirs from variety of sources. The vertical extend of a deep biosphere in the Gulf of Mexico remains poorly constrained and thus, no reliable rates of microbial activity in high-temperature environment can be applied. Nevertheless, our results derived from numerical simulation on gas hydrate formation from deeply-situated thermogenic and shallow biogenic methane originated from Pleistocene-age sediments support a significant contribution from deep fossil methane charging the seafloor vents and seeps, as well as gas hydrate accumulations in the Green Canyon area.

Therefore, we suggest interpreting results presented herein rather as general gas hydrate distribution pattern composed from two distinct methane sources which suggests the proportion and relationship between various CH₄ origins and their noticeably different migration efficiencies.

**UNCERTAINTIES**

Major uncertainties in the presented modeling study comprise source rock properties with a special focus on potential changes in Tithonian source rock thickness and initial petroleum generation properties (i.e. TOC content, HI value) which might occur laterally within the region of interest. In the proposed study, we have used rather maximum values of these two parameters which would favor hydrocarbon generation at the source and, potentially, gas hydrate saturation in the shallowest 500 meters of sedimentary column. We do not expect to see an overall change in the gas hydrate distribution pattern in case of lower source rock productivity but rather lower gas hydrate saturations in regions directly corresponding to fault-associated migration pathways for gas. A series of sensitivity studies would have to be performed in order to achieve a statistical relationship between source rock productivity parameters (including the layer thickness and local thinning) and gas hydrate saturation formed from thermogenic sources. We are aware of the fact that
structure II gas hydrates are commonly present in the Gulf of Mexico (Sassen and Macdonald, 1994; Sassen et al., 2001), however, due to two-component hydrocarbon generation kinetics used in the modeling study (oil and thermogenic methane gas) and software limitations (the GHSZ calculations provided for only structure I gas hydrates), it was not possible to fully explore a potential presence of structure II gas hydrates and the vertical extend of adequate stability zone.

Some assumptions were also needed regarding potential lateral heterogeneity in lithology of the Green Canyon sediments. Due to a complex geometry of a paleo-levee-channel systems present in the Green Canyon, some important geological features of local character could not be addressed with the presented model. It is highly probable that the grain size and distribution within the gas hydrate reservoir layers varies in three dimensions on a scale of meters. Lateral permeability is commonly thought to be more efficient way for fluid migration than its vertical analogue. In a contrary, upward gas phase migration due to the phase buoyancy within homogenous lithology is the fastest and most efficient way of transporting the free gas into the potential GHSZ. Numerical solution presented here does not account for gas hydrate and free gas phase co-existence within stability zone of hydrates (all methane is immediately trapped as gas hydrate, see Fig. 11 and Fig. 12) and thus, does not answer the questions about timing and evolution of seafloor venting structures commonly observed at the Northern Gulf of Mexico seafloor.

Faults introduced in the model as high-permeable pathways open during their entire presence which allows for rapid fluid and gas ascends (see migration method paragraph) with a constant value of capillary entry pressure (CEP) are an assumption made for the purpose of this study. Precise timing of, potentially, multiple events of fault re-opening and closure might affect the rate of methane transportation towards the GHSZ. However, due to lack of reliable data on fault properties evolution in time, we have decided to keep these parameters constant. Additional shallow-rooted high-permeability pathways which were not recognized on the seismic images might exist in the region and thus, strongly affect the local gas hydrate concentrations especially at moderate GHSZ depths.
3D interpretation of seismic data and available literature on the subject allowed us to reconstruct the history of salt invasion and development within the Green Canyon area and its direct vicinity. Special attention was paid to previously published basin reconstructions where salt layer deposition and re-mobilization events were coupled with some constrains on fluid and gas migration pathways affected by salt dome formations. Nevertheless, we are aware of several possible scenarios describing the salt invasion with different timing and volumetric rates. Presence of salt underlying gas hydrate-filled sediments modifies local thermal properties of surrounding strata and pore water chemistry leading to an increase of dissolved cation concentrations and thus, strongly affects the extend of gas hydrate stability zone in all three dimensions (especially visible in the paleo-gas hydrate stability zone reconstructions). It should be also noted that perfect sealing properties of salt tend to deviate originally vertical fluid and gas phase migration pathways towards more horizontal and following only the local topographic heights. Variable and parameter-dependent rates of hydrocarbon expulsion from the source rock might not be effective (or might not correlate with predictions) in case of invalid relationship between phase migration and timing of salt invasion. To resolve for these issues, a specific study on salt front invasion, deformation, and salt diapirism influencing the quantity and quality of fluid and gas phase migration performed with adequate spatial resolution should be addressed.

CONCLUSIONS

The Northern Gulf of Mexico contains all required components for abundant gas hydrate deposits: mature source rocks producing large amounts of hydrocarbon gases, efficient migration pathways along fault structures, paleo-channel-levee systems in the uppermost Pleistocene sediments providing a perfect reservoir for gas hydrate storage within 500 – 600 meters (locally up to 1,000 meters) thick gas hydrate stability zone. Moreover, high rates of sedimentation and large organic matter supply to the seafloor assure efficient microbial in-situ gas production directly within the GHSZ. Direct presence of gas hydrates in the Green Canyon region was confirmed by JIP Leg II operation which revealed moderate (about 20 vol. %) to high (about 80 vol. %) gas hydrate concentrations on several
litho-stratigraphical levels with a special attention paid to thick sandy intervals exhibited at depth of about 380 to 480 mbsf.

The general pattern of the simulated gas hydrate distribution (showing high concentrations of > 80 vol.% close to the base of the GHSZ) is primarily caused by gas hydrate-free gas recycling process fueled by methane generation from in-situ microbial sources and migration of thermogenic methane from great sediment depth (see Fig. 11). These results are consistent with findings of the JIP Leg II cruise (Guerin et al., 2009; Hutchinson et al., 2009; McConnell et al., 2010). Moreover, we were able to distinguish between gas hydrate of microbial in-situ origin and those of thermogenic origin (see Fig. 11). Relatively low gas hydrates concentrations (up to 3 vol.%) were found in the uppermost Pleistocene sediments and attributed to a) in-situ microbial formation of methane (see Fig. 12) not capable of producing sufficient amounts of CH₄ to produce significant gas hydrate saturations, b) high gas hydrate concentration at the base of the GHSZ blocking additional methane migration, and c) potential presence of locally developed fault structures transporting methane directly to the GHSZ but not recognized in the study.

Following the hypothesis of Sassen et al., 2003 who postulated mixed-microbial and thermogenic origin of methane but without a significant contribution from modern carbon sources in the Green Canyon area, we suggest an existence of deep fossil methane source charging the gas hydrate stability zone in the region. Fault structures which have been implemented into the numerical model have a major impact on enhancing gas migration into the GHSZ. Large volumes of methane attributed to the thermogenic origin have been consequently re-charging previously existing hydrocarbon reservoirs due to major geological re-structuring of the basin. However, large amounts of gas was vented out through the upper modeling boundary over the basin history and were, most likely, not able to contribute as significantly as previously thought to the total amount of gas hydrates present in the region.

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SUMMARY AND CONCLUSIONS

The primary focus of scientific projects presented herein was to a) quantify and evaluate present-day estimates of gas hydrates stored within marine sediments, b) develop a comprehensive and parameter-based numerical tool in order to resolve for bio-geochemical processes associated with gas hydrate formation and dissolution along the entire history of a basin, and c) investigate the 3D effects of high permeability pathways (i.e. faults) on gas and fluid migration within gas hydrate-bearing environment experiencing salt tectonism and rapid sedimentation.

As a result, a world-wide estimate on the total amount of gas hydrates being stored within marine sediments was performed. This study based on multi-1D numerical approach comprising geological, geophysical, and geochemical global data sets provided a detailed 1°x1° resolution maps of gas hydrate and free gas distribution in the world marine sediments. We estimate a total amount of ~1000 Gt C gas hydrates currently stored in the world marine sediments. However, the estimated amount of carbon trapped within gas hydrate structure should be considered as a lower-end of expected global amount as the mechanism of gas hydrate formation in this study was restricted to the in-situ biogenic methane formation and did not consider methane transport via bubbles or enhanced fluid flow. These results have important implications for future assessment of global gas hydrate deposits accounting for active fluid flow regions (i.e. active continental margins), climate studies investigating the fate of gas hydrate deposits under global warming (see Appendix 2 and Appendix 3), and understanding of the main processes controlling gas hydrate and free gas dynamics (see Appendix 1).

Gas hydrate and free gas formation and dissolution dynamics at the Blake Ridge site, offshore South Carolina were presented within a frame-scale representative of the entire basin history (10 Ma – present). It is concluded that the co-existence of gas hydrate and free gas phases within the stability zone of hydrates could explain relatively low gas hydrate saturations revealed by drilling and upward net fluid velocities at the seafloor. The amount
of dissolved methane representing a deep hydrocarbon source and entering the system through the lower boundary is estimated at CH₄ mass flux of 1.6·10¹¹ kg s⁻¹ m⁻² (corresponding to ~170 mM of CH₄). Presence of, most likely, mobile free gas phase at the great depths with concentrations reaching up to ~7.3 vol. % is suggested here as an explanation for slightly higher gas hydrate concentration at the base of the GHSZ due to gas hydrate-free gas recycling process. However, the time frame of such process is not constrained and therefore, more research investigating the efficiency of gas hydrate recycling on a basin-scale is required (see Chapter 3). Moreover, due to the influence of the Western Boundary Undercurrent (WBUC) on bottom water temperatures at the Blake Ridge, gas hydrate deposits are especially vulnerable to the climate change and potential large reductions of the GHSZ volume (second major reduction after the Arctic Ocean) are expected for this region within the next 500 years (see Appendix 3).

Based on the 3D numerical study of the Green Canyon, Gulf of Mexico, including salt diapirism, presence of faults, and high Neogene sedimentation rates, we identify two main mechanisms responsible for the location of high (>80 vol. %) gas hydrate concentrations predicted in the model. Prominent gas hydrate deposits extending vertically from the base of the GHSZ up to the seafloor are strictly related to the presence of faults developing at the top of uprising salt structures and acting as efficient high-permeability pathways for methane gas transportation. On the other hand, wide-spread gas hydrate deposits located at topographic lows and plateaus are located at the base of the GHSZ and mostly limited in their vertical extent. We attribute these abundant gas hydrate accumulations to the process of the free gas-gas hydrate recycling at the lower boundary of the GHSZ. According to our numerical model, the time-frame of this formation mechanism is directly related to the high sedimentation rates during the Neogene period. This large sedimentary load caused a significant and rapid subsidence of the basin followed by development of secondary intra-salt mini basins and therefore, shifted already existing gas hydrate deposits outside the stability zone which resulted in a formation of a free gas phase.
Potential economical importance of gas hydrate deposits as well as their high sensitivity to the climate change (see Chapter 1, Appendix 2, and Appendix 3) strength the need for further quantification and processes-based studies at regional and global scale. Our findings already suggest that long time-scale impacts of greenhouse effect and atmospheric warming are most likely less influential than it was previously postulated (see Appendix 2, Appendix 3). Therefore, the focus of future research should be shifted towards short time-scale and region-limited processes. The risk of e.g. sudden seabed subsidence due to dissociating gas hydrates seems to be more probable, especially in the context of potential gas hydrate recovery. Such hazardous events are dangerous for underwater infrastructure and in-situ biosphere accompanied with potential local ocean acidification. Further research on gas hydrate dissociation dynamics (see Chapter 2, Appendix 1) and time-resolved ocean response to increasing methane concentration is required (see Appendix 2). Finally, our findings strongly suggest that basin-scale studies should include the effect of high-permeability pathways such as fault structures associated with salt tectonics (see Chapter 3). These geological features provide an efficient migration potential to the hydrocarbon gas and methane-rich fluids and which, as an important part of the complex gas hydrate systems, should be incorporated into numerical models on a larger scale.
APPENDIX 1: THE GLOBAL INVENTORY OF METHANE HYDRATE IN MARINE SEDIMENTS: A THEORETICAL APPROACH

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ABSTRACT
The accumulation of methane hydrate in marine sediments is controlled by a number of physical and biogeochemical parameters including the thickness of the gas hydrate stability zone (GHSZ), the solubility of methane in pore fluids, the accumulation of particulate organic carbon at the seafloor, the kinetics of microbial organic matter degradation and methane generation in marine sediments, sediment compaction and the ascent of deep-seated pore fluids and methane gas into the GHSZ. Our present knowledge on these controlling factors is discussed and new estimates of global sediment and methane fluxes are provided applying a transport-reaction model at global scale. The modeling and the data evaluation yield improved and better constrained estimates of the global pore volume within the modern GHSZ (≥44 x 10¹⁵ m³), the Holocene POC accumulation rate at the seabed (~1.4 x 10¹⁴ g yr⁻¹), the global rate of microbial methane production in the deep biosphere (4 – 25 x 10¹² g C yr⁻¹) and the inventory of methane hydrates in marine sediments (≥ 455 Gt of methane-bound carbon).
Keywords: methane, gas hydrate, marine sediments, global change

1. INTRODUCTION

The global abundance of methane hydrate in marine sediments is still poorly constrained. Estimates are based on extrapolation of field data Kvenvolden and Lorenson, 2001; Milkov, 2004 and geochemical transport-reaction modeling Archer et al., 2008; Buffett and Archer, 2004; Burwicz et al., 2011b; Klauda and Sandler, 2005. They range over three orders of magnitude (500 – 55 700 Gt of C) and a clearly constrained consensus value has not emerged over the past decades. This is a major draw-back for gas hydrate research since the resource potential and the possible impact of methane hydrates on past and future climate change cannot be evaluated without a better constrained estimate of global methane hydrate abundance. Models and observations clearly show that methane hydrate formation is basically controlled by the following key parameters: 1. accumulation of particulate organic carbon at the seafloor; 2. kinetics of microbial organic matter degradation and methane generation in marine sediments; 3. thickness of the gas hydrate stability zone (GHSZ); 4. solubility of methane in pore fluids within the GHSZ; 5. sediment compaction; 6. ascent of deep-seated pore fluids and methane gas into the GHSZ. In the following, we present a comprehensive review on the key parameters listed above and identify major knowledge gaps. Subsequently, a geochemical transport-reaction model is applied to investigate the effects of the key parameters on gas hydrate accumulation in marine sediments on a quantitative basis. The model is finally used to constrain the global gas hydrate inventory in marine sediments.

2. ACCUMULATION OF PARTICULATE ORGANIC CARBON AT THE SEAFLOOR

Methane production and methane hydrate formation are fueled by the accumulation of particulate organic carbon (POC) at the seabed. The mass accumulation rate of sediments (MAR in g cm\(^{-2}\) yr\(^{-1}\)) and the POC accumulation rate (\(A_{\text{POC}}\) in g cm\(^{-2}\) yr\(^{-1}\)) are calculated as:
\[ MAR = \rho_s \cdot (1 - \Phi) \cdot w \]

\[ A_{POC} = \frac{POC_0 \cdot MAR}{100} \quad (1) \]

where POC_0 is the concentration of particulate organic carbon in surface sediments (in wt-%), \( \rho_s \) is the density of dry solids (in g cm\(^{-3}\)), \( \Phi \) is porosity and \( w \) is burial velocity (in cm yr\(^{-1}\)). The density of dry solids in continental margin sediments varies from 2.65 g cm\(^{-3}\) for quartz to 2.1 – 2.76 g cm\(^{-3}\) for different types of clay minerals. Here, we adopt \( \rho_s = 2.5 \text{ g cm}^{-3} \) as mean density of dry solids at continental margins Burwicz et al., 2011b. The porosity of bioturbated surface sediments (0 – 10 cm sediment depth) usually falls into a range of 0.7 – 0.9 at most continental margins. Thus, a mean value of \( \Phi = 0.8 \) is applied in the following to convert burial velocities of surface sediments into mass accumulation rates Burwicz et al., 2011b.

### 2.1. Holocene POC Accumulation Rates

POC concentrations in Holocene surface sediments have been measured at several thousand sites covering most depositional areas at the seabed Romankevich et al., 2009b; Seiter et al., 2004b. The available data have been compiled and evaluated to produce a global map of POC concentrations in marine surface sediments (Fig. 1).

**Figure 1.** Concentration of particulate organic carbon (POC) in Holocene surface sediments Romankevich et al., 2009b; Seiter et al., 2004b. The color coding indicates POC values in wt-%. Regions of the seafloor where data are not available are shown in white.
For some parts of the global seafloor POC concentrations are not available (see white areas in Fig. 1). In the following, we assume a POC value of 1 wt-\% for these areas. Burial velocities of Holocene surface sediments have also been determined at several hundred locations Burwicz et al., 2011b. The published data clearly show that burial velocities are high on the continental shelf and decrease with increasing water depth. Most of the sediments accumulating at the seabed are derived from the continents. Moreover, the solid remains of marine plankton (carbonate, biogenic opal) are deposited at the deep-sea floor as pelagic sediments. The global accumulation rate of sediments at the modern seafloor amounts to about 19.6 x 10^{15} g yr^{-1}. This number has been derived considering the transport of riverine, eolian and ice-rafted sediments to the ocean, the accumulation of neritic carbonates at the continental shelf and the accumulation of pelagic sediments at the deep-sea floor Burwicz et al., 2011b. The depth-distribution of sediment accumulation and the global accumulation rate can be used to constrain parameter values of a logistics equation defining the burial velocity as function of water depth Burwicz et al., 2011b:

\[
w = \frac{w_1}{1 + \left( \frac{Z}{Z_1} \right)^{c_1}} + \frac{w_2}{1 + \left( \frac{Z}{Z_2} \right)^{c_2}} \quad (2)
\]

with \( w_1 = 0.117 \) cm yr\(^{-1} \), \( w_2 = 0.006 \) cm yr\(^{-1} \), \( Z_1 = 200 \) m, \( Z_2 = 4000 \) m, \( c_1 = 3 \), \( c_2 = 10 \), and \( Z \) in m. Eq. (2) yields a global sediment accumulation of 19.6 x 10^{15} g yr\(^{-1} \) for \( \Phi = 0.8 \) and \( \rho_s = 2.5 \) g cm\(^{-3} \) when applied to the global bathymetric data set given by Menard and Smith Menard and Smith, 1966b. The equation predicts that most of the global sedimentation takes place on the continental shelf (14.1 x 10^{15} g yr\(^{-1} \) at 0 – 200 m water depth). These estimates are consistent with other data recently presented by Baturin Baturin, 2007. Baturin derived a total sedimentation rate of 18.9 x 10^{15} g yr\(^{-1} \) with a shelf and upper slope contribution of 13.6 x 10^{15} g yr\(^{-1} \). Sediments accumulating at shallow water depths (<200 m) cannot contribute to gas hydrate accumulation since marine methane hydrates are only formed at significantly higher pressures i.e. water depths. During the Holocene, the
accumulation of methane hydrates is thus severely limited by the continental shelf acting as a trap for the continental sediment input.

Holocene POC accumulation rates are calculated at global scale applying Eq. (1) and Eq. (2) with $\Phi = 0.8$ and $\rho_s = 2.5$ g cm$^{-3}$ and the POC concentrations shown in Fig. 1. The resulting global map shows high $A_{POC}$ values at the shelf of productive continental margins where POC is rapidly buried in terrigenous sediments (Fig. 2). Burial velocities vary over several orders of magnitude from less than 1 cm kyr$^{-1}$ in Pacific deep-sea basins to more than 100 cm kyr$^{-1}$ on the continental shelf while most of the POC concentrations fall into the range of 0.1 to 1 wt-%. The $A_{POC}$ variability is thus mainly induced by the strong contrast in burial velocity between pelagic and continental margin settings. The global POC accumulation rate in Holocene surface sediments calculated from the distribution shown in Fig. 2 amounts to $1.37 \times 10^{14}$ g yr$^{-1}$. Since continental margins are the main locus for sediment accumulation, 88 % of the global POC accumulation occurs within 500 km distance from the coastline (Fig. 2). Our new estimate of Holocene POC accumulation ($1.37 \times 10^{14}$ g yr$^{-1}$) is very close to a previous estimate ($1.40 \times 10^{14}$ g yr$^{-1}$) given by Baturin Baturin, 2007 even though Baturin’s global rate is based on an independent data set and modeling approach. This surprising conformity strongly supports the validity of the new approach presented by Burwicz et al. Burwicz et al., 2011b.

Figure 2. Accumulation rate of POC in Holocene surface sediments in g m$^{-2}$ yr$^{-1}$ at 0.5° x 0.5° spatial resolution.
2.2. QUATERNARY POC ACCUMULATION RATES

Most of the methane produced in marine sediments does not originate from Holocene surface sediments. The thickness of these Holocene deposits rarely exceeds 10 m while the gas hydrate stability zone extends several hundred meters into the sub-surface. Thus, mean POC accumulation rates averaged over a period of several million years are more appropriate for the prediction of hydrate accumulation than Holocene accumulation rates. During the Holocene, most riverine particles are deposited on the continental shelf because the shelf is not at isostatic equilibrium with the present sea level but is still affected by the much lower glacial sea level stand Hay and Southam, 1977. The sea level was 120 m below its present value during the last glacial maximum Rohling et al., 1998 reducing the water-covered shelf and marginal sea areas by more than 50 % Ludwig et al., 1999; Menard and Smith, 1966b; Peltier, 1994. Under glacial conditions, the anomalous Holocene shelf accumulation rate may have been diminished by an order of magnitude Hay, 1994 shifting the focus of sedimentation from the shelf to the continental rise and slope. Moreover, the transport of ice-rafted material and the deposition of eolian dust were strongly enhanced further increasing the accumulation rates at the margin seafloor Lisitzin, 1996. Hydrates only accumulate in margin sediments deposited at more than 200 m water depth at the continental slope and rise. The mean Quaternary sedimentation rate in this environment is certainly much higher than the Holocene value. The sediment accumulation at 200-3000 m water depth would rise by a factor of 5 if most of the Holocene shelf sedimentation was shifted to larger water depth under glacial conditions as proposed by Hay Hay, 1994. Quaternary burial velocities were thus calculated increasing the sedimentation rate at the continental slope and rise (>200 m water depth) at the expanse of shelf deposits Burwicz et al., 2011b. The global sediment accumulation rate was maintained while the slope and rise burial velocities were enhanced by a factor of 5 over a 500 km wide zone around the continental margins Burwicz et al., 2011b. This 500 km zone includes the continental slope and a major portion of the continental rise. The resulting burial velocities were then applied to calculate Quaternary POC accumulation rates. These calculations were then applied to calculate Quaternary POC accumulation rates. These calculations were then applied to calculate Quaternary POC accumulation rates. These calculations were then applied to calculate Quaternary POC accumulation rates. These calculations were then applied to calculate Quaternary POC concentrations
are not available at global scale. The error involved in the map of the Quaternary POC accumulation (Fig. 3) thus exceeds the error of the corresponding Holocene distribution (Fig. 2). Nevertheless, methane generation and gas hydrate accumulation in the modern ocean are controlled by the Quaternary mean values (Fig. 3) rather than the anomalous Holocene accumulation rates (Fig. 2). The global POC accumulation rate for Quaternary surface sediments calculated from the distribution shown in Fig. 3 amounts to $1.55 \times 10^{14}$ g yr$^{-1}$. In the Quaternary reconstruction, 89.5 % of the global POC accumulation occurs within a distant of 500 km from the coastline. The accumulation is, however, shifted from the shelf to the continental rise and slope.

Figure 3. Accumulation rate of POC in Quaternary sediments (in g m$^{-2}$ yr$^{-1}$).

2.3. CENOZOIC – CRETACEOUS POC ACCUMULATION RATES

Global accumulation rates of terrigenous sediments at the seafloor reconstructed over the last 150 Myr Wallmann, 2001 show a strong increase towards the Quaternary induced by high rates of continental erosion (Fig. 4). Quaternary erosion was accelerated by the waxing and waning of continental ice shields, rapid sea-level change and intense mountain building in the Himalayas and Tibetan High Plateau. Global rates of POC accumulation at the seafloor were reconstructed using the δ$^{13}$C record of marine carbonates Wallmann, 2001. They feature a maximum during the Quaternary induced by high rates of sediment accumulation (Fig. 4). However, the contrast to the previous periods is not as strong as observed for terrigenous sedimentation. It thus seems that average concentrations of POC
in marine sediments were higher in the geological past (Eq. 1). Very high POC concentrations may have prevailed prior to the Paleocene-Eocene Thermal Maximum (PETM) at 55.5 Myr. These high concentrations may have favored the built-up of a large marine gas hydrate inventory which was possibly destabilized during the PETM to induce the large negative δ¹³C excursion observed in the geological record. Dickens et al., 1997.

**Figure 4.** Accumulation of POC and terrigenous sediments over the last 150 Myr. The solid line shows the global marine POC accumulation rate normalized to the Quaternary value while the dotted line gives the global rate of terrigenous sedimentation at the seafloor normalized to the Quaternary Wallmann, 2001. The Paleocene-Eocene Thermal Maximum (PETM, at 55.5 Myr) is indicated by the vertical arrow.

3. **Microbial degradation of organic matter and methane formation in marine sediments**

Stable carbon isotope data show that methane hydrates are usually formed from biogenic methane produced by the anaerobic degradation of organic matter in the deep marine biosphere. It is thus important to understand the mechanisms and kinetics of organic matter degradation and microbial methane formation in the marine subsurface. Organic matter deposited at the seabed is degraded by microorganisms and other benthic biota using oxygen as terminal electron acceptor. The remaining organic matter is degraded by anaerobic bacteria and archaea using dissolved nitrate and manganese (+IV) and iron (+III) minerals as oxidizing agents. Berner, 1980. These additional electron acceptors are usually consumed within the bioturbated surface layer (0 – 10 cm sediment depth). Field
data show that only a small fraction of the POC raining to the seafloor is buried below 10 cm depth Flögel et al., 2011. The data reveal a marked contrast between fine-grained continental margin and deep-sea sediments Burdige, 2007. While at continental margins about 10 % of the POC raining to the seafloor is conserved and buried below 10 cm sediment depth, this fraction is reduced to about 1 % at the deep-sea floor Flögel et al., 2011. Due to the very low preservation of POC in open ocean environments, gas hydrates are usually not found in pelagic sediments but only at continental margins where a significant POC fraction is buried and therefore available for microbial methane formation in the deep subsurface.

POC buried below the bioturbated surface layer is further degraded by anaerobic bacteria and archaea using dissolved sulfate as electron acceptor:

\[ \text{C(H}_2\text{O)} + \frac{1}{2} \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \frac{1}{2} \text{H}_2\text{S} \]  \hspace{1cm} (3)

where C(H_2O) represents sedimentary POC.

Microbial methane production and accumulation starts below the depth of sulfate penetration. Several steps are needed before methane is finally produced as stable end product of anaerobic microbial POC degradation. In a first step, biogenic polymers are hydrolyzed and converted into monomers. These monomers (sugars, amino acids, lipids, etc.) are then fermented into CO_2, H_2 and a number of organic acids. Methane is finally formed by methanogenic microorganisms converting CO_2 and H_2 into methane Whiticar et al., 1986:

\[ \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \]  \hspace{1cm} (4)

The stoichiometry of the overall process of organic matter degradation and methanogenesis is given by the following reaction:

\[ \text{C(H}_2\text{O)} \rightarrow \text{CH}_4 + \text{CO}_2 \]  \hspace{1cm} (5)
Eq. (5) does not imply that methane is directly formed by POC degradation. It rather defines the substrate and the final products. The intermediate steps including fermentation and CO₂ reduction with H₂ are included in the overall stoichiometry Wallmann et al., 2006a.

Methane formed at depth is transported upwards into the sulfate-methane transition zone (SMTZ) via molecular diffusion and advection. Within this zone, methane is oxidized by consortia of bacteria and archaea using sulfate as terminal electron acceptor Boetius et al., 2000. The overall stoichiometry of anaerobic oxidation of methane (AOM) within the SMTZ is given by:

\[ \text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O} \]  

(6)

Considering this complex network of microbial processes, the key questions that need to be answered to estimate the global rate of methane formation may be formulated as: How much POC is reaching the methanogenic zone and how much of that POC can be microbially converted into methane? To answer these questions not only the POC burial rates but also the down-core changes in POC reactivity need to be defined. Since more than three decades marine geochemists and microbiologists have observed that the POC reactivity decreases strongly with sediment age and depth. In his classical paper on POC degradation kinetics in marine sediments Middelburg showed that the down-core decrease in POC reactivity can be represented by the following equation Middelburg, 1989:

\[ k_{\text{age}} = 0.16 \cdot (\text{age}_0 + \text{age})^{0.95} \]  

(7)

where \( k_{\text{age}} \) is the age-dependent reactivity (in yr⁻¹) and \( \text{age}_0 \) is the initial age of POC (in yr). The rate of POC degradation (\( R_{\text{POC}} \) in g C g⁻¹ yr⁻¹) is calculated as:

\[ R_{\text{POC}} = -\frac{\partial C_{\text{POC}}}{\partial t} = k_{\text{age}} \cdot C_{\text{POC}} \]  

(8)

where \( C_{\text{POC}} \) is the POC concentration (in g C per g of dry sediment). The equation was calibrated by a large number of rate measurements showing that the reactivity of POC
decreases by 10 orders of magnitude going from fresh marine plankton to POC buried in deep-sea sediments. More recently, ODP drilling confirmed the presence of living microorganisms in pelagic and terrigenous sediments down to the underlying oceanic crust Arndt et al., 2006; D’Hondt et al., 2004; Jørgensen and D’Hondt, 2006; Roy et al., 2012. The number of prokaryotic cells (bacteria and archaea) decreases from more than $10^8$ cm$^{-3}$ in the upper few meter of the sediment column to less than $10^6$ cm$^{-3}$ at depth Jørgensen and D’Hondt, 2006; Parkes et al., 2000. The logarithmic down-core decrease in cell numbers and the microbial POC degradation rates in the deep subsurface are broadly consistent with the rates predicted by the Middelburg model D’Hondt et al., 2002; D’Hondt et al., 2004; Parkes et al., 1994.

The main uncertainty of the Middelburg model is associated with the initial age parameter ($\text{age}_0$) defined as the average age of POC buried below the bioturbated zone. Initial ages of 300 – 30000 years were applied to reproduce the pore water profiles in sediment cores retrieved from the Sakhalin slope Wallmann et al., 2006a. An even larger range of 800 – 180000 years was needed to reproduce pore water profiles measured in ODP sediment cores Marquardt et al., 2010. These large ranges probably reflect the ambient variability in burial velocity, the deposition of refractory organic matter and the possible loss of surface sediments during core retrieval Wallmann et al., 2006a. The largest initial ages were observed at Blake Ridge where drift sediments are deposited containing pre-aged organic matter of terrigenous and marine origin Marquardt et al., 2010; Wallmann et al., 2006a.

Equations (7) and (8) can be combined and solved to estimate the POC loss within the sulfate reduction zone and thereby the input of POC into the methanogenic zone. The fraction of POC reaching the methanogenic zone results in:

$$f_{\text{MI}} = \exp \left( 3.2 \cdot \text{age}_0^{1/20} - 3.2 \cdot \left( t_{\text{exp}} + \text{age}_0 \right)^{1/20} \right)$$  \hspace{1cm} (9)

where $t_{\text{exp}}$ is the sulfate exposure time and $f_{\text{MI}}$ is the concentration of POC in sediments reaching the methanogenic zone divided by the POC concentration in sediments buried
below the bioturbated zone at 0.1 m depth. The sulfate exposure time depends on sulfate penetration depth \(z_s\) in m and burial velocity \(w\) in m yr\(^{-1}\):

\[ t_{\text{exp}} = \frac{z_s - 0.1}{w} \]  

(10)

Burial velocities at the deep-sea floor typically range from 0.1 to 10 cm kyr\(^{-1}\) (Eq. 2) while sulfate penetrates usually more than 100 m into pelagic sediment. A compilation of sulfate penetration depths in open ocean sediments confirmed that sulfate is usually not fully depleted in these pelagic deposits D’Hondt et al., 2002. This observation is partly explained by the deep penetration of dissolved oxygen into pelagic sediments Roy et al., 2012 and the delivery of sulfate through the base of the sediment column via sulfate-rich fluids circulating through the underlying oceanic crust. Deep-sea sediments are thus typically exposed to sulfate over their entire life span (up to ~150 Myr). Microbial rate measurements and pore water profiles obtained in pelagic sediments revealed that methanogenesis may occur already within the sulfate-bearing sediment horizons D’Hondt et al., 2004. Methane produced by this process is, however, consumed within the sulfate-bearing zone via AOM. Methane concentrations in pelagic sediments are therefore several orders of magnitude lower than the ambient saturation value with respect to methane hydrate Tishchenko et al., 2005. Due to this strong undersaturation of pore fluids, methane hydrates have never been documented in pelagic sediments.

**Figure 5.** Fraction of buried POC entering the methanogenic zone \(f_{\text{hi}}\) as calculated from Eq. (9) for initial ages of 1000 years, 10 000 years, and 100 000 years.
In most continental margin settings, sulfate dissolved in ambient pore fluids is completely consumed at 10 – 100 m sediment depth Borowski et al., 1999; D’Hondt et al., 2002. The sulfate exposure time results as $t_{exp} = 10^4 - 10^6$ yr for burial velocities of 10 – 100 cm kyr$^{-1}$. Thus, about 30 – 90 % of the buried POC is reaching the methanogenic zone in continental margin sediments (Fig. 5). The microbial degradation of POC delivered to the sulfate-free methanogenic zone may lead to the accumulation of methane in pore fluids and to the formation of methane hydrates pending on the rate of methane formation and the local pressure and temperature conditions.

Dissolved sulfate profiles often show an almost linear decrease with sediment depth suggesting that only a minor sulfate fraction is used for POC degradation while most of the sulfate is consumed via AOM in the underlying sulfate-methane transition zone Borowski and Paull, 1996; Dickens, 2001. Eq. (9) implies that only 10 % of the POC buried in continental margin sediments is consumed via microbial sulfate reduction where pre-aged organic matter ($age_0 = 10^5$ yr) is deposited at the seabed (Fig. 5). It is thus likely that linear sulfate profiles are induced by the deposition of old POC at the seabed. Terrestrial POC delivered to the margins by continental erosion is a likely source for this pre-aged material. However, sulfate profiles with significant curvature documenting strong sulfate depletion via anaerobic POC degradation are also commonly observed Wallmann et al., 2006a. They probably reflect the deposition of young marine organic matter since Eq. (9) implies that up to 80 % of this young POC ($age_0 = 10^3$ yr) is consumed via microbial sulfate reduction (Fig. 5).

The kinetics of microbial methane formation in marine sediments was studied in detail by Wallmann et al. Wallmann et al., 2006a. Evaluating pore water and sediment data from the Sakhalin Slope and the Blake Ridge, the authors showed that the rate of methane formation within the methanogenic zone ($R_{CH4}$ in g of methane carbon g$^{-1}$ yr$^{-1}$) can be calculated as:

$$R_{CH4} = -0.5 \frac{dC_{POC}}{dt} = \frac{0.5K_C}{C_{CH4} + C_{DRC} + K_C} k_{age} C_{POC}$$

(11)
where $K_C$ is an inhibition constant ($K_C = 30 - 50$ mM), $C_{DIC}$ is the concentration of dissolved inorganic carbon in ambient pore fluids and $C_{CH_4}$ the dissolved methane concentration (in mM). The factor 0.5 defines the fraction of POC being converted into methane. The remaining POC fraction is decomposed into carbon dioxide for sedimentary POC with an oxidation state of carbohydrates (Eq. 5). This extension of the Middelburg model was subsequently tested and applied at a number of ODP drill sites in prominent gas hydrate provinces Marquardt et al., 2010. The evaluation of pore water profiles showed that kinetic equation (11) gives indeed a good approximation of the down-core changes in microbial methane formation within the GHSZ.

Eq. (11) can be solved to calculate the fraction of POC being converted into methane carbon within the methanogenic zone:

$$f_M = 0.5 \left(1 - \exp \left( \frac{20K_C (\text{age}_0^{1/20} - (t + \text{age}_0)^{1/20})}{6.25(C_{CH_4} + C_{DIC} + K_C)} \right) \right)$$  \hspace{1cm} (12)$$

where $t$ is the residence time of sedimentary POC within the methanogenic zone while $\text{age}_0$ is the initial age of POC entering the methanogenic zone from above. The organic matter entering the methanogenic zone of typical margin sediments has initial ages of $10^4 - 10^6$ yr considering ambient sedimentation rates and sulfate exposure times. Methane formation is further inhibited by the accumulation of dissolved metabolites (DIC and CH$_4$) within ambient pore fluids. Assuming typical concentrations of $C_{DIC} = C_{CH_4} = 50$ mM and an inhibition constant of $K_C = 40$ mM, Eq. 12 can be applied to calculate the POC fraction being converted into methane within the sulfate-free methanogenic zone (Fig. 6).
**Figure 6.** Fraction of POC converted into methane carbon within the methanogenic zone of continental margin sediments ($f_{\text{ch}}$). The marked area indicates the range of POC residence times ($t = 3$–$30$ Myr) within the methanogenic zone at continental margins.

The residence time of sediments within the methanogenic zone is limited by the geothermal gradient since microbial methane formation cannot proceed at temperatures above $\sim$100°C. Assuming a geothermal gradient of $30$ – $40$°C/km, the deep biosphere may extend to a sediment depth of about 3 km. At continental margins with typical burial velocities of $10$ – $100$ cm kyr$^{-1}$, the residence time within the methanogenic zone may thus fall into a range of $t = 3$ – $30$ Myr. Fig. 6 and Eq. 12 show that about $10$ – $20$% of the POC entering the methanogenic zone is microbially converted into methane under these assumptions (for $age_0 = 10^5$ yr). Since $30$ – $90$% of POC buried below the bioturbated surface zone of continental margin sediments is reaching the methanogenic zone (Fig. 5), about $3$ – $18$% of the buried POC is converted into methane by the deep biosphere residing in underlying sulfate-depleted sediment layers.

Considering the arguments and equations presented above it is now possible to estimate the rate of microbial methane formation in continental margin sediments at global scale (Tab.1).
Table 1. Quaternary POC and methane balance for global continental margins

<table>
<thead>
<tr>
<th></th>
<th>Range</th>
<th>Best estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>POC burial at continental margins (10^11 g C yr⁻¹)</td>
<td>1.21 - 1.39</td>
<td>1.3</td>
</tr>
<tr>
<td>Fraction of buried POC reaching the methanogenic zone (%)</td>
<td>30 - 90</td>
<td>50</td>
</tr>
<tr>
<td>Fraction of buried POC microbially converted into methane (%)</td>
<td>3 - 18</td>
<td>8</td>
</tr>
<tr>
<td>Microbial methane production rate (10^12 g C yr⁻³)</td>
<td>4 - 25</td>
<td>10</td>
</tr>
</tbody>
</table>

This new estimate of microbial methane production in margin sediments (4 – 25 Tg C yr⁻¹, Tab. 1) is significantly lower than previous estimates of the global microbial methane production ranging from 60 Tg C yr⁻¹ Reeburgh et al., 1993 to 240 Tg C yr⁻¹ Hinrichs and Boetius, 2002. These previous estimates approach or even exceed the global rate of POC burial below the bioturbated zone. Our best estimate of ~10 Tg C yr⁻¹ would lead to an accumulation of up to 100 000 Gt CH₄·C over an accumulation period of 10 Myr if none of the methane would be lost by upward diffusion, AOM, fluid flow and gas ascent. However, field data clearly show that a large fraction of methane is lost by upward diffusion and fluid flow into the overlying sulfate-bearing zone where methane is consumed by microbial consortia using sulfate as terminal electron acceptor Boetius et al., 2000. The biogenic methane inventory is thus certainly much smaller than the time-integrated rate of biogenic methane formation derived above. Nevertheless, the number of 100 000 Gt C is a useful upper limit for biogenic methane accumulation. Interestingly, the global methane hydrate inventory estimated by Klauda and Sandler Klauda and Sandler, 2005 approaches this upper limit value.

The kinetic models of Middelburg and Wallmann can also be used to estimate the total POC degradation rate within the deep marine biosphere. The Middelburg model (Eq. 8) yields a rate of 1.2 x 10¹⁴ g yr⁻¹ applying a mean POC input flux of 1.4 x 10¹⁴ g yr⁻¹, an initial age of 10⁴ yr and a POC residence time in the deep biosphere of 10 Myr. It predicts that almost 90% of the buried POC would be consumed within the deep biosphere. Applying the same parameter values, an inhibition constant of 40 mM and mean methane and CO₂ concentrations of 50 mM, the Wallmann model (Eq. 11) predicts a POC consumption rate of 0.7 x 10¹⁴ g yr⁻¹ corresponding to ~50% of the burial flux. The remaining POC is further
decomposed below the deep biosphere via chemical processes yielding thermogenic gas, oil, kerogen and other products of high-temperature (>100°C) thermal maturation. It should, however, be noted that the numbers given above are very rough estimates since microbial organic matter degradation in the deep biosphere is a very complex and poorly understood process.

4. Thickness of the Gashydrate Stability Zone

Methane hydrates are only stable at low temperatures and high pressures. The stability field of structure type-I methane hydrate is well defined Sloan Jr., 1998. Pitzer equations can be used to constrain the effects of seawater salinity and porewater composition on methane hydrate stability Tishchenko et al., 2005. The stability field for sulfate-free seawater with a salinity of 35 PSU is shown in Fig. 7. The sharp phase boundary depicted in Fig. 7 is however not strictly valid for sediments and other porous media. Capillary forces acting on gas hydrates and free gas residing in sediment pores of different sizes create a broad transition zone where free gas and gas hydrate coexist Liu and Flemings, 2011. The thickness of this zone has been estimated as 20 – 28 m for Hydrate Ridge and Blake Ridge Liu and Flemings, 2011. The seismic bottom simulating reflector (BSR) indicating the top of the free gas occurrence zone is therefore often located at shallower depths than predicted by the bulk phase boundary. Moreover, the composition of the hydrate-forming natural gas has a strong effect on the positioning of the phase boundary. Biogenic gas formed by the microbial degradation of organic matter is composed of methane and CO₂ and contains only trace amounts of higher hydrocarbons (C₂+). CO₂ hydrates are usually not formed in marine sediments since their solubility clearly exceeds the CO₂ concentration in ambient pore fluids. Methane hydrates are less soluble and therefore the major product of biogenic gas formation in marine sediments. The hydrate-bound gas thus typically contains more than 99.9 % methane with only trace amounts of CO₂ and C₂+, Milkov, 2005. The low abundance of higher hydrocarbons in biogenic gas supports the formation of structure type I methane hydrate. However, thermogenic gas ascending from larger sediment depths contains significant amounts of C₂+, favoring the formation of structure type II and/or the
inclusion of C_{2r}-components in structure type I methane hydrate. These hydrates are stable over a significantly broader P-T range and thus induce a down-core displacement of the phase boundary Sloan Jr., 1998.

Figure 7. Phase diagram for methane hydrate (structure type I) for sulfate-free seawater with a salinity of 35 Tishchenko et al., 2005. Arrows indicate the formation of a transition zone by capillary forces and the broadening of the gas hydrate stability zone by higher hydrocarbon compounds (C_{nr}).

The thickness of the gas hydrate stability zone (GHSZ) in marine sediments is usually estimated considering the temperature (T) and pressure (P) conditions at the seabed and the increase in T and P with sediment depth. High-resolution data sets are available to define temperatures and pressures at the seafloor on global scale Burwicz et al., 2011b while the conductive heat flux has been measured at more than 9000 sites Hamza et al., 2008b. Most of these heat flow data have been generated by measuring the temperature gradient within the upper few meters of the sediment column. The conductive heat flux (q_{H}) is then calculated from the temperature gradient considering the ambient thermal conductivity of bulk sediments (\lambda_{B}):

\[ q_{H} = \lambda_{B} \cdot \frac{\partial T}{\partial z} \]  

(13)

Heat flow data rather than temperature gradients (dT/dz) have been compiled at global scale Hamza et al., 2008b. Geothermal gradients defining the thickness of the gas hydrate stability zone, thus, need to be derived from the heat flux data applying appropriate
estimates for ambient thermal conductivity. Thermal conductivities of bulk sediments quantify the efficiency of heat transport which involves transport (1) from grain to grain, (2) from grain to liquid to grain, and (3) through pore-filling liquid Waite et al., 2009. Rather than calculate the contribution of each heat transport path explicitly, thermal conductivity is often estimated using a two-phase mixing model to combine the thermal conductivities of the sediment grains with the pore fluid. The thermal conductivities of methane hydrate and water differ by <10% at the temperatures found in hydrate-bearing sediments Waite et al., 2009. For this reason, first-order thermal conductivity estimates can neglect the presence of methane hydrate and assume that the sediment pore space contains only water Grevemeyer and Villinger, 2001. The following two-phase mixing model provides a reasonable approximation for thermal conductivity in the uppermost 500 – 1000 m of the sediment column Grevemeyer and Villinger, 2001:

$$\lambda_B = \lambda_w \Phi \cdot \lambda_s^{(1-\Phi)}$$

(14)

where $\lambda_B$, $\lambda_w$, and $\lambda_s$ are thermal conductivities of bulk sediment, seawater and solids, respectively. The thermal conductivity of seawater increases with pressure and temperature Castelli et al., 1974. It varies from 0.56 to 0.60 W m$^{-1}$ K$^{-1}$ over the P-T range encountered within the GHSZ Castelli et al., 1974. A mean value of $\lambda_w$ = 0.58 W m$^{-1}$ K$^{-1}$ is thus representative for the marine hydrate stability zone. Quartz has a conductivity of 7.7 – 8.4 W m$^{-1}$ K$^{-1}$ Waite et al., 2009 while calcite has an average conductivity of 3.6 W m$^{-1}$ K$^{-1}$ Brigaud and Vasseur, 1989. Thermal conductivities of clay minerals vary from 5.2 W m$^{-1}$ K$^{-1}$ for chlorite to 1.8 – 2.7 W m$^{-1}$ K$^{-1}$ for smectite, illite and kaolinite Brigaud and Vasseur, 1989. Data measured in ODP cores retrieved at various continental margin sites indicate a mean value of $\lambda_s$ = 2.5 W m$^{-1}$ K$^{-1}$ for the dry solids in fine-grained margin sediments Grevemeyer and Villinger, 2001. The average porosity within the upper few meter of the sediment column is typically close to 0.75 Grevemeyer and Villinger, 2001. Applying Eq. 14, the thermal conductivity of clay-rich surface sediments results as $\lambda_B = 0.836$ W m$^{-1}$ K$^{-1}$ for $\lambda_w = 0.58$ W m$^{-1}$ K$^{-1}$ and $\lambda_s = 2.5$ W m$^{-1}$ K$^{-1}$. The geothermal gradient in surface
Appendix I

sediments is thus derived by dividing the ambient heat flux data by $\lambda_b = 0.836$ W m$^{-1}$ K$^{-1}$ (Eq. 13).

Thermal conductivity changes, however, with sediment depth due to the compaction of sediments inducing a down-core decrease in porosity. Porosity change is often described by the following equation Berner, 1980:

$$\Phi = \Phi_f + (\Phi_0 - \Phi_f) \cdot e^{-pz}$$  \hspace{1cm} (15)

where $\Phi_0$ is the porosity at the sediment surface, $\Phi_f$ the porosity at the base of the sediment column and $p$ is an attenuation coefficient. The mean porosity profile observed in ODP cores can be approximated applying $\Phi_0 = 0.74$, $\Phi_f = 0.3$ and $p = 1/600$ m$^{-1}$ Einsele, 2000.

The steady-state temperature profile in marine sediments is usually controlled by heat conduction. Neglecting heat production and convection, it can be described by the following differential equation Cussler, 1984:

$$\frac{\partial}{\partial z} \left( \lambda_B \cdot \frac{\partial T}{\partial z} \right) = 0$$  \hspace{1cm} (16)

This equation can be solved applying the following boundary conditions at the top of the sediment column at $z = 0$:

$$\frac{\partial T}{\partial z} = T_{Grad} = \frac{q_H}{\lambda_B} \quad T = T_{BW}$$  \hspace{1cm} (17)

where $T_{Grad}$ is the temperature gradient recorded in surface sediments, $q_H$ is the heat flow calculated from the gradient and the thermal conductivity of surface sediments while $T_{BW}$ is the temperature of ambient bottom water. The solution of this equation for constant $\lambda_B$ results as:

$$T = T_{BW} + T_{Grad}$$  \hspace{1cm} (18)
The equation can also be solved for variable \( \lambda_b \) considering the down-core changes in porosity and \( \lambda_b \) defined in Eq. 14 and 15. The resulting temperature profile is depicted in Fig. 8 for typical continental margin sediments (solid black line in the right panel). It shows a clearly non-linear shape since the down-core decrease in porosity induces a significant \( \lambda_b \) increase with depth (left panel in Fig. 8). The linear profile calculated from the \( \lambda_b \) value in surface sediments (\( \lambda_b = 0.836 \) W m\(^{-1}\) K\(^{-1}\), red dotted line in the left panel, Eq. 16) overestimates sediment temperatures at depth and thus underestimates the thickness of the GHSZ by almost 150 m (Fig. 8). It is thus important to consider the non-linear nature of sedimentary temperature profiles. The temperature profile and GHSZ thickness can, however, be approximated applying a constant \( \lambda_b \) of 1 W m\(^{-1}\) K\(^{-1}\) (blue dotted-broken line in right panel of Fig. 8). This mean value is thus often applied to estimate the vertical extent of the GHSZ in marine sediments Grevenmeyer and Villinger, 2001.

**Figure 8.** Down-core change in porosity (\( \Phi \), Eq. 15), thermal conductivity of bulk sediment (\( \lambda_b \), Eq. 14) and temperature (\( T \), Eq. 16) in typical continental margin sediments (\( \Phi_b = 0.74, \Phi_k = 0.3 \) and \( p = 1/600 \) m\(^3\), \( q_b = 0.03 \) W m\(^{-2}\), \( \lambda_w = 0.58 \) W m\(^{-1}\) K\(^{-1}\), \( \lambda_s = 2.5 \) W m\(^{-1}\) K\(^{-1}\)). The phase boundary for methane hydrate (structure type I) shown in the right panel (black broken line) is calculated for sediments deposited at 2000 m water depth, hydrostatic pressure conditions and sulfate-free sediment porewater with a salinity of 35 Tishchenko et al., 2005.

Global maps of the GHSZ thickness were produced by Burwicz et al. (2011b) and Pinero et al. Piñero et al., submitted assuming constant temperature gradients and applying the same global data sets for water depth, bottom water temperature, heat flow
and sediment thickness. The base of the GHSZ is defined by the intersection of the sedimentary temperature profile and the phase boundary for sulfate-free pore water (Fig. 8). Pinero et al. Piñero et al., submitted assumed a constant thermal conductivity of $\lambda_B = 1.0 \text{ W m}^{-1} \text{ K}^{-1}$ over the entire ocean. The map produced under this assumption gives a good approximation for the GHSZ thickness in fine-grained continental margin sediments (Fig. 9). The vertical extend of the GHSZ is, however, underestimated where sediments are dominated by sand, chlorite and calcite since sedimentary bulk conductivity is strongly enhanced by these components Brigaud and Vasseur, 1989. Moreover, the map is based on a thermodynamic model valid for pure methane hydrate of structure type I Tishchenko et al., 2005. It may thus underestimate the vertical extent of the GHSZ where methane hydrate is stabilized by C$_2$ components entrained into the GHSZ by the ascent of thermogenic gas (Fig. 7). Burwicz et al. Burwicz et al., 2011b applied a constant $\lambda_B$ value of $1.5 \text{ W m}^{-1} \text{ K}^{-1}$ which over-predicts the GHSZ thickness in margin sediments composed of smectite, illite and kaolinite but may give a better approximation for pelagic sediments. Both maps show an extended and deep-reaching GHSZ at high latitudes and around passive continental margins whereas a thin GHSZ is derived for the open ocean where the thickness of the GHSZ is limited by the thin sedimentary cover.

**Figure 9.** Thickness of the gas hydrate stability zone calculated from global heat flux data Hamza et al., 2008b considering bathymetry, bottom water temperature, sediment thickness data and a bulk thermal conductivity of $1.0 \text{ W m}^{-1} \text{ K}^{-1}$ Piñero et al., submitted.
The global volume of the GHSZ is estimated to be $67 \times 10^{15}$ m$^3$ integrating the data shown in Fig. 9. This value should be considered as a minimum estimate since the thickness of the GHSZ may be underestimated in those areas where solid phases with high thermal conductivity and C$_{2+}$-bearing gas hydrates are deposited. The pore space available for gas hydrate accumulation amounts to $44 \times 10^{15}$ m$^3$ considering the decay of porosity over the sediment column (Fig. 8, Eq. 15). Up to $4 \times 10^{21}$ g CH$_4$-C could reside in the GHSZ if the entire pore space ($44 \times 10^{15}$ m$^3$) would be filled by methane hydrate. This maximum estimate clearly exceeds the total methane pool generated via microbial POC degradation over a period of 10 Myr ($1.0 \times 10^{20}$ g CH$_4$-C, see section 3). Thus, only 2.5 % of the global GHSZ pore space could be occupied by gas hydrates if the entire biogenic methane pool would be fixed as gas hydrate.

5. Solubility of Methane in Sedimentary Pore Fluids

Methane produced by the microbial degradation of organic matter is dissolved in ambient pore fluids. The solubility of methane in water is however limited by the low polarity and hydrophobic nature of methane molecules. Excess methane formed by pervasive methane production thus precipitates as gas hydrate or forms a free gas phase pending on the local P-T conditions. Methane hydrate precipitates when the methane concentration in the pore fluids exceeds the solubility of methane hydrate. The equilibrium concentration with respect to methane hydrate is restored by hydrate precipitation extracting excess methane from solution. The solubility of methane hydrate has been measured experimentally and calculated using various thermodynamic approaches Waite et al., 2009. It increases with temperature and decreases with pressure and salinity whereas the solubility of methane gas in water is enhanced under high pressure and reduced by an increase in temperature and salinity. The down-core rise in sediment temperature thus promotes an increase in dissolved methane concentrations within the GHSZ and a decrease in dissolved methane in the underlying free gas zone (Fig. 10).
Appendix 1

Figure 10. Solubility of methane in marine sediments deposited at 2000 m water depth. Solubility is calculated for methane hydrate (blue circles) and methane gas (red crosses) in sulfate-free seawater with $S = 35$ assuming hydrostatic conditions, a bottom water temperature of $2^\circ$C and a linear geothermal gradient of 0.03$^\circ$C m$^{-1}$ Duan et al., 1992a; Tishchenko et al., 2005. The black line indicates the dissolved methane concentration attained in methane-saturated pore fluids (in mmol per kg solution). The base of the gas hydrate stability zone (GHSZ) is located at the intersection of the gas hydrate and free gas solubility curves.

Capillary forces affect the stability and solubility of gas hydrate and gas in fine-grained marine sediments. A transition zone is formed where the solubility ranges of gas bubbles and hydrate crystals residing in sediment pores of different sizes overlap Liu and Flemings, 2011. The discontinuity at the base of the GHSZ (Fig. 10) is thus replaced by a smooth and continuous transition in methane solubility Liu and Flemings, 2011; Waite et al., 2009.

6. SEDIMENT COMPACTION, FLUID FLOW AND GAS ASCENT

Gas hydrates are formed from methane being produced within the GHSZ (section 3) and by methane ascending into the GHSZ from below. Upward flow of methane is induced by numerous processes including sediment compaction, tectonic over-pressuring and the buoyancy of methane gas and methane charged fluids. Sediment compaction is driven by the overburden load of younger sediments being continuously deposited at the seabed Einsele, 2000. In most marine settings, it induces an exponential decrease in porosity ($\Phi$) and water content with sediment depth (Fig. 8). Therefore, exponential equations such as Eq. 15 are used to describe the compaction-driven down-core decrease in porosity.
Applying Eq. 1 and Eq. 15, the burial velocity of pore water \( (v_B) \) and solids \( (w_B) \) are calculated as Berner, 1980:

\[
  v_B = \frac{\Phi_f \cdot w_f}{\Phi}, \quad w_B = \frac{(1 - \Phi_f) \cdot w_f}{(1 - \Phi)}
\]  \hspace{1cm} (19)

The equations above are valid for steady state conditions, i.e. for homogenous deposits formed by continuous sedimentation. The porosity of marine sediments deposited on oceanic crust is usually not completely eliminated by compaction. The residual porosity at the base of the sediment column (i.e. the crust-sediment interface) is given by \( \Phi_f \) while \( w_i \) is the burial velocity of water and solids which is attained after the porosity has been reduced to \( \Phi_f \) via steady-state compaction. Compaction promotes the burial of solids while pore water burial is diminished since water is expelled and transported upwards due to the down-core reduction in pore space (Fig. 11). However, steady-state compaction does not induce a flow of water into the overlying water column: The pore fluids do not escape into the bottom water since the pore water burial velocity induced by the continuous deposition of young sediments at the seabed exceeds the velocity of the compaction-driven upward fluid flow.

Seepage of pore fluids is frequently observed at continental margins where sediments are compressed by tectonic forces Judd, 2003 since marine sediments subducted below continental crust and accreted at active continental margins are over-pressured and dewatered to such an extent that pore fluids escape into the bottom water Hensen et al., 2004; Ranero et al., 2008; Suess et al., 1998; Wallmann et al., 1997a. Salt diapirism, sediment erosion and slope failure induce additional fluid seepage at passive and active continental margins. Upward fluid flow is ultimately driven by excess pressures as described by the Darcy equation Bear, 1972:

\[
  u = -\frac{k}{\mu_w} \left( \frac{\partial P}{\partial z} - \rho_w \cdot g \right)
\]  \hspace{1cm} (20)
where the Darcy flow $u$ (m$^3$ m$^{-2}$ yr$^{-1}$) is the volume of water (m$^3$) being transported through a cross-sectional sediment area (m$^2$) over a period of time (yr). Upward fluid flow occurs when the sedimentary pressure gradient ($\partial P/\partial z$ in Pa m$^{-1}$) exceeds the hydrostatic pressure gradient defined as product of water density ($\rho_w$ in kg m$^{-3}$) and gravitational acceleration ($g = 9.81$ Pa m$^{-2}$ kg$^{-1}$). The velocity of fluid flow is modulated by the intrinsic permeability of bulk sediments (k in m$^2$) and the viscosity of water ($\mu_w \approx 10^3$ Pa s). The intrinsic permeability of marine sediment varies over several orders of magnitude. It increases with porosity and grain size: Terrigenous marine sediments containing fine-grained clay have typical permeability values of $10^{-18}$ – $10^{-14}$ m$^2$ while clean sands have values of $10^{-12}$ – $10^{-10}$ m$^2$ Bear, 1972.

**Figure 11.** Burial velocity of pore fluids ($v_p$) and solids ($w_p$) in marine sediments subject to steady-state compaction. Velocities are calculated applying Eq. (19) with $\Phi_0 = 0.74$, $\Phi_i = 0.3$, $p = 1/600$ m$^2$, and $w_i = 50$ cm kyr$^{-1}$.

The sedimentary pressure gradient is enhanced in compressive tectonic settings and may approach the lithostatic pressure gradient defined as the product of $g$ and the bulk density of sediments. The bulk density of sediments $\rho_B$ is calculated as:

$$\rho_B = \rho_w \cdot \Phi + \rho_s \cdot (1 - \Phi)$$

(21)

The Darcy flow at lithostatic pressure $u_l$ is thus calculated as:
\[ u_L = -\frac{k}{\mu_w} \cdot (\rho_R \cdot g - \rho_w \cdot g) = -\frac{k \cdot g}{\mu_w} \cdot (\rho_w \cdot (\Phi - 1) + \rho_s \cdot (1 - \Phi)) \] (22)

The inter-granular fluid flow velocity \( v \) is related to the Darcy flow velocity \( u \) as:

\[ v = \frac{u}{\Phi} \] (23)

Both velocities, \( u \) and \( v \), attain a positive sign for a downward movement with respect to the sediment-water interface while a negative sign indicates the ascent of pore fluids towards the sediment surface. Fluids ascending through a constantly growing homogenous sediment deposit subject to steady-state compaction have an inter-granular fluid flow velocity of:

\[ v_N = v + v_b = \frac{u + \Phi \cdot f \cdot w_f}{\Phi} \] (24)

Fluids are thus expelled across the sediment-water interface into the overlying water column when the velocity of fluids infiltrating the sediment column from below \( (v) \) exceeds the burial velocity of pore fluids \( (v_b) \). Upward fluid flow velocities \( (v) \) have been measured at various cold seep sites and mud volcanoes located at active and passive continental margins Hensen et al., 2004; Linke et al., 2005; Luff and Wallmann, 2003; Tryon et al., 2002; Tryon et al., 1999; Wallmann et al., 2006b; Wallmann et al., 1997a; Wallmann et al., 1997b. They typically range from 0.1 to 100 cm yr\(^{-1}\). These flow velocities are consistent with \( u \) values predicted for over-pressured clay-bearing sediments deposited at continental margins (Fig. 12).
Figure 12. Velocity of Darcy fluid flow at lithostatic pressure \( (u_d) \) in marine sediments as function of intrinsic permeability. Darcy flow is calculated applying density values of \( p_w = 1036 \) kg m\(^{-3} \) and \( p_s = 2500 \) kg m\(^{-3} \) and a porosity of \( \Phi = 0.5 \).

Gaseous methane occurs below the GHSZ and in the transition zone at the base of the GHSZ. The bottom simulating reflector (BSR) observed in many seismic surveys marks the boundary between hydrate-bearing sediments and the underlying gas-bearing sediment zone. The density of methane gas is lower than the density of pore fluids. Therefore buoyancy forces may induce an upward flow of gas into the GHSZ. For sediments containing both gas and water, Darcy’s law is formulated as Bear, 1972:

\[
\begin{align*}
    u_w &= -\frac{k \cdot k_{RW}}{\mu_w} \left( \frac{\partial p_w}{\partial z} - \rho_w g \right) \\
    u_G &= -\frac{k \cdot k_{RG}}{\mu_G} \left( \frac{\partial p_G}{\partial z} - \rho_G g \right)
\end{align*}
\]

(25)

where the subscripts W and G indicate water and gas, respectively. Relative permeability appears as additional non-dimensional parameter in the equations above (\( k_{RW} \) and \( k_{RG} \)). Various equations have been proposed to quantify the relative permeability of water and gas in marine sediments at different saturation values Bear, 1972; Waite et al., 2009. One of the more commonly used forms is given by Parker et al., 1987:

\[
\begin{align*}
    k_{RW} &= S_{WN}^{1/2} \cdot \left( 1 - \left( 1 - S_{WN}^{1/m} \right)^m \right)^2 \\
    k_{RG} &= \left( 1 - S_{WN} \right)^{1/2} \cdot \left( 1 - S_{WN}^{1/m} \right)^m
\end{align*}
\]

(26)

where \( m \) is the pore-size-distribution index. The normalized water saturation \( S_{WN} \) is defined as:
\[ S_{WN} = \text{Min} \left[ \frac{S_W - S_{WC}}{1 - S_{WC} - S_{GC}}, 1 \right] \] (27)

where \( S_W \) is the water saturation, i.e. fraction of pore space occupied by water \( (S_W = 1 - S_c) \). The irreducible water saturation has a typical value of \( S_{WC} = 0.3 \) while the corresponding gas saturation falls into the range of \( S_{GC} = 0.01 - 0.1 \) Garg et al., 2008. The irreducible gas saturation is the most critical parameter for the prediction of upward gas migration in marine sediments since gas migration occurs only when the gas saturation \( S_G \) exceeds \( S_{GC} \).

A high \( S_{GC} \) value of 0.1 indicates that gas migration is inhibited if less than 10% of the pore space is occupied by gas \( (S_G < 0.1, S_{WN} = 1, k_{RG} = 0, q_G = 0, \text{s. Eqs. 25 - 27}) \). This would imply that gas migration across the BSR is effectively suppressed since the methane gas produced by microbial POC degradation below the GHSZ rarely builds up to saturations of \( S_G > 0.1 \). The BSR is produced by the strong seismic contrast between gas below the GHSZ and gas hydrate within the GHSZ. Seismic surveys show a wide-spread occurrence of the BSR indicating that a significant fraction of methane gas is not mobile but retained and buried in sediments underlying the GHSZ. However, seismic chimneys indicating the ascent of free gas are also frequently observed at continental margins and are often associated with high gas hydrate saturations in the overlying GHSZ. It thus seems that the free gas is usually immobile but locally mobilized and transported into the GHSZ. The controls on gas migration into the GHSZ are poorly understood and this lack of physical understanding causes a large degree of uncertainty in the prediction of gas hydrate accumulation in marine sediments.

The gas pressure \( P_G \) is related to the water pressure \( P_W \) as Bear, 1972:

\[ P_G = P_W + P_c \] (28)

where \( P_c \) is the capillary pressure. \( P_c \) may be calculated as Doughty, 2007:

\[ P_c = \frac{P_{cc}}{S_{WN} \left( -\frac{np_c}{np_c-1} \right) - 1} \] (29)
Appendix 1

where $P_{CC}$ has a value of 13300 Pa in low permeability sediments while npc takes a value of 1.7 Doughty, 2007.

Darcy gas flow at constant gas saturation ($\partial P_c/\partial z = 0$) and hydrostatic pressure ($\partial P_w/\partial z = \partial P_w/\partial z = g \cdot \rho_w$) can be calculated as function of gas saturation ($S_G$) and intrinsic permeability to quantify the buoyancy driven gas ascent into the GHSZ:

$$u_{G-H} = -\frac{k \cdot k_{BG} \cdot g}{\mu_G} \cdot (\rho_G - \rho_w)$$

(30)

Figure 13 shows this buoyancy driven flux for typical continental margin sediments deposited at 2000 m water depth. Applying a geothermal gradient of 30°C/km, the temperature at the base of the GHSZ is 19.1°C while the hydrostatic pressure at the phase boundary amounts to 257 bar (Fig. 8). The densities of methane gas and water are $\rho_G = 198$ kg m$^3$ Duan et al., 1992b and $\rho_w = 1036$ kg m$^3$ Chester, 2000 under these P-T conditions while the dynamic viscosity of methane gas amounts to $\mu_G = 11 \times 10^6$ Pa s Friend et al., 1989. The gas flow is completely inhibited at $S_G < S_{GC}$ and increases rapidly with increasing $S_G$ at $S_G > S_{GC}$. Buoyancy forces would thus induce a rapid ascent of gas into the GHSZ if the gas saturation exceeds the critical value. Under these conditions the methane hydrates buried and dissociated below the GHSZ would not be lost from the system but would be constantly recycled into the GHSZ via upward gas migration. The methane hydrate inventory would expand over time until the pore space available for gas migration is clocked by methane hydrate. Very high methane hydrate saturations could be attained by this recycling mechanism.

It is important to note that gas ascent is a much more efficient mechanism for the transport of methane into the GHSZ than fluid flow. For the conditions shown in Fig. 13, an upward Darcy gas flow of 1 cm yr$^{-1}$ introduces a methane flux of 1980 g m$^{-2}$ yr$^{-1}$ (for $\rho_G = 198$ kg m$^{-3}$) while a corresponding water flow of 1 cm yr$^{-1}$ induces a methane flux of only 24 g m$^{-2}$ yr$^{-1}$ at a dissolved methane concentration of 150 mM (Fig. 10).
The POC accumulation rates that are fueling methane production at depth rarely exceed 10 g m\(^{-2}\) yr\(^{-1}\) (Fig. 3). The entire methane pool potentially formed by the microbial and thermal decomposition of buried POC would thus be transported into the GHSZ at gas and water flow velocities as low as \(u_g \approx 0.002 \text{ cm yr}^{-1}\) and \(u_w \approx 0.2 \text{ cm yr}^{-1}\).

A better understand of the physical controls on gas and water ascent into the GHSZ is thus a high priory requirement for the prediction of gas hydrate accumulation at local and global scale.

**Figure 13.** Relative permeability of gas (\(k_{RG}\) upper panel, Eq. 26) and buoyancy-driven gas flow (\(u_{g_{BP}}\) lower panel, Eq. 30) in fine-grained marine sediments as function of gas saturation (\(S_g = 1 - S_w\)). \(k_{RG}\) is calculated applying Eq. 26 and 27 with \(S_{WC} = 0.3\), \(S_{GC} = 0.01\) and \(m = 0.75\). The gas flux is calculated for hydrostatic pressure conditions applying Eq. 30 with \(\rho_w = 1036 \text{ kg m}^{-3}\), \(\rho_G = 198 \text{ kg m}^{-3}\), \(k = 10^{-15} \text{ m}^{2}\), \(\mu_g = 11 \times 10^{-6} \text{ Pa s}\) and the relative gas permeability depicted in the upper panel.

### 7. Controls on Gas Hydrate Accumulation in Marine Sediments

In the following section we will present a series of model runs obtained with the transport-reaction model introduced by Wallmann et al. Wallmann et al., 2006a to investigate the controls on gas hydrate accumulation. We will start this analysis by presenting the results
of a reference simulation. The sensitivity tests presented in the following sections are based on this reference case.

7.1. Reference case

The reference case presents a continental margin site at about 2000 m water depth with moderately high concentrations of POC and very high sedimentation rates. Porosity and temperature profiles applied in the standard case are shown in Fig. 8, the corresponding methane solubility values are depicted in Fig. 10 while the burial velocities of solids and pore fluids are shown in Fig. 11. Parameter values used in this reference model run are listed in Tab. 2.

Table 2. Parameter values and upper boundary conditions applied in the reference case

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Depth-independent parameter values</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density of pore water</td>
<td>( \rho_w )</td>
<td>1036 kg m(^{-3})</td>
</tr>
<tr>
<td>Density of dry sediments</td>
<td>( \rho_s )</td>
<td>2500 kg m(^{-3})</td>
</tr>
<tr>
<td>Density of methane hydrate</td>
<td>( \rho_{\text{GH}} )</td>
<td>912 kg m(^{-3})</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>( \lambda_B )</td>
<td>1.0 W m(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>Heat flow</td>
<td>( q_{\text{hi}} )</td>
<td>0.03 W m(^{-2})</td>
</tr>
<tr>
<td>Pressure gradient (hydrostatic)</td>
<td>( \partial P / \partial z )</td>
<td>0.1016 bar m(^{-1})</td>
</tr>
<tr>
<td>Length of the model column</td>
<td>( L )</td>
<td>590 m</td>
</tr>
<tr>
<td>Thickness of the GHSZ</td>
<td>( L_{\text{GHSZ}} )</td>
<td>567 m</td>
</tr>
<tr>
<td>Simulation time</td>
<td>( t )</td>
<td>( \geq 5 ) Ma</td>
</tr>
<tr>
<td>Inhibition constant for POC degradation</td>
<td>( K_C )</td>
<td>40 mM</td>
</tr>
<tr>
<td>Initial age of POC</td>
<td>( \text{age}_0 )</td>
<td>10,000 yr</td>
</tr>
<tr>
<td>Kinetic constant for AOM</td>
<td>( k_{\text{AOM}} )</td>
<td>10 dm(^{3}) mol(^{-1}) yr(^{-1})</td>
</tr>
<tr>
<td>Kinetic constant for gas hydrate precipitation</td>
<td>( k_{\text{GHIP}} )</td>
<td>( 10^{-3} ) wt-% yr(^{-1})</td>
</tr>
<tr>
<td>Kinetic constant for gas hydrate dissolution</td>
<td>( k_{\text{GHD}} )</td>
<td>( 10^{-4} ) yr(^{-1})</td>
</tr>
<tr>
<td>Porosity at the sediment surface</td>
<td>( \Phi_0 )</td>
<td>0.74</td>
</tr>
<tr>
<td>Porosity after compaction</td>
<td>( \Phi_s )</td>
<td>0.3</td>
</tr>
<tr>
<td>Attenuation coefficient for porosity decrease</td>
<td>( \rho )</td>
<td>( 1/600 ) m(^{-1})</td>
</tr>
<tr>
<td>Burial velocity at the sediment surface</td>
<td>( v_w )</td>
<td>( 134.6 ) cm yr(^{-1})</td>
</tr>
<tr>
<td>Burial velocity after compaction</td>
<td>( v_l )</td>
<td>( 0.05 ) cm yr(^{-1})</td>
</tr>
<tr>
<td>Mass accumulation rate</td>
<td>( \text{MAR} )</td>
<td>875 g m(^{2}) yr(^{-1})</td>
</tr>
</tbody>
</table>

**Conditions at the upper boundary**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>( P_0 )</td>
<td>200 bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>( T_0 )</td>
<td>2(^\circ)C</td>
</tr>
<tr>
<td>Dissolved sulfate concentration</td>
<td>( C_s(0) )</td>
<td>28.9 mM</td>
</tr>
<tr>
<td>Dissolved methane concentration</td>
<td>( C_A(0) )</td>
<td>( 10^{6} ) mM</td>
</tr>
<tr>
<td>Dissolved inorganic carbon concentration</td>
<td>( C_I(0) )</td>
<td>2.3 mM</td>
</tr>
<tr>
<td>POC concentration</td>
<td>( C_{\text{POC}}(0) )</td>
<td>1 wt-%</td>
</tr>
<tr>
<td>Gas hydrate concentration</td>
<td>( C_{\text{GH}}(0) )</td>
<td>0 wt-%</td>
</tr>
</tbody>
</table>
The model simulates the reactive transport of 3 dissolved species (DIC, sulfate, methane) and two solid species (POC and methane hydrate). Molecular diffusion, burial and compaction are considered as transport processes. The simulated reactions include POC degradation via sulfate reduction, AOM, methanogenesis, gas hydrate formation and gas hydrate dissolution. Fixed concentration values are applied at the upper boundary (Tab. 2) while zero gradients are used as lower boundary conditions for all dissolved species. The model domain excludes the upper bioturbated zone of the sediment column and includes the transition zone at the base of GHSZ where the saturation concentration of dissolved methane is assumed to be constant over a depth interval of 23 m (see section 4) Liu and Flemings, 2011. All model results shown in the following figures and tables are valid for steady state conditions which were reached after a simulation time of ~3 Ma. The reference model does not consider gas and fluid ascent into the GHSZ from below.

The dissolved inorganic carbon concentrations calculated in the reference run show a continuous increase with sediment depth reflecting the microbial degradation of POC (Fig. 14). Dissolved methane production starts at ~8 m sediment depth after sulfate is almost completely consumed by organic matter degradation and AOM (Fig. 15). Dissolved methane increases down-core and reaches the saturation value with respect to methane hydrate at a sediment depth of ~86 m. At this point gas hydrate starts to form in the sediment column (Fig. 14). Methane hydrate formation continues since the microbial production of methane within the GHSZ over-compensates the down-core increase in methane hydrate solubility. Close to the base of the GHSZ at ~545 m sediment depth, methane hydrate dissolves since the saturation level is no longer maintained by the sluggish methane production from aging POC. The saturation level is restored by methane hydrate dissolution in the deeper portion of the GHSZ (545 – 567 m) and by a combination of dissolution and dissociation in the underlying transition zone (567 – 590 m). Methane hydrate buried below the model domain to sediment depths >590 m dissociates to form dissolved and gaseous methane.
Figure 14. Concentrations of dissolved inorganic carbon (DIC), dissolved methane (CH₄), particulate organic carbon (POC) and methane hydrate saturation (GH-Sat.) in the reference model run. The dotted line in the upper right panel indicated the concentration of methane in equilibrium with methane hydrate.

Figure 15. Concentrations of dissolved sulfate (solid line) and dissolved methane (dotted line) in surface sediments calculated in the reference model run. The shaded bar indicates the sediment layer where methane is oxidized by microbial consortia using sulfate as terminal electron acceptor (AOM zone). The AOM zone is equivalent to the sulfate-methane transition zone (SMTZ).

The modeling shows that only ~22 % of the POC being deposited below the bioturbated zone (729 mmol m⁻² yr⁻¹, Tab. 3) is degraded within the GHSZ. The remaining portion is buried to larger sediment depths. Sulfate reduction contributes ~26 % to the total POC degradation while most of the POC degradation (~74 %) occurs within the methanogenic zone of the GHSZ. Sulfate diffusing into the sediment from above (52.8 mmol m⁻² yr⁻¹) is
consumed via AOM (~60 %) and POC degradation (~40 %). The slight curvature of the sulfate pore water profile (Fig. 15) is induced by sulfate reduction via POC degradation occurring within the top ~8 m of the sediment column. Methane produced via POC degradation within the GHSZ (60.4 mmol m⁻² yr⁻¹) is consumed by AOM (~52 %) and buried below the GHSZ (39 %). Only a small portion (~9 %) is permanently fixed in gas hydrates (5.5 mmol m⁻² yr⁻¹, Tab. 3). The resulting gas hydrate saturations are very low. The maximum saturation of 0.35 vol-% is reached at ~470 m sediment depth. At this depth 99.65 % of the pore space is filled by water while only 0.35 % is occupied by methane hydrate. The depth-integrated inventory of carbon bound in methane hydrate amounts to 62 kg m⁻². Most of the carbon resides in the sedimentary organic carbon pool and in the pore water as dissolved methane and DIC (Tab. 3).

In the following sections (7.2 – 7.6) selected parameter values of the reference simulation are varied to explore the controls on gas hydrate accumulation in marine sediments.

**Table 3.** Fluxes at the upper boundary of the model column, depth-integrated rates and carbon inventories calculated in the reference simulation

<table>
<thead>
<tr>
<th>Flux/Rate</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluxes at the upper boundary</strong></td>
<td>in mmol m⁻² yr⁻¹</td>
</tr>
<tr>
<td>POC deposition</td>
<td>729</td>
</tr>
<tr>
<td>DIC release into bottom water</td>
<td>99.6</td>
</tr>
<tr>
<td>CH₄ release into bottom water</td>
<td>0.0</td>
</tr>
<tr>
<td>SO₄ flux into sediment</td>
<td>52.8</td>
</tr>
<tr>
<td><strong>Depth-integrated rates</strong></td>
<td>in mmol m⁻² yr⁻¹</td>
</tr>
<tr>
<td>Total POC degradation</td>
<td>163.1</td>
</tr>
<tr>
<td>POC degradation via sulfate reduction</td>
<td>42.3</td>
</tr>
<tr>
<td>POC degradation via methanogenesis</td>
<td>120.8</td>
</tr>
<tr>
<td>Sulfate reduction via POC degradation</td>
<td>21.2</td>
</tr>
<tr>
<td>Methane production via POC degradation</td>
<td>60.4</td>
</tr>
<tr>
<td>Methane and sulfate consumed by AOM</td>
<td>31.6</td>
</tr>
<tr>
<td>Gas hydrate formation</td>
<td>7.7</td>
</tr>
<tr>
<td>Gas hydrate dissolution</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Depth-integrated carbon inventories</strong></td>
<td>in kg m⁻²</td>
</tr>
<tr>
<td>C in DIC</td>
<td>734</td>
</tr>
<tr>
<td>C in dissolved methane</td>
<td>379</td>
</tr>
<tr>
<td>C in POC</td>
<td>5000</td>
</tr>
<tr>
<td>C in methane hydrate</td>
<td>62</td>
</tr>
</tbody>
</table>
7.2. Effects of POC Concentration, Burial Velocity and GHSZ Thickness on Gas Hydrate Accumulation

Model runs were executed to study the sensitivity of gas hydrate accumulation to the POC concentration and the burial velocity at the upper boundary of the model (Fig. 16). Methane hydrate accumulation within the GHSZ is enhanced under high POC since more substrate is available for microbial methane production (left panel in Fig. 16). The relationship between gas hydrate accumulation and burial velocity \(w_0\) is more complicated. At \(w_0\) values of 10 – 150 cm kyr\(^{-1}\), gas hydrate accumulation increases with \(w_0\) since the supply of POC into the methanogenic zone is promoted by increasing \(w_0\) values. Moreover, POC reactivity is enhanced due to the decrease in burial age. However, a further increase in burial velocity does not induce an expansion of the gas hydrate inventory (Fig. 16). A decline in the gas hydrate inventory is observed at extremely high burial velocities (\(>150\) cm kyr\(^{-1}\) for 2 wt-% POC; \(>250\) cm kyr\(^{-1}\) for 1 wt-% POC). These trends are induced by the accelerated burial of gas hydrate and dissolved methane below the GHSZ. They are further supported by the decrease in the residence time of POC within the GHSZ which reduces the time-integrated rate of methane production within the GHSZ. It is important to note that model runs with identical values for the POC accumulation rate may yield very different gas hydrate inventories. Thus, the hydrate inventory increases to 427 kg m\(^2\) at POC = 5 wt-% and \(w_0 = 20\) cm kyr\(^{-1}\) while a value of only 154 kg m\(^2\) is attained at POC = 2 wt-% and \(w_0 = 50\) cm kyr\(^{-1}\) even though the POC accumulation rate amounts to 6.5 g m\(^2\) yr\(^{-1}\) in both model runs (Eq. 1). The POC accumulation rate is thus not a useful master parameter for the calculation of gas hydrate inventories especially at high POC concentrations and burial velocities.
Figure 16. Effect of POC concentration and burial velocity on methane hydrate accumulation in marine sediments. POC_0 and w_0 are the concentration of particulate organic carbon and the burial velocity of solids in surface sediments while GHI is the depth-integrated inventory of carbon bound in methane hydrate. R indicates the reference case.

An expansion of the GHSZ induces an exponential increase in gas hydrate inventories since the prolonged residence time of sediments within the GHSZ allows for more microbial methane formation and gas hydrate accumulation (Fig. 17).

Figure 17. Effect of GHSZ thickness on methane hydrate accumulation in marine sediments. L_{GHSZ} denotes the thickness of the gas hydrate stability zone. It was varied by changing the heat flow applied in the reference model run over a range of q_{ht} = 0.02 – 0.1 W m^2 corresponding to temperature gradients of 20 – 100 °C km^1. In the left panel, the burial velocity at the interface was maintained at the reference value (w_0 = 134.6 cm ky^r). The right panel shows model results with diminished w_0 values. R indicates the reference case.
Results of the individual model runs (Figs. 16 - 17) were analyzed to derive a simple transfer function:

\[
GHI = a \cdot L_{\text{GHSZ}}^b \cdot \left( POC_0 - \frac{c}{w_0} \right) \cdot \exp \left( - \left( e^{POC_0^2} + f \cdot \ln \left( \frac{w_0}{POC_0} \right) \right)^2 \right)
\]  

(31)

where GHI is the inventory of methane hydrate within the GHSZ (in kg methane-C m\(^2\)), \(L_{\text{GHSZ}}\) is the thickness of the gas hydrate stability zone (in m) while POC\(_0\) (in wt-%) and \(w_0\) (in cm kyr\(^{-1}\)) are the POC concentration and the burial velocity of solids in surface sediments. Parameter values of the equation were determined by a minimization procedure using the FindMinimum object in MATHEMATICA 8.0. The best fit to the individual model runs depicted in Figs. (16) and (17) was obtained with (parameter values ± standard deviations):

\[
a = 0.003171 \pm 0.00042; \quad b = 1.862 \pm 0.020; \quad c = 54.83 \pm 6.9; \quad d = 1.092 \pm 0.039; \quad e = 1.183 \pm 0.022; \quad f = 0.01537 \pm 0.0043
\]

The results of the more than 100 model runs are well reproduced by the transfer function (Fig. 18).

**Figure 18.** Gas hydrate inventories (GHI in kg m\(^2\)) within the GHSZ calculated by individual runs of the transport-reaction model (\(GHI_m\); s. Figs. 16 - 17) and with the transfer function (\(GHI_t\), Eq. 31) for the same set of parameter values. The solid line shown in the left panel has a slope of unity and serves as a reference for the transfer function values. The residuals shown in the right panel are calculated as \(GHI_t - GHI_m\).
The error in the gas hydrate inventory introduced by the transfer function may be quite significant at low GHI values but is always <10% at GHI ≥ 200 kg m\(^2\) (see residuals in the right panel of Fig. 18). The function is valid for the parameter values applied in the reference simulation (Tab. 2). It can be used to estimate GHI from ambient \(L_{GHSZ}\), \(w_0\), and POC\(_0\) values for GHI ≥ 0 over a range of \(L_{GHSZ} = 0 – 1000 m\); \(w_0 = 10 – 600 \text{ cm kyr}^{-1}\), and \(\text{POC}_0 = 0.5 – 5 \text{ wt-}\%\). It is more reliable than our previously published transfer function using POC accumulation rates as master variable for the prediction of gas hydrate inventories Marquardt et al., 2010.

Controls on the gas hydrate inventory (GHI) are shown in Fig. 19. GHI increases with \(\text{POC}_0\) and \(L_{GHSZ}\). Maximum values of >1000 kg m\(^2\) are obtained at \(\text{POC}_0 > 3.5\) and \(L_{GHSZ} > 750\) m. GHI also increases with burial velocity at \(w_0 = 10 – 100 \text{ cm kyr}^{-1}\) while a further \(w_0\) increase beyond 100 cm kyr\(^{-1}\) has no significant effect on gas hydrate accumulation. GHI values are zero for \(\text{POC}_0 < 0.5 \text{ wt-}\%\).

Figure 19. Controls on gas hydrate accumulation as predicted by the transfer function (Eq. 31). The contour lines indicate gas hydrate inventories (GHI) in kg C m\(^2\). The contour plot on the left hand side is calculated for \(w_0 = 100 \text{ cm kyr}^{-1}\) while the contour plot on the right shows the results for \(L_{GHSZ} = 400\) m.
7.3. Effects of Sediment Compaction on Gas Hydrate Accumulation

The accumulation of gas hydrates is also strongly affected by sediment compaction since the burial velocity of solids and pore water is not only controlled by the mass accumulation rate but also by the down-core decrease in sediment porosity. Compaction accelerates the velocity of sediment and gas hydrate burial while the burial of pore fluids is diminished (Fig. 11). Gas hydrate accumulation is favored by a decrease in pore water burial since less dissolved methane is lost to the sediments underlying the GHSZ while a more rapid burial of solids decreases the residence time of POC and gas hydrate within the GHSZ and thereby the accumulation of gas hydrates. However, compaction also increases the solid to water ratio within the GHSZ. Thus, for a given unit volume of bulk sediment more methane is released from the decaying POC while less methane is needed to saturate the pore fluids. The overall effect of compaction is thus a strong increase in the gas hydrate inventory within the GHSZ (Fig. 20).

Figure 20. Effect of sediment compaction on gas hydrate accumulation. The porosity after compaction ($\Omega$) and the attenuation coefficient for the down-core decrease in porosity ($p$) are varied while the porosity at the sediment surface is maintained at the reference value of $\Omega_0 = 0.74$ (s. Eq. 15). Compaction decreases towards the right in both plots. R indicates the reference case.

The porosity data measured within the GHSZ give some constraints on the degree of compaction. However, different interpretations of the porosity profile are possible since the base of the sediment column is usually located below the GHSZ. Sedimentary deposits
at continental margins are often several kilometers deep such that the base of the sediment column is not reached by conventional scientific drilling. The porosity at the base of margin deposits is thus poorly constrained. It may be significantly lower than the value assumed in the reference simulation (Φ_l = 0.3). Fig. 21 shows that a complete compaction at large sediment depth is also consistent with the porosity observations within the GHSZ at continental margins. Complete compaction (Φ_l = 0) is however inhibiting the burial of pore fluids (Eq. 19 and Fig. 21) and thus greatly enhancing the accumulation of gas hydrates within the GHSZ.

**Figure 21.** Porosity, burial velocity of sediments (w_b) and pore waters (v_w) applied in the reference case (solid lines) and in margin sediments with complete compaction at the base of the sediment column (broken lines). The following values were applied to calculate the depth profiles (s. Eq. 15): Reference: Φ_0 = 0.74, Φ_l = 0.3, p = 1/600 m^3, w_b = 134.6 cm kyr^-1; Margin: Φ_0 = 0.74, Φ_l = 0.0, p = 1/1300 m^3, w_b = 134.6 cm kyr^-1.

Complete compaction may occur at the base of thick sedimentary deposits and in compressive tectonic settings. This situation may be more representative for many continental margin sites than the conditions applied in the reference simulation. Therefore, an additional set of model runs was performed to explore gas hydrate accumulation for a complete compaction scenario applying the parameter settings defined in Tab. 2 with Φ_l = 0.0, p = 1/1300 (Fig. 21). The simulations show that the gas hydrate inventories are significantly enhanced by complete compaction (Fig. 22). In these simulations dissolved methane is only lost by upward diffusion into the AOM zone while the loss via burial of
dissolved methane at the base of GHSZ is inhibited (Fig. 21). The largest increase in GHI is observed at moderately low burial velocities and mass accumulation rates. Thus, the GHI at \( w_0 = 50 \) cm ky \( r^{-1} \) and \( \text{POC}_0 = 1 \) wt.-% amounts to 55.8 g C m \( ^2 \) at complete compaction (Fig. 22) while a value of only 2.8 g C m \( ^2 \) is calculated for the reference scenario (Fig. 16). The burial velocity in surface sediments has only a small effect on gas hydrate accumulation for fully compacting sediments. At \( \text{POC}_0 = 2 \) wt.-% almost the same GHI value is calculated over a \( w_0 \) range of 50 – 150 cm ky \( r^{-1} \) (Fig. 22).

**Figure 22.** Effect of POC concentration and burial velocity on methane hydrate accumulation in continental margin sediments experiencing complete compaction (\( \Phi_t = 0.0, \ p = 1/1300 \) m\(^3\)). See legend of Fig. 16 for further information.

Additional model runs were performed to explore the gas hydrate inventory for different GHSZ thicknesses (\( \text{L}_{\text{GHSZ}} = 150 - 900 \) m). Results of the individual model runs were analyzed to derive the following transfer function for completely compacting margin sediments:

\[
\text{GHI} = a \cdot \text{L}_{\text{GHSZ}}^b \cdot \left( \frac{c_0}{w_0} \right) \cdot \exp \left( - \left( e + f \cdot \ln(w_0) \right)^2 \right)
\]

(32)

where GHI is the inventory of methane hydrate within the GHSZ (in kg methane-C m\(^2\)), \( \text{L}_{\text{GHSZ}} \) is the thickness of the gas hydrate stability zone (in m) while \( \text{POC}_0 \) (in wt.-%) and \( w_0 \) (in cm ky \( r^{-1} \)) are the POC concentration and the burial velocity of solids in surface sediments. Parameter values of the equation were determined by a minimization procedure.
using the FindMinimum object in MATHEMATICA 8.0. The best fit to the model runs was obtained with:

\[ a = 0.002848 \pm 0.00049, \quad b = 1.681 \pm 0.027, \quad c = 24.42 \pm 7.2, \quad d = 0.9944 \pm 0.10, \quad e = -1.441 \pm 0.19, \quad f = 0.3925 \pm 0.032 \]

The results of the 80 model runs are well reproduced by the transfer function (Fig. 23). The function is valid for the parameter values applied in the reference simulation (Tab. 2 with \( \Phi_1 = 0.0, \ p = 1/1300 \) for GHI \( \geq 0 \) over a range of \( L_{\text{GHSZ}} = 0 - 1000 \) m; \( w_0 = 10 - 150 \) cm kyr\(^{-1} \), and \( \text{POC}_0 = 0.2 - 5 \) wt-%.

**Figure 23.** Gas hydrate inventories (GHI in kg m\(^{-2}\)) within the GHSZ calculated by individual runs of the transport-reaction model (GHI\(_{\text{pr}}\)) and with the transfer function (GHI\(_{\text{tr}}\), Eq. 32) for fully compacting margin sediments (see legend of Fig. 18 for further information).

![Figure 23](image)

Controls on GHI are shown in Fig. 24. The contour plots look similar to those produced for the reference simulation (Fig. 19). However, significant differences arise at \( w_0 = 20 - 100 \) cm kyr\(^{-1} \) and \( \text{POC}_0 = 1 - 2 \) wt-% where the function for full compaction predicts significantly higher gas hydrate inventories in margin sediments. These differences are relevant since the POC concentrations and burial velocities observed in margin sediments often fall into these \( w_0 \) and \( \text{POC}_0 \) ranges.
Figure 24. Controls on gas hydrate accumulation as predicted by the transfer function for margin sediments subject to complete compaction. The contour lines indicate gas hydrate inventories (GHI) in kg C m\(^{-2}\). The contour plot on the left hand side is calculated for \(w_0 = 100\) cm kyr\(^{-1}\) while the contour plot on the right shows the results for \(I_{GHSZ} = 400\) m.

7.4. EFFECTS OF FLUID AND GAS FLOW ON GAS HYDRATE ACCUMULATION

The accumulation of gas hydrates is strongly supported by the ascent of pore fluids into the GHSZ. Model runs under reference conditions (Tab. 2) show that the gas hydrate inventory is greatly enhanced already at low upward fluid flow velocities (Fig. 25). The inventory increases by two orders of magnitude at an upward Darcy flow of \(u_n = 1.5\) cm yr\(^{-1}\). The gas hydrate saturation at the base of the GHSZ increases to \(\sim 90\%\) at \(u_n = 2.2\) cm yr\(^{-1}\). At this point the infiltration of fluids into the GHSZ is effectively suppressed since the pore space is almost completely clocked by methane hydrate. The effect of gas inflow was estimated assuming that the ascending gas is completely dissolved at the base of the GHSZ (Fig. 25). The modeling showed that under this assumption an almost complete saturation of the pore space is achieved at an upward gas flow of \(u_g = 0.025\) cm yr\(^{-1}\). Fluid and gas infiltration are thus effectively supporting the accumulation of gas hydrates in marine sediments. The model runs based on the reference scenario produced a maximum gas hydrate saturation of only \(\sim 3\%\) without gas and fluid flow. It is thus very likely that the much higher saturations that have been observed at many continental margin sites have been created almost exclusively by the ascent of pore fluids and/or methane gas into the GHSZ.
7.5. Effects of POC degradation kinetics on gas hydrate accumulation

The initial age ($\text{age}_0$) and the inhibition constant ($K_e$) are used in the model to define the reactivity of POC (Eq. 7 and Eq. 11). Both parameters are varied to study their effect on gas hydrate accumulation applying the parameter settings of the reference simulation (Tab. 2). The model runs show that GHI increases with age, until a maximum is reached at age$_0 = 5$ kyr (Fig. 26). A further increase causes a significant contraction of the GHI until gas hydrate formation is almost completely suppressed at age$_0 = 100$ kyr. The initial increase is related to a better preservation of POC within the sulfate reduction zone supporting methanogenesis in the underlying sediments. A further increase in age$_0$ reduces the rate of methanogenesis within the GHSZ and thereby the accumulation of gas hydrates. The dissolved sulfate profile attains an almost linear shape at age$_0 = 100$ kyr since most of the sulfate is consumed via AOM rather than POC degradation under this parameter setting (Fig. 27). Similar sulfate profiles have been observed at many continental margin sites. The modeling strongly suggests that they are related to the deposition of old POC at the sediment surface. The high initial age of this material (100 kyr) may reflect the deposition of POC previously eroded at other locations and subsequently re-deposited at the study site (i.e. drift deposits such as Black Ridge). It may also reflect the deposition of terrigenous POC eroded from adjacent continental areas.
The inhibition constant \( (K_C) \) has a very strong effect on gas hydrate accumulation. Methanogenesis is strongly suppressed at low \( K_C \) values while high values allow for significantly more methane production and gas hydrate accumulation (Fig. 26). The down-core increase in dissolved ammonium, bromide, iodide, total alkalinity and DIC observed in ODP cores provides important constraints on the POC degradation rates and can thus be used to constrain the ambient \( K_C \) value. The evaluation of these pore water profiles at major gas hydrate provinces showed that \( K_C \) usually falls into a range of 30 – 50 mM Marquardt et al., 2010; Wallmann et al., 2006a.

**Figure 26.** Kinetic controls on gas hydrate accumulation. \( \text{age}_0 \) is the initial age of POC while \( K_C \) is a constant defining the inhibition of POC degradation induced by the accumulation of dissolved metabolites (DIC, \( \text{CH}_4 \)) in ambient pore fluids. \( R \) indicates the reference case.

**Figure 27.** Dissolved sulfate and methane profiles at \( \text{age}_0 = 100 \) kyr. See legend of Fig. 15 for further information.
The Middelburg model (Eq. 7 and 8) was integrated into the transport-reaction model to further test the effects of reaction kinetics on gas hydrate accumulation. It allows for more gas hydrate formation than the model used in this paper Wallmann et al., 2006a since methanogenesis is not inhibited by DIC and methane accumulating in ambient pore fluids (Fig. 28). The GHI value of 910 kg C m$^{-2}$ calculated with Middelburg’s kinetic rate law is almost identical to the GHI values calculated with Wallmann’s kinetic equation at high $K_C$ values (GHI = 907 kg C m$^{-2}$ at $K_C = 100 000$ mM, s. Fig. 26).

A new kinetic rate law for POC degradation was recently introduced by Burdige Burdige, 2011. Burdige proposed that microbial POC degradation rates increase with sediment temperature and that this increase can be described by a simple Arrhenius equation:

$$k(T) = A \cdot \exp \left( -\frac{E_a}{R \cdot T} \right)$$  \hspace{1cm} (33)

where $k(T)$ is a temperature-dependent kinetic constant, $E_a$ is the activation energy, $T$ is sediment temperature and $R$ is the gas constant ($R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$). The corresponding non-dimensional constant describing the down-core increase in reactivity is defined as:

$$k_r = \frac{\exp \left( -\frac{E_a}{R \cdot T} \right)}{\exp \left( -\frac{E_a}{R \cdot T_{bw}} \right)}$$  \hspace{1cm} (34)

where $T_{bw}$ is bottom water temperature. We introduced this constant into our rate law to calculate gas hydrate accumulation for the reference case considering the effects of both metabolite inhibition and temperature on POC degradation:

$$R_{POC} = -\frac{dC_{POC}}{dt} = \frac{K_C}{C_{CH_4} + C_{POC} + K_c k_{ext} \cdot k_r \cdot C_{POC}}$$  \hspace{1cm} (35)

Applying an activation energy of $E_a = 200 \text{ kJ mol}^{-1}$ Burdige, 2011 the value of the kinetic constant $k_r$ increases exponentially from 1 at the sediment surface to 197 at the base of the sediment column. The rates of POC degradation are thus strongly enhanced in the lower
section of the model column (Fig. 28). The gas hydrate inventory is expanded to 520 kg C m$^{-2}$ due to the temperature effect. Hydrate saturations calculated with the Middelburg model (Eq. 7 and 8) and the Burdige model (Eq. 35) vary within the same order of magnitude (Fig. 28). It should, however, be noted that the strong down-core decrease in POC and increase in DIC produced by the Middelburg and Burdige models are not consistent with observations. The POC profiles measured in ODP cores from major gas hydrate provinces show only a minor decrease with sediment depth while the DIC concentrations do not exceed 300 mM Hensen and Wallmann, 2005; Marquardt et al., 2010; Wallmann et al., 2006a. The rates of POC degradation, methane production and gas hydrate formation are thus strongly over-estimated by the Middelburg and Burdige models. The Middelburg equation is purely empirical while the Arrhenius equation applied by Burdige is valid for elementary reactions but not for complex multi-step process such as the microbial degradation of POC. Both approaches are thus not based on solid theoretically concepts. The chosen apparent activation energy of 200 kJ mol$^{-1}$ has been determined for abiotic hydrocarbon generation from kerogen while values reported for microbial POC degradation in surface sediments span a large range between 23 and 132 kJ mol$^{-1}$ with values clustering between 50 and 60 kJ mol$^{-1}$ and 70 and 90 kJ mol$^{-1}$ Middelburg et al., 1996; Westrich and Berner, 1988.

Figure 28. Concentrations of dissolved inorganic carbon (DIC), dissolved methane (CH$_4$), particulate organic carbon (POC) and methane hydrate saturation (GH-Sat.) calculated by integrating the kinetic rate laws introduced by Middelburg (Eq. 7 and 8) and Burdige (Eq. 35) into the reaction-transport model.
In the following we use OPD Site 799A (Leg 128) featuring a strong geothermal gradient and high-quality dissolved ammonium data to test our model at elevated temperatures of up to 50°C. The shape of the ammonium depth profile is giving us important constraints on the down-core change in organic matter reactivity since the biogeochemistry of ammonium is very simple in anoxic sediments: Ammonium is released into the porewater by the microbial degradation of organic matter while a minor portion is adsorbed on the solid phase until an adsorption/desorption equilibrium is attained. The stoichiometry of ammonium release is constrained by field data (POC/PON ratios) while the adsorption constant has been defined experimentally Mackin and Aller, 1984. OPD Site 799A is located in the Japan Sea, a marginal sea in a continental arc setting Ingle et al., 1990. Sediments were taken at about 2000 m water depth from the Kita-Yamato Trough, a narrow graben structure filled with sediments featuring a very high geothermal gradient of about 100°C km⁻¹. Sediments cored in Hole 799A include biosiliceous sediments and fine-grained detrital sediments intercalated with carbonate-rich intervals and numerous ash layers. They accumulate at an average rate of about 70 m Myr⁻¹ and contain abundant organic matter of mostly marine origin with particulate organic carbon values (POC) ranging from 0.24% to 5.66%. Porosity values scatter around a mean value of 0.75. Both, POC and porosity show no significant down-core trends. Pore water data indicate that sediments retrieved from Hole 799A are subject to in-situ diagenetic processes including microbial degradation of sedimentary organic matter. Pore water gradients and concentrations are not significantly affected by upward fluid flow Ingle et al., 1990. Our transport-reaction model Wallmann et al., 2006a was applied to site 799A to simulate the microbial degradation of POC and particulate organic nitrogen (PON) and the turnover of ammonium. The reaction network of the model includes degradation of particulate organic matter via sulfate reduction and methanogenesis, anaerobic oxidation of methane, the release of dissolved ammonium from degrading PON, and ammonium adsorption. The effects of porosity, tortuosity and temperature on diffusion coefficients of dissolved sulfate, methane, ammonium and dissolved inorganic carbon (DIC) were considered in the model applying appropriate empirical equations Boudreau, 1997. Constant concentrations were
prescribed at the upper boundary of the model column while zero gradients were used as lower boundary condition. The following parameter values were applied in the modeling: porosity: 0.75 (constant), molar PON/POC ratio: 0.1, burial velocity: 70 m Myr$^{-1}$, geothermal gradient: 100°C km$^{-1}$, $K_S$: 40 mM, age$_{e}$: 10 kyr, adsorption constant for ammonium: 1.7 cm$^3$ g$^{-1}$ Mackin and Aller, 1984.

The model results clearly show that the kinetic model for POC degradation introduced by Wallmann et al. Wallmann et al., 2006a is able to reproduce the data measured at OPD site 799A (s. Figure 29). The ammonium profiles calculated by the model are very close to observations and the model results are consistent with solid phase data (POC and total N). ODP site 799A was also simulated applying the original Middelburg model without inhibition term. The model results shown in Figure 29 confirms that the Middelburg model overestimates rates of organic matter degradation at large sediment depths since the predicted ammonium concentrations clearly exceed the measured values. This observation is consistent with a recent study on microbial sulfate reduction rates in fjord sediments showing a more pronounced down-core decrease in POC reactivity than predicted by the Middelburg model Jorgensen and Parkes, 2010. The data were used to further test the Burdige model for a moderate activation energy of only $E_a = 50$ kJ mol$^{-1}$. Even with this modest temperature sensitivity the model strongly over-predicts ammonium release and POC degradation rates at large sediment depths (s. Fig. 29).

Microbial organic matter degradation in the deep biosphere is a very complex and poorly understood process. Nevertheless, our model is clearly giving a good approximation to the general trends observed in geochemical ODP data and can thus be used to predict organic matter degradation and microbial methane formation in anoxic marine sediments to sediment temperatures of up to 50°C. The good correspondence between observations and model results is very encouraging but also surprising since our model does not explicitly consider effects of temperature on microbial degradation rates even though the microbial degradation of labile organic matter in marine surface sediments is promoted under high temperatures Middelburg et al., 1996; Westrich and Berner, 1988. A weak temperature
effect is implicitly considered in our model: Rates are suppressed by the built-up of high metabolite concentrations in ambient pore fluids which is partly controlled by the diffusive flux of these species towards the sediment surface. Since diffusion coefficients increase with temperature, elevated temperatures promote the diffusive loss of metabolites and thereby the rate of organic matter degradation. Thus, the rate of POC degradation amounts to 5.9 \( \mu \text{mol m}^{-3} \text{yr}^{-1} \) at the base of the model column (450 mbsf) in the model run depicted in Fig. 29 and decreases to 5.5 \( \mu \text{mol m}^{-3} \text{yr}^{-1} \) when the sediment temperature is kept at a constant value of 2°C throughout the model column. Considering this very modest temperature sensitivity, our model should significantly underestimate degradation rates at about 50°C if microbial turnover rates in the deep biosphere would strongly respond to temperature. It thus seems that temperature is not having a strong effect on the kinetics of refractory organic matter degradation in the deep biosphere. Rates are rather controlled by the strong down-core decrease in reactivity induced by the preferential degradation of labile organic matter at shallow depth levels and the inhibition of degradation processes by the accumulation of dissolved metabolites. Considering the long time periods available for adaptation in slowly accumulating sediments, it might be possible that each sediment level is harboring microorganisms being adapted to ambient temperature. This would suggest a down-core succession of microbial communities along the geothermal gradient with each community operating close to its temperature optimum. In this scenario, ambient temperature would have a negligible effect on the microbial degradation of refractory organic matter in the deep biosphere. However, much more basic research on microbial processes, diversity, and adaptation in the deep biosphere is needed to test this hypothesis.
Appendix 1

Figure 29. Model results for ODP site 799A. Concentrations of dissolved ammonium (NH₄), particulate nitrogen (N), particulate organic carbon (POC) and POC degradation rates obtained applying the kinetic rate laws introduced by Wallmann et al. (Eq. 11), Middelburg (Eq. 7 and 8) and Burdige (Eq. 35) with an activation energy of $E_a = 50 \text{ kJ mol}^{-1}$. N concentrations are the sum of particulate organic nitrogen (PON) and adsorbed ammonium. Symbols indicate the data measured at ODP site 799A while lines indicate model results.

8. CONSTRAINING THE GLOBAL METHANE HYDRATE INVENTORY IN THE MODERN OCEAN

In the following section, the transfer functions derived in sections 7.2 and 7.3 are applied on a global grid to estimate the abundance and distribution of methane hydrate in marine sediments. The global grid was defined by the POC concentrations in marine surface sediments (POC₀) and burial velocities (w₁) reported in Burwicz et al. Burwicz et al., 2011b and the GHSZ map ($L_{GHSZ}$) shown in Fig. 9.

Transfer function Eq. (31) which is valid for sediments experiencing a low degree of compaction was applied with Holocene burial velocities to provide a minimum estimate for the accumulation of gas hydrates in marine sediments. The global inventory of methane hydrates in marine sediments amounts to only 3 Gt of C under these boundary conditions. Low-grade gas hydrate occurrences are predicted for some high productivity areas with depth-integrated hydrate inventories of less than $40 \text{ kg m}^{-2}$. These low values are consistent with the previous model results for Holocene boundary conditions presented by Burwicz et al., 2011 yielding a global gas hydrate inventory of only 4 Gt of C.
The transfer function valid for low compaction (Eq. 31) was also applied on a grid with Quaternary burial velocities to consider the down-slope transport of sediments during glacial sea-level low-stands (Fig. 30). The global inventory of methane hydrates in marine sediments expands to 122 Gt of C due to the increase in burial velocity. The map shows extended hydrate-bearing areas at productive continental margins. Elevated inventories of up to 230 kg m\(^{-2}\) are found at the highly productive margin off Peru.

Our best estimate of the global distribution of marine sediments is shown in Fig. 31. It is based on the assumptions that margin sediments are completely compacted at large sediment depths and that shelf sediments are eroded and deposited on the continental slope and rise under glacial conditions. The global inventory of gas hydrates derived from our best estimate map (Fig. 31) is 455 Gt of C. The map predicts gas hydrate accumulations of \(~10\) kg m\(^{-2}\) over extended margin areas with elevated values of \(>100\) kg m\(^{-2}\) in high productivity zones at the western continental margins and in the Arabian Sea. High values are also calculated at the Argentinean margin and north of Madagascar. The background concentration of methane hydrates in margin sediments of \(~10\) kg m\(^{-2}\) corresponds to very low gas hydrate saturations of less than 0.1 Vol-% which are not resolved by geophysical methods and drilling. The true distribution of gas hydrates is probably patchier than the distribution shown in Fig. 31 since sediments are not always experiencing full compaction such that dissolved methane is buried and lost below the GHSZ. Fluid flow is implicitly considered in the map since pore fluids are not buried below the GHSZ. This approach is probably valid for passive continental margins. However, it does not consider the additional fluid flow at active margins where pore fluids of the incoming oceanic plate are mobilized and released into the GHSZ. The gas hydrate abundance at active margins is thus systematically underestimated in Fig. 31.
Figure 30. Global distribution of methane hydrate in marine sediments. The map was calculated applying low compaction (Eq. 31) and Quaternary burial velocities. The color coding indicates depth-integrated hydrate inventories in kg C m$^{-2}$.

Figure 31. Global distribution of methane hydrate in marine sediments. The map was calculated applying complete compaction (Eq. 32) and Quaternary burial velocities. The color coding indicates depth-integrated hydrate inventories in kg C m$^{-2}$.

It should also be noted that steady-state conditions were applied in all model runs. The models were run over a period of several million years until the depth-integrated inventory of gas hydrates reached a constant value. It was assumed that geothermal gradients and POC accumulation rates at the seafloor have been constant over the entire model period.
Thus, the model runs do not consider subsidence, thermal evolution and the changes in POC accumulation during basin formation.

Gas ascent and focused fluid flow at active continental margins are not considered in the map. These processes are responsible for the formation of high-grade gas hydrate accumulations which have been documented at an ever increasing number of sites Boswell and Collett, 2011a; Moridis et al., 2009. The global picture that emerges from our modeling exercise may be summarized as: Gas hydrates occur at many continental margin sites at very low saturations of less than 0.1 %, Higher saturations of 1 – 3 % appear at productive continental margins where abundant organic matter is delivered to the seafloor by the sinking of biogenic detritus. High-grade deposits with saturations of >3 % are formed only where fluid and/or gas have migrated into the GHSZ. These deposits are not shown on the map since it is currently not possible to constrain the global distribution of these high-grade gas hydrate deposits.

Our estimate of the global abundance of marine gas hydrates is certainly too low since gas ascent and focused fluid flow are not considered. Fluid and gas flow have an enormously strong effect on gas hydrate accumulation. The gas hydrate inventory is enhanced by about two orders magnitude already at very low velocities of fluid and gas ascent \( u_r < 2 \text{ cm kyr}^{-1} \); \( u_G < 0.02 \text{ cm kyr}^{-1} \), s. Fig. 25). It is currently not possible to constrain the global number and abundance of these hot spots for gas hydrate accumulation. However, the modeling presented in this contribution suggests that the global inventory of methane in these hot spot areas may exceed the global hydrate inventory of low-grade deposits if only 1% of the global seafloor would be affected by upward gas or fluid flow.

The gas hydrate distribution shown in Fig. 31 may be used for prospection purposes while Eq. (32) can be applied to estimate the gas hydrate inventory where ambient data for \( w_\phi \), \( L_{GHSZ} \) and \( \text{POC}_o \) are available. It should, however, be noted that detailed local surveys will almost certainly reveal inventories differing considerably from the predicted values since the regional basin evolution and the local pathways for fluid and gas flow are not resolved.
in our global estimates. Seismic surveys and drilling data are needed to constrain local gas hydrate inventories. Moreover, new 3-D basin modeling tools have recently been developed that can be used to better constrain gas hydrate inventories in well characterized sedimentary basins Piñero et al., 2011. These models can be used to simulate in detail the thermal and sedimentary history and the ascent of gas and fluids through faults and fractures at selected sites. However, it will not be possible to apply these basin models at global scale in the foreseeable future.

The first model-based estimate of the global methane hydrate inventory under Holocene boundary conditions was presented by Buffett and Archer Buffett and Archer, 2004. They used the POC rain rate to the seabed as a major external driving force for the simulation of hydrate formation in marine sediments. The rain rate was calculated as a function of water depth and applied as an upper boundary condition for an early diagenesis model simulating the degradation of POC in the top meter of the sediment column Archer et al., 2002. The POC burial rate at 1 m sediment depth calculated with this “muds” model was applied as upper boundary condition for the simulation of methane turnover in the underlying sediment sequence. The later simulations consider the microbial degradation of POC via sulfate reduction and methanogenesis and the anaerobic oxidation of methane within the sulfate-methane transition zone Davie and Buffett, 2003a, b. POC was separated into an inert fraction and a labile fraction that was degraded over the top km of the sediment column following first order reaction kinetics (rate constant $3 \times 10^{13} \text{s}^{-1}$). The model also considers an externally imposed rate of upward fluid flow. It was calibrated using field data obtained at Blake Ridge (a passive margin site) and the Cascadia margin (active continental margin). The best fit to observations was obtained assuming that the 25 % of the total POC is labile and using upward fluid flow velocities of 0.23 mm yr$^{-1}$ (passive margin) to 0.4 mm yr$^{-1}$ (active margin). Applying these parameter values on a global grid and assuming a compensating downward fluid flow over 50 % of the global seafloor area resulted in a total methane hydrate inventory of 3000 Gt C Buffett and Archer, 2004. The hydrate inventory was to a large degree controlled by the velocity of upward fluid flow.
Without imposed fluid flow, the global hydrate inventory was reduced to 600 Gt C Buffett and Archer, 2004. Subsequently, the authors discovered an extrapolation error in the calculation of POC rain rates as function of water depth Archer et al., 2008. The model-based estimate of the global hydrate inventory was reduced from 3000 Gt C to approximately 700 – 900 Gt C after correction for this error Archer et al., 2008.

Klauda and Sandler Klauda and Sandler, 2005 used a modified version of the Davie and Buffett model Davie and Buffett, 2003a, b to estimate the global marine hydrate inventory under Holocene boundary conditions. The entire POC pool was assumed to be completely degradable with a reduced decay constant of $1.5 \times 10^{-14} \text{ s}^{-1}$. The upper boundary of the model domain was constrained by field data. POC concentrations measured in surface sediments and Holocene sedimentation rates averaged over the major ocean basins were applied to define the POC burial flux at the sediment surface. The global hydrate inventory estimated with this approach was surprisingly high (55 700 Gt C) even though the model was run without imposing upward fluid flow. Unfortunately, Klauda and Sandler Klauda and Sandler, 2005 did not consider POC degradation via sulfate reduction. The large difference to our estimate may be explained by the neglect of microbial sulfate reduction and AOM since the accumulation of methane in pore fluids and gas hydrates is strongly diminished by these processes.

Burwicz et al. Burwicz et al., 2011b performed the first simulation of gas hydrate formation under Quaternary boundary conditions at global scale. Their estimate of the global gas hydrate inventory in marine sediments (995 Gt C) is larger than our Quaternary estimates for low and complete compaction (122 Gt C and 455 Gt C, respectively). Burwicz et al. Burwicz et al., 2011b applied a different compaction law and assumed very low porosities for GHSZ sediments. Moreover, they used a significantly higher value for the mean thermal conductivity of marine sediments ($1.5 \text{ W m}^{-1} \text{ K}^{-1}$) resulting in a very strong expansion of the GHSZ with respect to our modeling (s. discussion in section 4). To test the effect of the GHSZ expansion, we applied their GHSZ grid in an additional model run. We obtained a global GHI value of 937 Gt C for Quaternary conditions and full
compaction (Eq. 32) which is close to the value derived by Burwicz et al. Burwicz et al., 2011b (995 Gt C). We conclude that the difference between our best estimate (455 Gt C) and the previous estimate (995 Gt C) by Burwicz et al. Burwicz et al., 2011b is mainly caused by the different choice of thermal conductivity values. The maps presented by Burwicz et al. Burwicz et al., 2011b were produced by performing a full-scale 1-D transport-reaction simulation at each grid point. They are thus more precise than our estimates which are affected by additional errors introduced by the transfer functions. However, the available data strongly suggest that the thermal conductivity of most continental margin sediments is smaller than 1.5 W m\(^{-1}\) K\(^{-1}\) and close to the value applied in our modeling (1.0 W m\(^{-1}\) K\(^{-1}\)). We thus conclude that the gas hydrate distribution shown in Fig. 31 and our new best estimate of the global gas hydrate abundance (455 Gt C) are more realistic than previous results.

9. ACCUMULATION OF GAS HYDRATES UNDER PETM BOUNDARY CONDITIONS

The strong negative isotopic carbon excursion observed during the PETM (55.5 Ma ago) has been ascribed to the dissociation of methane hydrates in marine sediments Dickens et al., 1997; Dickens et al., 1995; Zachos et al., 2005. About 1000 Gt of methane carbon release are required to explain the isotope values observed in marine carbonates. The conditions at the PETM were very different from today. The bottom water temperatures were close to 10\(^\circ\)C, the burial velocities of terrigenous sediments were reduced by a factor of \(\sim 4 - 5\) while the POC concentrations in surface sediments were probably much higher than today (Fig. 4).

To test the potential for gas hydrate formation prior to onset of the PETM, the standard simulation with full compaction was run at a bottom water temperature of 10\(^\circ\)C, a POC concentration of 4 wt-% and a burial velocity of \(w_o = 33.7\) cm kyr\(^{-1}\) (Fig. 32). The thickness of the GHSZ was reduced to \(\sim 265\) m due to the elevated bottom water temperature while methane production rates were enhanced due to the increase in POC concentration. The resulting gas hydrate saturation values were similar to the saturations obtained under
modern conditions (Fig. 32). However, the overall effect was a decrease in the GHI from 99 kg C m$^{-2}$ in the modern ocean to 19 kg C m$^{-2}$ in the PETM.

These model results suggest that the potential for gas hydrate accumulation before the onset of the PETM was lower than today. Wide-spread ascent of pore fluids and/or methane gas into the GHSZ has to be postulated for the period prior to the PETM to explain the isotopic excursion by gas hydrate dissociation.

**Figure 32.** Concentrations of dissolved inorganic carbon (DIC), dissolved methane (CH$_4$), particulate organic carbon (POC) and methane hydrate saturation (GH-Sat.) calculated for the modern ocean and the PETM. The modern ocean simulation was done for the reference case with complete compaction ($\Phi_t = 0.0$, $p = 1/1300$ m$^3$). The PETM simulation was based on the reference case with complete compaction applying a bottom water temperature of 10°C, a POC concentration of POC$_0 = 4$ wt-% and a reduced burial velocity of $w_b = 33.7$ cm kyr$^{-1}$.

10. CONCLUSIONS AND OPEN QUESTIONS

A number of improved global estimates can be derived from the data and model results presented above:

- The global POC accumulation rate in the modern ocean amounts to $\sim 1.4 \times 10^{14}$ g yr$^{-1}$.
- The global rate of microbial methane formation in marine sediments is lower than previously assumed and falls into the range of $4 - 25 \times 10^{12}$ g C yr$^{-1}$. 

185
• The pore volume within the GHSZ is extensive and can be constrained as $\geq 44 \times 10^{15}$ m$^3$.

• The global inventory of methane hydrates in marine sediments is $\geq 455$ Gt C.

The global distribution maps of methane hydrate presented in this contribution are representative for methane hydrate being formed by the microbial degradation of POC within the GHSZ. The maximum pore space saturation reached under these conditions is 3 vol. %. However, sediment cores and logs obtained at an ever growing number of sites have clearly shown that the saturation values are much higher than 3 vol. % under favorable geologic conditions. Our model results clearly show that these highly concentrated gas hydrate deposits have been formed by the migration of dissolved or gaseous methane into the GHSZ. Potentially exploitable gas hydrate reservoirs are thus only formed where gas or water has been transported into the GHSZ via upward advection. Fluid and gas flow have an enormously strong effect on gas hydrate accumulation. The gas hydrate inventory is enhanced by about two orders magnitude already at very low velocities of fluid and gas ascent ($u_w < 2$ cm kyr$^{-1}$; $u_g < 0.02$ cm kyr$^{-1}$). The global distribution of methane hydrates is probably characterized by the wide-spread occurrence of low-grade hydrate saturations ($<0.1$ vol-%) along continental margins superimposed by elevated saturations in highly productive regions (1 - 3 vol-%). Observational data reveal a large number of “sweet spots” where saturations are enhanced by methane migration (>3 vol-%). However, it is currently not possible to constrain the global number and abundance of these high-grade deposits by numerical modeling.

The Quaternary is characterized by very low bottom water temperatures and extremely high rates of POC accumulation at the seabed. It offers unusually favorable conditions for gas hydrate accumulation since the inventory of gas hydrates in marine sediments increases under low temperature and high POC input. The conditions were much less favorable during most of the Cenozoic and Cretaceous. This is also true for the PETM where large-scale gas hydrate dissociation has been evoked to explain a global negative excursion observed in the $\delta^{13}$C record. Thus, wide-spread ascent of pore fluids and/or
methane gas into the GHSZ has to be postulated for the period prior to the PETM to explain the isotopic excursion by large-scale gas hydrate dissociation.

More work is needed to better constrain the global gas hydrate inventory in the seabed. This work should address at least some of the following open questions:

- What are the major geochemical and biological control mechanisms regulating the rate of microbial methane production in the deep biosphere?
- What precisely are the physical and geological controls on gas transport into the GHSZ? Is gas ascending into the GHSZ already at low gas saturation values? What defines the critical gas saturation value that needs to be overcome to allow for gas migration?
- What fraction of the global seabed is affected by upward gas and fluid flow?
- How does the hydrate inventory evolve under non-steady state conditions?

### List of Symbols and Abbreviations Used in the Contribution

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
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<tr>
<td>Anaerobic oxidation of methane</td>
<td>AOM</td>
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<tr>
<td>Accumulation rate of particulate organic carbon</td>
<td>( \dot{A}_{POC} )</td>
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<td>Bottom Simulating Reflector</td>
<td>BSR</td>
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<td>Gravitational acceleration</td>
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<td>Depth-integrated inventory of methane hydrate</td>
<td>GHI</td>
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<td>Saturation of the pore space by methane hydrate</td>
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<td>Gas hydrate stability zone</td>
<td>GHSZ</td>
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<td>Permeability</td>
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<td>Relative permeability of gas in porous media</td>
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<td>Inhibition constant for POC degradation</td>
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<td>Thickness of the gas hydrate stability zone</td>
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<td>Mass accumulation rate of sediments</td>
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<td>Attenuation coefficient for porosity decrease</td>
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**APPENDIX 2: RISING ARCTIC OCEAN TEMPERATURES CAUSE GAS HYDRATE DESTABILIZATION AND OCEAN ACIDIFICATION**

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**ABSTRACT**

Vast amounts of methane hydrates are potentially stored in sediments along the continental margins, owing their stability to low temperature – high pressure conditions. Global warming could destabilize these hydrates and cause a release of methane (CH₄) into the water column and possibly the atmosphere. Since the Arctic has and will be warmed considerably, Arctic bottom water temperatures and their future evolution projected by a climate model were analyzed. The resulting warming is spatially inhomogeneous, with the strongest impact on shallow regions affected by Atlantic inflow. Within the next 100 years, the warming affects 25% of shallow and mid-depth regions containing methane hydrates. Release of methane from melting hydrates in these areas could enhance ocean acidification and oxygen depletion in the water column. The impact of methane release on global warming, however, would not be significant within the considered time span.
INTRODUCTION
Formed under low temperature – high pressure conditions [Tishchenko et al., 2005] vast amounts of methane hydrates are considered to be locked up in sediments of continental margins [Buffett and Archer, 2004; Klauda and Sandler, 2005]. In the Arctic Ocean (AO), hydrates are deposited at shallow water depths close to shelf edges, stabilized by year-round cold temperatures [Hester and Brewer, 2009]. Because the Arctic has warmed considerably during the recent decades and because climate models predict accelerated warming if global greenhouse gas emissions continue to rise [Solomon et al., 2007], a destabilization of shallow Arctic hydrate deposits has been debated [Reagan and Moridis, 2007; Kerr, 2010]. Methane (CH₄), a gas with a global warming potential ~25 times higher than CO₂ [Solomon et al., 2007], could be released from the melting hydrates and enter the water column and atmosphere [Krey et al., 2009]. Recent field studies indicate an increase in methane fluxes from submarine Arctic permafrost and the seafloor [Westbrook et al., 2009; Shakhova et al., 2010]. Our multi-disciplinary analysis provides a closer look into regional developments of submarine Arctic gas hydrate deposits under future global warming scenarios and reveals where and over which time scales gas hydrates could be destabilized and affect oceanic pH, oxygen, and atmospheric methane.

TEMPERATURE EVOLUTION IN THE MID-DEPTH ARCTIC OCEAN
For an evaluation of the general distribution and the natural variability we investigated the spatio-temporal variability of Arctic bottom water in a hindcast experiment with the ocean/sea-ice NEMO (v2.3) [Madec, 2006], carried out by the DRAKKAR collaboration [The DRAKKAR Group, 2007]. The global simulation was performed at 1/2° resolution (ORCA05) and 46 levels in the vertical, whereby partial bottom cells allowed realistic topographic slopes. The experiment, that demonstrated its fidelity in simulating the salient features of the Atlantic circulation variability [Biastoch et al., 2008], was forced by inter-annually varying atmospheric boundary conditions of the past decades [Large and Yeager, 2004]. To exclude a potential model drift in the water masses a second experiment under repeated-year forcing was subtracted from the hindcast. The bottom water temperatures to
first order reflect water depth (Fig. 1a), featuring colder values around 0 °C below 1000 m and warmer values on the shelves. However, a clear impact of the ocean circulation is seen as a band of temperatures around 1 °C surrounding the AO at ~400 m, an expression of the Atlantic inflow below the Arctic halocline [Polyakov et al., 2004]. Colder temperatures appear on the Russian and Canadian shelves due to the exposure of the surface waters to continental cold air outbreaks during winter.

Fig. 1 (a) Map of the time-mean (1985-2004) bottom water temperatures in the ocean hindcast simulation and (b) ensemble-mean trend in (in °C per 100 years) in the climate model simulation under CO₂ increase. The contour line depicts the 400 m isobath. The Laptev shelf area used for Fig. 2c is marked by black stippling. Acronyms mark the Arctic Ocean (AO), European Nordic Seas (ENS) and the Laptev Sea (LS).

The Atlantic inflow from the European Nordic Seas (ENS) into the AO exhibits pronounced variability on decadal time scales [Biastoch et al., 2008], following temperature and transport changes in the branch of the North Atlantic Current flowing through the ENS [Holliday et al., 2008]. The flow of Atlantic water towards the AO south of Svalbard (Fig. 2a) shows a remarkable consistency with observations, both in mean temperature (3.70 ± 0.60 °C vs. 3.96 ± 0.69 °C [Holliday et al., 2008]) and variability, with minima in the late 1970s, mid 1980s and late 1990s. Changes towards warmer temperatures were reported for the past few decades [Holliday et al., 2008], which are supported by the simulated long-
term trend (0.014 °C yr⁻¹). Although the long-term trend (< 0.005 °C yr⁻¹) of the bottom water is weaker (Fig. 2b), a decadal variability by the Atlantic inflow is also present: changes over a single pentad repeatedly reach 0.75 °C (red lines). The inflow signal extends to the shelf areas off Russia as part of the cyclonic circulation around the AO [Dmitrenko et al., 2008]. Although the Arctic Intermediate Water also varies on a decadal time scale [Polyakov et al., 2004], bottom water temperatures along the Russian slope remain almost unaffected (Fig. 2c). Only the shallow and potentially methane-rich [Shakhova et al., 2010] shelf regions in the Laptev Sea show significant annual variations.

![Variability of temperatures in the hindcast simulation, shown by monthly and inter-annually filtered temperatures of (a) the Atlantic inflow (50-200 m depth) off Svalbard and bottom water temperatures (b) along the eastern continental slope in the ENS off Svalbard and Norway (water depth 416-793 m) and (c) along the Russian continental slope, (black, 416-793 m, 90-180°E) and on the shelf (blue, 0-100 m) in the Laptev Sea. The red lines mark trends in particular 5-year periods.](image)

The future evolution of bottom water temperatures was analyzed in an ensemble of greenhouse warming integrations with a coupled climate model (KCM) [Park et al., 2009]. This configuration utilizes the same numerical framework, but at lower resolution.
(ORCA2, 2° horizontally, 31 levels) and the atmospheric model ECHAM5 [Roeckner et al., 2003] as an active atmosphere. In addition to a 430 year control experiment with present day greenhouse gas concentrations (CO₂ = 348 ppm), an ensemble of eight 100-year long global warming simulations, each starting from different states of the control run, were performed with 1% increase in the CO₂ equivalent concentration [Park et al., 2009]. The linear trend of the ensemble average was combined with the ORCA05 distribution. The temperature changes (Fig. 1b) show a highly inhomogeneous distribution, with increases of 1-2 °C along the continental slopes and even higher values on the shelves due to the direct influence from the atmosphere. Individual ensemble members resembles strong inter-annual to decadal variability in the Nordic Seas (Fig. S2) due to different states of the Atlantic Ocean circulation, but all feature a consistent long-term trend of 2.5 °C per century. Anomalies take some decades to protrude into the Laptev Sea, depending on the state of the Arctic circulation [Polyakov et al., 2004]; consistent trends are starting typically after 50 years.

**IMPACT ON METHANE HYDRATE STABILITY AND OCEAN ACIDIFICATION**

Methane hydrate stability in marine sediments is mainly a function of temperature and pressure [Tishchenko et al., 2005]. A thermodynamic analysis (Fig 3b) of selected Arctic regions illustrates that in the ENS the methane hydrate will experience a phase shift from hydrate to free gas in mid-depth levels at around 500 m within the next 100 years. Natural decadal variability can easily add another 0.75 °C (Fig. 2) to the long-term increase. Along the Russian slope only shallower depths (~300 m) undergo a phase shift.
Fig. 3 (a) Changes in thickness of the GHSZ caused by temperature increase of the ensemble mean of the global warming, (b) phase diagram of methane hydrate as a function of pressure and temperature (constant salinity of S=35 p.s.u.). Open symbols mark the bottom water temperatures along the ENS (cycles) and Russian (squares) slopes in the present climate run, closed symbols the greenhouse warming experiments. Vertical bars indicate the vertical resolution of the ocean model. (c) Volumetric GHSZ thickness changes north of 60ºN as a function of time. A value of 100% corresponds to the worst case scenario. The shaded range marks estimates for 0 and 10m sulfate reduction zone thickness.

For the overall impact of future bottom water warming on the stability of methane hydrates potentially stored in the Arctic seafloor we explored the thickness of the gas hydrate stability zone (GHSZ) below the seafloor. The GHSZ is defined as that part of a sediment column where hydrostatic fluid pressures are higher than the temperature and salinity dependent dissociation pressure of gas hydrates. The dissociation pressure was calculated according to [Tishchenko et al., 2005] using the fields from the ocean model and steady-state temperatures computed from global heat flow values in combination with an average sediment conductivity of 1.5 W m⁻¹ K⁻¹ for present (Fig. S3) and future climates. To roughly estimate the amount of hydrate within the GHSZ we used simple constant mean hydrate pore filling estimates of 2.4% (60-70ºN) to 6.1% (north of 70ºN) based on ODP data and numerical modeling [Klauda and Sandler, 2005]. Inhibition of hydrate formation
by sulfate reduction is approximated by including a 5m thick hydrate free zone below the seafloor. Assuming a mean porosity of 0.5 and standard values for density and methane content of hydrate, we estimated a total inventory of 900 Gt carbon (C) north of 60° N for the present climate. This value is not too far off the estimated 500 Gt C based on studies offshore Alaska [Kvenvolden, 1988] representing a fraction of the still largely unknown global hydrate inventory of 500-64,000 Gt C [Hester and Brewer, 2009]. Under the global warming scenario most affected regions are distributed around the AO and the ENS. Areas exhibiting decreases ≥ 20 m in the GHSZ thickness sum up to a total size of ~850,000 km² resulting in a total methane release of ~100 Gt C. However, these estimates are too high for the considered 100-year time window and need to be adjusted for the sluggish diffusion of heat into marine sediments. Using a constant thermal diffusivity of 4 × 10⁻⁷ m² s⁻¹ and neglecting the latent heat of hydrate melting, we find that only 12% of the worst-case hydrate volume is reduced after 100 years for sulfate reduction zone thicknesses 5 m (Fig. 3c). Note that sensitivity runs with 0 and 10 m sulfate reduction zone thicknesses show reductions of 14 and 10%, respectively.

What could happen to the released methane? It is conceivable from environmental hydrate studies that, depending on the release rate, at least ~50% of the methane that dissolves into the sediment porewater, could be retained inside the seafloor by microbial anaerobic oxidation of methane (AOM) [Knittel and Boetius, 2009; Treude et al., 2003]. AOM represents a long-term sink for methane-derived carbon, converting methane into bicarbonate and eventually precipitating it as authigenic carbonates [Peckmann et al., 2001]. However, methane rising through sediments as free gas could bypass the benthic methane filter [Knittel and Boetius, 2009] and, depending on water depth [McGinnis et al., 2006], immediately reach the atmosphere. Methane that on the other hand dissolves into the water column could be utilized by microbial aerobic oxidation of methane [Valentine et al., 2001]. Different to its counterpart AOM in sediments, aerobic oxidation of methane converts methane with oxygen into CO₂ – a molecule that can impact oceanic pH.

For the following scenario we assume that 50% of the methane from the transient GHSZ thickness change is released into the water column and consumed by aerobic
methanotrophs. A Lagrangian analysis of the oceanic currents (Suppl. Material) shows that (within a given year) the bulk of the water affected by methane is kept within 100 m above the bottom and along the mid-depth topographic slope. Changes in seawater carbonate chemistry were calculated by adding the microbial produced CO₂ to the background dissolved inorganic carbon (Suppl. Material). Some areas of the AO revealed pH values to drop by up to 0.25 units (Fig. 4) within the next 100 years. Additionally, the aerobic consumption of methane could locally decrease bottom water oxygen concentrations by up to 25% (Suppl. Material, data not shown). Regional methane-induced seawater acidification from the seafloor would occur in addition to an ocean-wide acidification caused by the uptake of anthropogenic CO₂ from the atmosphere [Solomon et al., 2007]. The combined effect of the two processes would accelerate ocean acidification in parts of the AO, including deeper waters which otherwise would be exposed to ocean acidification with a considerable time delay. Research on that topic so far has been conducted under the premises of a projected pH decrease due to the anthropogenic CO₂-uptake of about 0.3 units until the end of this century. Methane-induced acidification could nearly double this decrease in parts of the AO.

Fig. 4 Changes in pH due to the release of 50% of the methane from hydrates within the first 100 years and distributed over the first 100 m above the bottom.
If, in a rather unrealistic scenario, all of the liberated methane would reach the atmosphere, global warming could be amplified [Bartordoř et al., 2008]. Under transient conditions we estimated an additional average methane flux of only 162 Mt CH₄ yr⁻¹ from melting Arctic hydrates over the next 100 years (Suppl. Material) – a value lower than the current anthropogenic input of (600 Mt yr⁻¹) [Bartordoř et al., 2008]. Sensitivity experiments with the climate model confirm the negligible feedback of the climate system under this limited additional amount of methane (Fig. S3). On a longer time scale, however, the transient heat conduction leads to a faster methane release; the methane released from the steady-state GHSZ calculation causes an upper limit of 0.7 ºC increase in surface air temperature on top of global warming.

**CONCLUSIONS**

The present study is to our knowledge the first combining ocean hindcasts and future climate projections with GHSZ calculations and potential consequences. It should be noted that the overall model still has its limitation with respect to the resolution of the bottom water temperatures, the actual distribution of sub-seafloor methane hydrates and the individual response of the microbial community in the sediment and water column. Nevertheless, the study clearly shows that hydrate destabilization can occur in the Arctic in response to global warming, and that the potential methane release is substantial, but limited in the next 100 years. An important finding is that warming and variability of the Atlantic inflow will play a major role in the fate of Arctic gas hydrates. Recent observations [Westbrook et al., 2009; Reagan and Moridis, 2009] agree well with sensitive areas identified here. Our maps could represent a useful tool in identifying areas around the Arctic Ocean where increases in methane release are likely to occur now or in the near future.

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APPENDIX 3: MODELING THE FATE OF METHANE HYDRATES UNDER GLOBAL WARMING

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ABSTRACT

Large amounts of methane hydrate locked up within marine sediments are vulnerable to climate change. Changes in bottom water temperatures may lead to their destabilization and the release of methane into the water column or even the atmosphere. In a multi-model approach, the possible impact of destabilizing methane hydrates onto global climate within the next century is evaluated. The focus is set on changing bottom water temperatures to infer the response of the global methane hydrate inventory to future climate change. Present and future bottom water temperatures are evaluated by the combined use of hindcast high-resolution ocean circulation simulations and climate modeling for the next century. The changing global hydrate inventory is computed using the parameterized transfer function recently proposed by Wallmann et al. [2012]. We find that the present-day world’s total marine methane hydrate inventory is estimated to be 1146 Gt of methane carbon. Within the next 100 years this global inventory may be reduced by ~0.03 % (releasing ~453 Mt methane from the seafloor). Compared to the
present-day annual emissions of anthropogenic methane, the amount of methane released from melting hydrates by 2100 is small and will not have a major impact on the global climate. On a regional scale, ocean bottom warming over the next 100 years will result in a relatively large decrease in the methane hydrate deposits, with the Arctic and Blake Ridge region, offshore South Carolina, being most affected.

1. INTRODUCTION

The Earth’s climate system has experienced significant changes over the last century. Although strongly masked by natural variability on synoptic, interannual, and decadal time scales, it is clear that the long-term temperature trend is due to anthropogenic influences [Huber and Knutti, 2012; Santer et al., 2013]. Observational records reveal that not only the atmosphere but also the global ocean is subject to a warming trend. According to the fifth Assessment Report of the Intergovernmental Panel on Climate Change [IPCC, 2013], the upper ocean (0-75 m) temperature has risen from 1971 to 2010 by 0.11°C/10yrs, the temperature at 700 m by 0.015°C/10yrs. Few observations exist on the deep ocean (here referred to as the regions below 700 m water depth) and warming estimates largely rely on climate models. Owing to its vast volume, the deep ocean is likely to play a key role in modulating the evolution of global warming since it effectively removes heat from the atmosphere and surface ocean [Meehl et al., 2011; Lamarque, 2008].

With observations and climate projections pointing to significant ocean warming over the next 100 years, rising seafloor temperatures may lead to the destabilization of gas hydrates within marine sediments.

Methane (CH₄) is the most common gas found in naturally occurring gas hydrates, accompanied by hydrogen sulphide, carbon dioxide (CO₂), and, less frequently, by higher hydrocarbons [Sloan, 1990]. The pressure- and temperature-controlled stability limit of methane hydrates is such that the base of the gas hydrate stability zone (GHSZ) outcrops on the upper continental slope at around 300-500 meters water depth (Figure 1). Given that most ocean warming will occur within the first few hundred meters water depth, it will
be this region where hydrates are most susceptible to dissociation from rising bottom water temperatures.

Fig. 1. Schematic of a typical continental shelf margin depicting the present-day area of gas hydrate stability (light + dark orange). Within this zone, the accumulations most vulnerable to climate change are marked in dark orange [adapted from Boswell and Collett, 2011]. In boxes A and B, a detailed depiction of how the thickness of the GHSZ may change under climate change is shown. The blue dashed lines resemble the phase boundary for methane hydrate, calculated for an exemplary sediment deposited at 500m water depth and sulfate-free porewater with a salinity of 35. The solid and dashed dark red lines depict the steady-state temperature profiles under present-day conditions and a warming scenario of either 3.0 °C (box A) or 1.5 °C (box B) (red arrows). On the upper continental slope (300 - 500m water depth), the point where the GHSZ outcrops on the seafloor is shifted down the slope, which leads to complete dissociation (box A), whereas the lower continental slope and continental rise may face a reduction from the bottom (box B). This all happens on longer time scales, the transient temperature profiles in the sediment are indicated by green dotted lines (after 50, 100, 150, 200, and 500 years from left to right). The base of the GHSZ for present-day is denoted by the Bottom Simulating Reflector (BSR).

Figure 1 illustrates two possible scenarios resulting from a gradual increase in bottom water temperature over the next 100 years, followed by a several hundred years long thermal equilibration phase. If the temperature rise is sufficient to eventually result in the complete dissociation of the hydrate column, progressive hydrate melting will occur from both the top as well as bottom of the GHSZ until the entire stability zone vanishes (Figure
1A). This is the main process by which hydrates are likely to destabilize within the next century. However, due to the sluggish thermal diffusion rate in marine sediments, complete dissociation will only occur after several hundred years. If seafloor warming will only reduce the thickness of the stability zone, hydrate melting occurs at the bottom of the stability zone (Figure 1B). This, in turn, is the likely process by which the global hydrate inventory is reduced on centennial to millennium time scales in response to global warming. Since the stability of gas hydrates is more vulnerable to small changes in temperature than to pressure [Tishchenko et al., 2005], we concentrate on the influence of varying bottom water temperatures only. Hunter et al. [2013] recently found that even large changes in the sea level (of up to +20 mm/yr) do not lead to significant variations in the global gas hydrate inventory.

During the dissociation of methane hydrates, a free methane gas phase forms that may escape to the seafloor or even the atmosphere, which has important regional and global consequences. Through microbial aerobic oxidation [Valentine et al., 2001; Murrell, 2010], the water column can be affected by oxygen depletion and ocean acidification [Biastoch et al., 2011]. Only if enough methane passes through this microbial filter and reaches the atmosphere, its global warming potential (about 25 times higher than CO₂ [IPCC, 2007]) could lead to a further acceleration of climate change. As a consequence, it has been suggested that hydrates played an important role in past and future climate change.

The most prominent and best studied past warming event is the Paleocene-Eocene Thermal Maximum (PETM). Enormous amounts of carbon (>2000 Gt) were released into the atmosphere causing a surface temperature rise of ~6°C [Cohen et al., 2007; Higgins and Schrag, 2006]. The associated carbon isotope excursion points to an isotopically light source, which is consistent with methane released from dissociating gas hydrates [Dickens et al., 1995]. Doubts whether sufficient amount of hydrate were stable under warmer Paleocene marine conditions and the discrepancy between the amount of warming and the carbon excursion pose significant challenges to this hypothesis [Higgins and Schrag, 2006]. Methane hydrate dissociation, according to the clathrate gun hypothesis, may have also
played a role during Quaternary climate change [Kennett et al., 2003] but also this view has been convincingly challenged based on ice core data [Sowers, 2006].

Fueled by field studies that indicate an increase in methane fluxes from submarine Arctic permafrost and the seafloor [Westbrook et al., 2009; Shakhova et al., 2010], methane hydrates are also debated in the context of contemporaneous climate change. The sluggish rate of heat diffusion into marine sediments renders catastrophic and widespread hydrate dissociation triggered by warming bottom waters unlikely [Archer, 2007; Maslin et al., 2010; Ruppel, 2011; Biastoch et al., 2011], and recently discovered gas flares offshore Svalbard appear to be related to natural seepage processes rather than to global warming induced hydrate dissociation [Berndt et al., 2014].

A robust assessment of the role of methane hydrates in contemporaneous climate change comes down to the question of how large the current global marine gas hydrate inventory is and how much of it will be affected by warming seafloor temperatures. Despite the clear need to answer these questions, the global abundance of methane hydrates in marine sediments remains poorly constrained. Global estimates range over several orders of magnitude from 500 to 55,800 Gt C (cf. Figure 2) without clear convergence [cf. Kvenvolden and Lorenson, 2001; Buffett and Archer, 2004; Milkov, 2004; Klauda and Sandler, 2005; Archer et al., 2009; Boswell and Collett, 2011; Burwicz et al., 2011; Wallmann et al., 2012; Piñero et al., 2013]. Estimates based on the global extrapolation of known hydrate deposits [e.g. Milkov, 2004] suffer from the sparse global data coverage, while the uncertainty in model-based estimates [e.g. Klauda and Sandler, 2005; Archer et al., 2009; Burwicz et al., 2011; Wallmann et al., 2012] results from differences in model assumptions and variable quality of global input data sets.
Fig. 2. Global estimates of methane hydrate inventories (Gt C) with error bars indicating estimated ranges of the GHI.

Similar uncertainty exists for the projected warming of bottom waters. The observation-based average trends in warming given in the latest IPCC report are global averages, which are not necessarily representative for specific regions and problematic to extend into the future. We therefore have to rely on projections based on climate models to assess the spatial and temporal evolution of bottom water temperatures. However, climate models are currently run at a lateral resolution of 1-2° and a vertical resolution of tens to hundreds of meters, which may introduce interpolation errors into the prediction of bottom water temperatures, especially along the steep continental slopes.

The above considerations illustrate the need for improved tools for the assessment of the current global hydrate inventory and its fate under global warming. In this study, we present a new self-consistent methodology, which is based on the combination of a high-
resolution ocean hindcast simulation, future climate projections, and a parameterized reaction-transport model for the prediction of hydrates in marine sediments. One advantage of this approach is that the current distribution of marine gas hydrates, which represents the starting condition for the climate simulations, is fully consistent with both the ocean as well as the climate model and is derived from a process-based analysis and not extrapolated from sparse regional data. The high-resolution ocean hindcast simulation provides the baseline bottom water temperature onto which the warming trends predicted by the climate model are projected. This approach increases the effective resolution and assures the spatial accuracy and consistency with the initial temperature field and global input data sets.

2. DATA AND METHODS

2.1. MODEL CONFIGURATIONS

For analyzing present-day global climate conditions, data from a global ocean/sea-ice model, performed under atmospheric boundary conditions of the past decades (hindcast), were used. The model is based on the Nucleus for European Modelling of the Ocean (NEMO) [Madec, 2008] and consists of an eddy-active, z-coordinate global grid at 0.25° nominal resolution (ORCA025) [Barnier et al., 2006]. The effective resolution amounts to ~13.8 km at 60° latitude and gets coarser with decreasing latitude (being ~27.75 km at the equator).

With a total number of 46 levels in the vertical, the grid spacing is fine at the surface (ten levels in the upper 100 m), and then increases with depth to 250 m at the bottom. Bottom topography is described by partially filled bottom cells to better represent topographic slopes and providing a reasonable representation of the global oceanic circulation [Barnier et al., 2006]. Vertical mixing is parameterized using the turbulent kinetic energy (TKE) scheme of Blanke and Delecluse [1993], lateral mixing is aligned along isopycnal surfaces.

The model run is initialized with temperature and salinity fields combined from the Levitus climatology [Levitus et al., 1998] for mid- and low latitudes, the Polar Science Center Hydrographic Climatology (PHC 2.1) for high latitudes [Steele et al., 2001], and
from the Medatlas climatology for the Mediterranean Sea [Jourdan et al., 1998]. The model integration is spun up to a quasi-steady state using atmospheric fields for the years 1978-2007, then integrated over the hindcast period 1948-2007 [Behrens et al., 2013]. Momentum, heat, and freshwater fluxes at the sea surface are based on the atmospheric data sets developed by Large and Yeager [2004, 2009] and implemented through bulk formulae according to the CORE-II-protocol (Coordinated Ocean-ice Reference Experiments), suggested by Griffies et al. [2009]. These forcing data sets are originally based on the NCEP/NCAR (National Center for Environmental Prediction/National Center for Atmospheric Research) reanalysis products and corrected and adjusted using various observational (e.g. satellite) data sets to correct for known biases Large and Yeager [2009]. The forcing fields are provided at six hourly (windspeed, temperature, humidity), daily (short and long wave radiation), and monthly (precipitation) resolution. Annual mean river runoff was provided by Dai and Trenberth [2002].

For analyzing future climate change, simulations of the Kiel Climate Model (KCM) [Park et al., 2009], a coupled ocean/atmosphere/sea-ice general circulation model, were used. KCM consists of the atmospheric model ECHAM5 [Roeckner et al., 2003] and the ORCA2 model configuration, the latter also based on the same numerical framework as the ORCA025 model configuration, but at lower resolution (2° horizontally, 31 vertical levels). Here, two experiment series were used: A twentieth-century equivalent control experiment and a series of twenty-two 100-year-long global warming simulations. The control simulation describing “present-day” climate conditions was forced by constant greenhouse gas concentrations (CO₂=348 ppm) and was integrated for 1100 years in total. For the global warming experiments (twenty-first-century equivalent), the CO₂ concentration was increased by 1%/yr (compound) until CO₂ doubling is reached after about 70 years and stabilized thereafter for another 30 years. Those experiments were started from different initial conditions chosen semiregularly at 30- to 40-year intervals from the control run. According to Hawkins and Sutton [2009], future predictions of climate change are dominated by model uncertainty on decadal time scales. In order to reduce the model
uncertainty of KCM, an ensemble mean is used in this study to provide a robust assessment of temperature changes under future climate change.

2.2. Stability Analysis of Gas Hydrates

The stability of gas hydrates within marine sediments depends on temperature, pressure, and to a smaller extent on salinity. The boundary between the hydrate and free gas phase fields for structure I methane hydrates is obtained via the modified Pitzer-approach of Tishchenko et al. [2005]. Pore fluid pressures are assumed hydrostatic, and salinity within the sediment column is assumed to be the same as at the seafloor. The temperature gradient within the sediment column is computed from global heat flow data:

\[
\frac{\partial T}{\partial z} = -\frac{q_h}{\kappa_B}
\]  

(1)

where \( q_h \) is the conductive heat flow obtained from Hamza et al. [2008] and \( \kappa_B \) the bulk thermal conductivity of sediments. Throughout this study, a constant thermal conductivity of \( \kappa_B=1.5 \) W/m/K is used, which is based on the characteristic properties of shaly-sandstones [Hantschel and Kauerauf, 2010].

With these assumptions the steady-state geotherm can be calculated:

\[
T = \frac{\partial T}{\partial z} \cdot z + T_{BW}
\]

(2)

where \( T_{BW} \) is the bottom water temperature predicted by the ocean circulation model. To assess possible gas hydrate dissociation as a consequence of warming bottom waters, a transient thermal solution is necessary. The sedimentary temperature profile is then given by the solution of the heat conduction equation:

\[
\frac{\partial T}{\partial t} = \alpha_B \cdot \frac{\partial^2 T}{\partial z^2}
\]

(3)
where \( \alpha_b \) is the bulk thermal diffusivity (in \( m^2/s \)), which is defined as:

\[
\alpha_b = \frac{K_B}{(\rho \cdot c_p)_B}
\]

(4)

with \( \rho \) being the density (in \( kg/m^3 \)) and \( c_p \) the specific heat capacity at constant pressure (in \( J/kg/K \)) of bulk sediments. Furthermore, the volume-specific heat capacity, \( (\rho \cdot c_p)_B \), can be calculated by

\[
(\rho \cdot c_p)_B = (1 - \Phi) \cdot \rho_s \cdot c_{p_s} + \Phi \cdot \rho_f \cdot c_{p_f}
\]

(5)

where \( \Phi \) denotes porosity (ranges between 0 and 1) and the subscripts \( s \) and \( f \) represent solids and fluids, respectively. For the calculation of \( \alpha_b \), the following parameter values have been chosen: \( K_B = 1.5 \, W/m/K \), \( \rho_s = 2650 \, kg/m^3 \), \( \rho_f = 1025 \, kg/m^3 \), \( c_{p_s} = 835 \, J/kg/K \), and \( c_{p_f} = 4181.3 \, J/kg/K \). Although porosity changes with depth, a simple constant thermal diffusivity is assumed based on an average porosity of \( \Phi = 0.5 \). Equation (3) is solved using finite differences and thus the thickness of the GHSZ \( (L_{GHSZ}) \) in marine sediments for transient state conditions can be evaluated. All transient calculations start from the steady-state solution given by Eq. (2) and use the predicted changing bottom water temperature as top boundary condition and heat flow \( q_{bt} \) as bottom boundary condition.

We follow Wallmann et al. [2012] and compute the hydrate inventory, GHI, in kg C/m\(^2\) at every grid point with a transfer function that takes gas hydrate stability zone thickness, \( L_{GHSZ} \) (m), the particulate organic carbon (POC) concentration at the seafloor (wt. %), and sedimentation rate (cm/kyr) as input:

\[
GHI = a \cdot b^{L_{GHSZ}} \cdot \left( \frac{POC_0}{2 \cdot c_{max}} \right) \exp \left( - \left( e + f \cdot \ln \left( \frac{w}{w_0} \right) \right)^2 \right)
\]

(6)

The following fitting parameters (parameter value ± standard deviation) are used: \( a = 0.002848 \pm 0.00049 \), \( b = 1.681 \pm 0.027 \), \( c = 24.42 \pm 7.2 \), \( d = 0.9944 \pm 0.10 \), \( e = 1.441 \pm 0.19 \), and \( f = 0.3925 \pm 0.032 \). The derivation of the transfer function in Wallmann et al. [2012] was
done by parameterizing the predicted hydrate inventory computed by a transport-reaction model [Wallmann et al., 2006; Burwicz et al., 2011], which resolves kinetics-controlled microbial degradation of POC via sulfate reduction as well as methanogenesis, hydrate formation, and pore fluid chemistry (CH₄, DIC, SO₄). Equation (6) implicitly assumes a compaction law that describes exponential compaction with depth:

\[
\Phi(z) = \Phi_0 \cdot \exp(-c_0 \cdot z)
\]

(7)

where \( \Phi_0 \) is the initial porosity at the sediment surface and \( c_0 \) is the compaction length scale (in m⁻¹).

As sedimentation rates are not available on a global scale, water depth is used as a proxy to estimate them. The evaluation of sedimentation rates of Holocene surface sediments measured at different stations (in total more than 500) showed a decrease in the latter with increasing water depth [Burwicz et al., 2011]. Due to this depth dependency, Burwicz et al. [2011] were able to derive a parameterization that provides sedimentation rate \( w \) (in cm/yr) as a function of water depth (\( z \) in m):

\[
w = \frac{w_1}{1 + \left( \frac{z}{z_1} \right)^{c_1}} + \frac{w_2}{1 + \left( \frac{z}{z_2} \right)^{c_2}}
\]

(8)

with \( w_1 = 0.117 \) cm/yr, \( w_2 = 0.006 \) cm/yr, \( z_1 = 200 \) m, \( z_2 = 4000 \) m, \( c_1 = 3 \), and \( c_2 = 10 \). Evaluating Eq. (8) shows that most sedimentation (∼72%) takes place on the continental shelf (\( z = 0-200 \) m), where \( w \) ranges between 0.01 cm/yr and 10 cm/yr. While this is correct throughout the Holocene, direct observations revealed that the thickness of Holocene sediments is only a fraction of the actual GHSZ thickness. It is therefore more appropriate to consider mean sedimentation rates averaged over a period of several million years for the prediction of hydrate accumulation.
Hay [1994] found that under glacial conditions, as they have repeatedly occurred throughout the Quaternary, the anomalous Holocene shelf accumulation rate (as predicted by Eq. 8) might have been diminished by an order of magnitude. It is therefore reasonable to shift the main deposition areas from the shelf to the deeper continental slope and rise. Hence, the sedimentation rate was increased over a ~500 km wide range around the continental margins by moving deposited material from shelf regions (z=0-200 m) to continental slopes [Burwicz et al., 2011]. At distance greater than 500 km to the coast, sedimentation rates are computed via Eq. (8). It should be noted that the total amount of sediment supplied to the global ocean stays constant. For estimating the GHI of present-climate conditions we use this modified sedimentation mode as today’s marine hydrate accumulation rates are likely controlled by Quaternary mean values [Wallmann et al., 2012].

The total global methane inventory for present-climate conditions can be obtained by integrating the GHI (given by Eq. 6) over the surface area for each grid cell of the ocean model. To evaluate the possible impact of future climate change onto marine hydrates, the change in the total global methane inventory is calculated by firstly using present-day data, then inferring bottom temperature warming due to future projections, whereby the change in the global gas hydrate inventory under global warming is calculated by scaling the present GHI with the variations in the $I_{\text{GHSZ}}$. Note that this approach of scaling the GHI by the relative change in $I_{\text{GHSZ}}$ will slightly underestimate the change in the global gas hydrate inventory, as GHI scales exponentially with the exponent $b=\sim 1.7$ and not linearly. The reason for this lies in the non-linear pressure- and temperature-dependent solubility limit of methane in seawater. Example simulations with the full transient reaction-transport model upon which the employed transfer function is built [Burwicz et al., 2011], show that the time the system takes to re-equilibrate to a new steady-state is much longer than the here considered time scales of seafloor warming. It is therefore legitimate to assume that the GHI scales linearly with the reduction in the stability zone thickness in the global warming experiments.
For the present-day quantification, global water temperatures and salinities, averaged over the last 20 years of model integration (1988-2007), have been extracted from the lowest water grid box of the ORCA025 model. To evaluate future climate change, the temperature and salinity distributions extracted from the KCM have been three-dimensionally interpolated onto the tripolar grid of ORCA025. This allows a more accurate determination of the bottom slopes and values due to the higher horizontal and vertical resolution of ORCA025. Temperature changes and steady-state GHSZ changes are calculated from the differences between the 22 individual ensemble members (last 30 years) and their corresponding periods of the reference model. For the calculation of transient GHSZ changes, the ensemble mean was derived after the application of the individual gas hydrate stability analyses.

In many deep-sea areas the calculated thickness of the GHSZ is larger than the actual sediment thickness; in these cases the vertical extent was restricted to the sediment thicknesses. For this purpose a combined data set of global sediment thicknesses based on the data sets provided by the NOAA (National Oceanic and Atmospheric Administration) National Geophysical Data Center for the World's oceans and marginal seas [Divins, 2003] and by Laske and Masters [1997] for the Arctic region was used.

Global POC concentrations in marine surface sediments are based on the combination of the data sets provided by Seiter et al. [2004] and Romankevich et al. [2009]. For some areas (e.g. Southern Ocean, south western Pacific) POC concentrations are not available and a default value of 1 wt. % POC is assumed.

3. RESULTS

3.1. PRESENT-DAY CLIMATE CONDITIONS

The global map of the thickness of the GHSZ under steady-state conditions for present-day climate (Figure 3) shows values of up to 600-900 m in polar regions due to low bottom water temperatures (<0°C) and along continental margins where bottom water temperatures are low and a thick sediment cover exists. Thinner GHSZs (<150 m) are predicted for most of the deeper ocean, where the vertical extent is restricted by thin
sediment thicknesses. The shelf regions (above 300 m water depth) feature no stable conditions for structure I gas hydrates because of too high bottom water temperatures (except for permafrost regions but those are not considered in this study). The global volume of sediment within the GHSZ under present-day climate conditions is estimated to be \(87 \times 10^{15}\) m\(^3\). Reassuring is the good agreement with observational values of the depth of the Bottom Simulating Reflector (BSR), which is often used as an indicator for the base of the GHSZ [Haacke et al., 2007], for different regions (Table 1).

![Gas hydrate stability zone (present-day)](image)

Fig. 3. Global map of the gas hydrate stability zone thickness (LGHSZ in m) under present-day climate conditions (mean 1988-2007). The white shadings indicate areas where LGHSZ = 0 m. The dashed contour line marks the 300m isobath.

### Table 1. Thickness of the GHSZ and Depth of the Bottom Simulating Reflector

<table>
<thead>
<tr>
<th>Region</th>
<th>(I_{\text{GHSZ}})</th>
<th>BSR Depth</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arctic (Beaufort Sea)</td>
<td>452 m</td>
<td>300 – 700 m</td>
<td>Andreassen et al. [1997]</td>
</tr>
<tr>
<td>Blake Ridge</td>
<td>447 m</td>
<td>440 – 600 m</td>
<td>Kvenvolden and Lorenson [2000]</td>
</tr>
<tr>
<td>Cascadia Margin</td>
<td>202 m</td>
<td>230 m</td>
<td>Riedel et al. [2006]</td>
</tr>
<tr>
<td>Sea of Okhotsk</td>
<td>331 m</td>
<td>50–900 m</td>
<td>Lüdmann and Wong [2003]</td>
</tr>
<tr>
<td>Norwegian Continental Margin</td>
<td>456 m</td>
<td>270 – 300 m</td>
<td>Mienert et al. [2005]</td>
</tr>
</tbody>
</table>

*Comparison of the mean present-day thickness of the GHSZ (\(I_{\text{GHSZ}}\) in m), including all values > 0 m, estimated according to the method described in section 2.2 with recently published results obtained after calculating the depth of the Bottom Simulating Reflector (BSR in m) for different regions [adapted from Piñero et al., 2013]. Regions are depicted in Figure 6.*
Using the predicted $L_{GHZ}$ (Figure 3), the Quaternary sedimentation rates, and the POC concentration in surface sediments, the abundance and distribution of methane hydrates in marine sediments are calculated using Eq. (6). Figure 4 shows widespread accumulations of hydrate along the continental slopes. The shallower (<300 m water depth) and most of the deeper parts of the ocean do not contain any methane hydrate because the former features too warm bottom water temperatures and the latter is subject to too slow sedimentation as well as POC accumulation rates. In fact, the highest amounts of methane hydrates with values exceeding 260 kg C/m$^2$ are found in areas with high amounts of organic carbon and high sedimentation rates, i.e. off Colombia, Uruguay, the eastern coast of Africa, and the Arabian Sea (Figure 4). The present-day global inventory of marine methane hydrates calculated for Quaternary sedimentation rates amounts to 1146 Gt of methane carbon (Figure 2). In contrast, using Holocene sedimentation rates would provide a minimum estimate of methane hydrate accumulation in marine sediments of just 3 Gt C.

![Methane hydrate concentration](image)

Fig. 4. Present-day global distribution of methane hydrates (kg C/m$^2$) in marine sediments calculated for Quaternary sedimentation rates. For the performed calculations, the sedimentation rates were increased over a 500km wide range close to the coast line; at distance (> 500 km) sedimentation rates have been obtained according to Eq. (8). Note that our sedimentation model explains the predicted hydrate occurrence around e.g. Hawaii and the Galapagos islands, although no hydrate is observed there. The dashed contour line marks the 300m isobath.
3.2. Future Climate Conditions

Considering the ensemble mean trend of bottom water temperatures for future climate change (Figure 5), it is clearly visible that the most dominant changes will occur in the shelf regions, with shallow regions of the Arctic as well as off the coast of Australia and Nova Scotia, around Indonesia, and in the Yellow Sea rising by more than 3°C within the next century. However, the deep ocean appears to remain largely unaffected. Li et al. [2013] found that the deep ocean will respond to global warming with some delay on centennial to millennial time scales (refer to Figure 3 therein). These time scales are not considered in our 100-year approach. In the context of destabilizing methane hydrates, the changes in the deeper ocean play a minor role. The Labrador Sea is even predicted to cool by about 0.5° to 1.5°C at a depth below 1000 m because of a decreased northward heat transport related to a weakened Meridional Overturning Circulation (MOC) [Weaver et al., 2012; IPCC, 2013].

Fig. 5. Global distribution of the ensemble mean trend in bottom water temperatures (°C) over the next 100 years. The dashed contour line marks the 300m isobath.
Steady-state analysis

Under global warming conditions, the thickness of the GHSZ will decrease along the global continental slopes by up to 60 m if steady-state conditions are considered (Figure 6), i.e. the rate of heat diffusion is ignored and a steady-state geotherm for the changed bottom water temperature is assumed. This analysis provides a clearer picture of what may happen to marine gas hydrates under global warming conditions but over predicts the total volume of possible dissociating hydrates. More realistic volume estimates are provided later in the transient analysis. Under steady-state conditions, most changes occur in the depth range 300 to ~1500 m; the deeper ocean and the shelf regions will probably not be subject to any considerable changes due to temperatures remaining in the hydrate or in the gas phase because of the prevailing temperature and pressure conditions.

![Gas hydrate stability zone (ensemble mean trend)](image)

Fig. 6. Global map of the predicted thickness of the gas hydrate stability zone (LGHSZ in m), calculated under steady-state conditions for the ensemble mean trend, where the colored shadings indicate either a reduction (red) or an increase (blue) in the LGHSZ. The colored boxes mark the regions of the Cascadia Margin (CM), Gulf of Mexico (GOM), Blake Ridge (BR), Gulf Stream (GS), Norwegian Continental Margin (NOR), and Sea of Okhotsk (OS). The dashed contour line marks the 300m isobath.
By comparing the bottom water temperature trend (Figure 5) and predicted GHSZ change (Figure 6), it becomes evident that most warming will occur on the continental shelves and the upper parts of the continental slopes. As a consequence, most hydrate melting occurs on the upper continental slope due to the retreat of the GHSZ (Figures 1A and 6). The vertical reduction of the hydrate stability zone (Figure 1B) is of secondary importance within hundreds of years, due to the slow diffusion of heat, and only occurs on the lower parts of the continental slope. The deeper ocean is not significantly affected by seafloor warming and hydrate melting over the next century. In some areas, e.g. the Labrador Sea, the deeper ocean is even subject to a cooling trend. We do not, however, consider the (unlikely) formation of new hydrates over the next hundred years in those areas and for the following only the areas featuring a reduction of the L_{GHSZ} under the future global warming scenario (red shadings in Figure 6) are taken into consideration.

In the steady-state scenario the global volume of sediment within the hydrate stability zone will reduce by approximately 0.3%. In respect to the methane hydrate inventory, this results in a reduction of the global inventory by about 6.7 Gt C (-0.6%).

Table 2. Volume of Sediment Within the GHSZ and Methane Hydrate Inventories (Present-day Estimates and Future Changes)\(^a\)

<table>
<thead>
<tr>
<th>Region</th>
<th>Sediment Volume Within GHSZ</th>
<th>Gas Hydrate Inventory(^d)</th>
<th>Change in Gas Hydrate Inventory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arctic</td>
<td>(3.80 \cdot 10^5) m(^3)</td>
<td>116 Gt C</td>
<td>(-1.4%(^b), (-0.12%(^c))</td>
</tr>
<tr>
<td>Blake Ridge</td>
<td>(0.18 \cdot 10^3) m(^3)</td>
<td>1 Gt C</td>
<td>(-11.5%(^b), (-0.99%(^c))</td>
</tr>
<tr>
<td>Cascadia Margin</td>
<td>(0.11 \cdot 10^3) m(^3)</td>
<td>9 Gt C</td>
<td>(&lt; -0.1%(^b), &lt; -0.01%(^c))</td>
</tr>
<tr>
<td>Sea of Okhotsk</td>
<td>(0.91 \cdot 10^5) m(^3)</td>
<td>39 Gt C</td>
<td>(-0.7%(^b), (-0.05%(^c))</td>
</tr>
<tr>
<td>Gulf of Mexico</td>
<td>(0.54 \cdot 10^5) m(^3)</td>
<td>43 Gt C</td>
<td>(&lt; -0.9%(^b), &lt; -0.03%(^c))</td>
</tr>
<tr>
<td>Norwegian Continental Margin</td>
<td>(0.04 \cdot 10^3) m(^3)</td>
<td>1 Gt C</td>
<td>(&lt; -0.2%(^b), &lt; -0.04%(^c))</td>
</tr>
<tr>
<td>Gulf Stream</td>
<td>(0.12 \cdot 10^5) m(^3)</td>
<td>5 Gt C</td>
<td>(-0.9%(^b), (-0.05%(^c))</td>
</tr>
<tr>
<td>Global</td>
<td>(8.7 \cdot 10^5) m(^3)</td>
<td>1146 Gt C</td>
<td>(-0.6%(^b), (-0.03%(^c))</td>
</tr>
</tbody>
</table>

\(^a\) Present-day estimates of volume of sediment within the GHSZ (in m\(^3\)) and methane hydrate inventories (GHI in Gt C) for the different regions depicted in Figure 6. The changes in the methane hydrate inventories under global warming (in %) are related to present-day climate conditions. Note that no active fluid flow is considered for the calculation of the GHI.

\(^b\) Change in GHI under steady-state conditions.

\(^c\) Change in GHI within the next 100 years under transient state conditions.

\(^d\) The GHI values have been rounded to the nearest whole number.
We chose seven example regions (Table 2, Figure 7) with known hydrate occurrences for further detailed analysis [cf. Kvenvolden and Lorenson, 2001; Lüdemann and Wong, 2003; Riedel et al., 2006; Bohrmann and Torres, 2006; Heeschen et al., 2007; Hester and Brewer, 2009]. Assuming steady-state, the greatest relative changes in the methane hydrate inventory will occur at the Blake Ridge region offshore South Carolina (-11.5%), followed by the Arctic (-1.4%). In contrast, the Cascadian Margin will feature the smallest relative changes which amount to a reduction of about 5 Mt C (<-0.1%). The Norwegian Continental Margin will also be subject to a rather weak decrease in the GHI of 2 Mt C. Note that although covering only ~3% of the global seafloor, the Arctic Ocean accounts for ~24% of the global hydrate inventory loss in the steady-state analysis.

Fig. 7. The predicted change in the distribution of methane hydrates (kg C=m²) under steady-state conditions for the ensemble mean trend for (a) the Arctic and the Norwegian Continental Margin, (b) the Cascadia Margin, Gulf of Mexico, Blake Ridge, and Gulf Stream, and (c) the Sea of Okhotsk. The solid contour lines mark the 300m isobath.

Figure 8 shows seafloor warming over the next 100 years for the seven selected example sites in the context of the methane hydrate phase diagram. The open symbols indicate bottom water temperatures of the present-day climate and the filled symbols those of the
global warming experiment. Progressive (and eventual complete) dissociation of hydrate occurs where the seafloor temperature rises across the phase boundary (cf. Figure 1A). At mid-latitude regions this happens between 450 m (Sea of Okhotsk in Figure 8c) and 600 m (Blake Ridge in Figure 8b and Gulf of Mexico in Figure 8c). In the Arctic, this phase shift occurs already at shallower depths (~380 m) due to the lower bottom water temperatures. Regions where the seafloor is under present-day climate within the hydrate stability field and where warming does not result in a phase shift at the seafloor, a progressive vertical reduction in the GHSZ thickness from below occurs (cf. Figure 1B) on time scales of hundreds to thousands of years. At all example sites the magnitude of warming diminishes with increasing water depth.
Fig. 8. Phase diagrams of methane hydrate as a function of pressure (here denoted by water depth in m) and temperature (°C) considering a constant salinity of 35 for (a) the Arctic and Norwegian Continental Margin, (b) the Blake Ridge and Cascadian Margin as well as for (c) the Sea of Okhotsk, Gulf Stream, and Gulf of Mexico. The open symbols indicate bottom water temperatures of the present-day climate (time mean 1988 to 2007) and the closed symbols those of the global warming experiment. The error bars mark the vertical resolution of the ORCA025 model configuration. Note the different scales of the x-axes.

**Transient state analysis**

A steady-state will not be reached within the next century since heat penetration into marine sediments is relatively slow (see green dotted lines in Figure 1A, B) [Ruppel, 2011; Parmentier et al., 2013]. The more realistic calculation thus accounts for transient heat diffusion into the sediments (Eq. 3).
Fig. 9. (a) Global mean volume change in the GHSZ thickness (10^13 m^3) and (b) global mean change in the methane hydrate inventory (Mt C) as a function of time. The error bars indicate the standard deviations of the 22 ensemble members. The changes are related to present-day climate conditions (Figure 2, Table 2).

Figure 9a shows that within the next 100 years the global volume of sediment within the GHSZ will decrease on average by only 2.4 \times 10^{13} m^3 (~0.03\% of present-day volume). The here not considered consumption of latent heat during hydrate melting might reduce this value even further. Since the global warming scenario with KCM is limited to the next 100 years, it is assumed that bottom water temperatures will remain constant beyond that timeframe and volume changes of the GHSZ were estimated for the next 200 to 500 years (see Figure 9a) by considering a longer time of heat diffusion into the sediment. However, this also means that we calculate a lower estimate, since it is unlikely that bottom water temperatures remain constant after the stabilization of the greenhouse gas concentrations [Park et al., 2009].

Similar to the global values, the regional breakdown also features relative small reductions. Since comparisons of absolute changes make no sense for individual (somehow arbitrary defined) regions, we concentrate on the relative changes. As already indicated by the analysis of the bottom water temperature (Figure 8), largest relative changes are expected in the Arctic and at Blake Ridge offshore South Carolina. Accordingly, the amount of methane released from the seafloor varies among the investigation areas by three orders of magnitude. The largest relative changes will occur at Blake Ridge, where the inventory is on average going to be reduced by almost 6\% (-54 \pm 5 Mt C) after 500 years of heat
penetration into the sediment owing to the strong bottom water temperature increase at the end of the 21st century (cf. Figure 5). The largest absolute release of methane gas will occur in the Arctic, with between 140 ± 10 Mt C and 410 ± 30 Mt C entering the water column of the Arctic Ocean within the next 100 to 500 years. In contrast, changes along the Norwegian Continental Margin are relatively small (~0.9 ± 0.2 Mt C after 500 years), despite the strong exposure to the poleward flowing continuation of the North Atlantic Current. In total, the seven chosen investigation areas account on average for about 52% of the global hydrate inventory change when considering a transient warming of the sediment column over 100 years, whereby the global inventory reduces by ~355 ± 23.5 Mt C (Figure 9b).

4. DISCUSSION

For the present-day climate we estimate that about 1146 Gt C are stored within marine methane hydrate deposits. This value fits fairly well into the range of previously published global estimates (cf. Figure 2), which were either based on field observations or on model studies. Our study improves previous model-based estimates in that we use a high-resolution ocean hindcast model to predict current bottom water temperature and salinity values, global input data sets compiled at the resolution of the ocean model, and a transfer function that is based on a 1D reaction-transport model, which takes the full complexity of the problem into account and has been successfully verified at various test sites [Wallmann et al., 2006; Wallmann et al., 2012].

It should be noted that direct observations might point to very different local hydrate inventories compared to the predicted values shown in Figure 4. This mismatch arises as local pathways for fluid and gas flow are not considered in our approach. Both fluid and gas flow have a strong effect on the accumulation of gas hydrates in marine sediments and could enhance the hydrate inventory [Zatepina and Buffett, 1997; Xu and Ruppel, 1999; Buffett and Archer, 2004; Piñero et al., 2013]. Therefore, the value of 1146 Gt C should be considered as a minimum estimate based on the in-situ microbial degradation of POC. In order to match specific local observations on hydrate occurrences with numerical models,
detailed 3-D model-data integration is necessary. Such an approach is currently not feasible on a global scale due to limitations in both current models and available data sets.

In respect to future climate change, we have shown that the stability of methane hydrates as well as the total hydrate inventory is substantially affected by changing bottom water temperatures. Within the next century, hydrate dissociation will especially occur where the hydrate stability limit is shifted down the continental slope. Hydrate deposits that are located at greater depth will not be affected considerably within the next century owing to the long ventilation times of the deep ocean of up to 1000 years [Krey et al., 2009] and the slow rate of heat diffusion within marine sediments [Ruppel, 2011; Parmentier et al., 2013]. Only a small fraction of the global hydrate inventory is therefore affected by global warming over the next century. A possible effect on global climate thus only seems plausible on millennial and longer time scales [cf. Archer, 2007].

Nevertheless, warming bottom waters will destabilize hydrate deposits on the continental slopes at water depths of ~300-700 m over the next century (see Figure 8), which will result in the release of noticeable amounts of methane into the ocean and potentially into the atmosphere. Especially, the deposits found in the Arctic, at relatively shallow water depth, could undergo rapid dissociation. Observed gas flares and seepage sites [Westbrook et al., 2009; Shakhova et al., 2010] suggest that this is already happening but the evidence remains inconclusive and the observed venting may well be unrelated to global warming [Berndt et al., 2014]. What is clear, however, is that the absolute numbers of methane release will be low. Compared to the 354 Mt CH₄/yr of present-day annual anthropogenic methane emissions [IPCC, 2013], the here predicted ~473 Mt CH₄ of globally released methane covering the full time span of 100 years in the transient scenario is small. This is even an unrealistic upper estimate, since most of the methane released from the seafloor is utilized by microbial processes. Although highly uncertain, it is possible that at least 50% of the dissolved methane is retained inside marine sediments due to anaerobic methane oxidation (AOM) [Treude et al., 2003; Reeburgh, 2007; Knittel and Boetius, 2009]. Mau et al. [2007] recently investigated a massive seep field and found that only ~1% of the methane leaving the seafloor reaches the atmosphere.
Compared to Biastoch et al. [2011], we note that the amount of methane and carbon inventories in the Arctic presented here is much smaller. Specific details in the calculation of the GHSZ thickness (higher resolved ocean model, more global warming ensemble members, and a gradual temperature increase instead of a step function) are of minor importance, given the fact that the GHSZ volume north of 60°N is quite similar. Most important is certainly the inventory calculation. The constant mean hydrate pore filling of 2.4% to 6.1% in Biastoch et al. [2011] led to a much higher inventory of 9000 Gt C for the present climate (note that the inventory in the original version of Biastoch et al. [2011] was incorrectly given by 900 Gt C). The almost two orders of magnitude lower value of ~116 Gt C calculated here demonstrates that the main uncertainty in model-based hydrate estimates is not the volume of sediments within the hydrate stability zone but the computation of the amount of hydrate stored within it. Here we use a transfer function instead of simple pore filling estimates. Future models that further improve on this will help reducing the large uncertainty in current global estimates (cf. Figure 2). Since the amount of released methane is much lower compared to Biastoch et al. [2011], the large-scale impact on acidification and deoxygenation is also smaller. Regional refinement (which is beyond the scope of this study) is needed to identify the local imprint of released methane on the near-bottom chemistry.

Apart from the Arctic, hydrate deposits in relatively shallow waters (300-700 m) in the Gulf of Mexico or along the western North Atlantic Margin will, most likely, be affected by global warming as well [Reagan and Moridis, 2007; Phrampus and Hornbach, 2012; Skarke et al., 2014]. In addition, variations in the location of ocean currents and an additional warming on decadal time scales might lead to the local dissociation of marine gas hydrates. Phrampus and Hornbach [2012] found that the onset of methane hydrate destabilization can already be observed along the western North Atlantic Margin and is attributable to a northwestward shift in the Gulf Stream flow direction as warmer waters are introduced in regions, which have previously been exposed to colder bottom water currents. Both changes in the Gulf Stream flow direction and in ocean temperature could trigger the melting of methane hydrate deposits. It is likely that changing ocean currents, i.e.
variations in the flow direction and/or temperature distribution, might have a significant impact on the stability of methane hydrates in specific regions of the world ocean.

5. CONCLUSION

To improve our understanding of methane hydrates and their fate under global warming, detailed estimates of hydrate inventories are required. Here we provide improved present-day estimates, both for the global scale and specific regions in which hydrates were confirmed by observations.

Despite the significant ocean bottom warming over the next 100 years and the resulting potential phase shifts from methane hydrate to free gas at mid-depth along the continental margins, we find that the release of methane into the water column is very limited throughout the next century. On a global scale, it is negligible compared to the current anthropogenic releases of methane and other greenhouse gases. However, due to the long time scales of deep oceanic processes and the slow penetration of heat into the sediment, the decrease of methane hydrates will continue even beyond a potential recovery of the atmospheric warming.

On a regional scale, the relative decrease of methane hydrate is larger, with the Arctic and Blake Ridge region being most affected by climate change. In this regard, our maps could provide some guidance in which regions the interplay between ocean circulation changes, ocean bottom warming, sediment structure, and localization and quantification of methane hydrate deposits needs to be further investigated.

Apart from the physical and geological approaches, advances are also needed to better quantify the amount of released methane from the sediment and into the atmosphere. Uncertainties of methane consumption within the water column due to microbial consumption are too large to provide reliable estimates on the impact of decreasing methane hydrates onto the climate system.

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REFERENCES


Appendix 3


APPENDIX 4: GLOBAL MARINE SEDIMENTS AS MICROBIAL HABITATS:
DISTRIBUTION OF WATER, ORGANIC CARBON, TEMPERATURE, AND PORE SPACE
IN MARINE SEDIMENTS

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ABSTRACT

Marine sediments are vast biogeochemical reactors that contribute significantly to global element cycles on multiple time scales. Microbial degradation of organic matter is a key driver of not only these transformational processes, but also the modification of paleontological, isotopic and mineralogical signals contained in sediments that are used to decipher the history of the carbon cycle and climatic variation. However, it is unknown how the microorganisms in marine sediments will respond to global climate change and associated perturbations in ocean temperature, salinity, pH, redox chemistry and circulation patterns. In order to assess the extent to which these changes will impact microbially-driven cycles – and how they have influenced them in the past - global data sets describing sedimentation and organic delivery rates, bathymetry, heat conduction and sediment thickness have been combined with a continuum model describing organic
matter degradation to quantify the distribution of water, temperature and organic matter in marine sediments. The resulting quantitative description of the physiochemical properties of global marine sediments as a habitat for microorganisms has yielded new estimates for the global volume \((3.038 \times 10^8 \text{ km}^3)\) and average thickness of marine sediments (840 m) and their volumetric distribution on shelf, margin and abyssal settings. A porosity model adopted in this study has been used to generate the only known estimate of the global volume of marine sedimentary pore water \((8.103 \times 10^7 \text{ km}^3)\), 7% of the global oceans and larger than the Southern Ocean. In addition, a three-dimensional model for the thermal structure of marine sediments has revealed that \(\sim 42\%\) are above 40°C, suggesting a vast potential niche for thermophilic organisms. Furthermore, an organic matter degradation model has been applied on a global scale to reveal the 3-D distribution of particular organic matter in marine sediments deposited throughout the Quaternary, encompassing the most microbially active layers of marine sediment. Three levels of organic matter degradability were considered that effectively serve as proxies for global marine sediment microbial biomass and activity levels throughout the last 2.6 Ma of marine sediments. The results of these scenarios indicate that the rate of organic matter degradation in Holocene sediments is 361 Tg C yr\(^{-1}\), while the rate in the much more voluminous Pleistocene-aged sediments is only 11 Tg C yr\(^{-1}\). The fraction of organic matter that has escaped burial in both the Holocene and Pleistocene are geographically highly variable. These results are discussed in the context of the role of microbial activity in shaping diagenesis, influencing the carbon cycle, and the extent of life in the subsurface.

**Keywords:** deep biosphere, biogeochemistry, diagenesis, organic matter, element cycles

1. **INTRODUCTION**

Microorganisms have been found in numerous subsurface environments including marine and fresh water sediments, mines, the oceanic lithosphere, aquifers, hydrocarbon reservoirs, salt deposits, caves, permafrost, sedimentary rocks as well as on and under ice.
sheets and glaciers (Schrenk et al., 2010; Heim, 2011; Orcutt et al., 2011; Colwell and D’Hondt, 2013; Jungbluth et al., 2013). In many of these settings, little is known about what reactions the organisms are catalyzing or at what rate they are active. As a result, the influence that microorganisms have driving global element cycles in a significant fraction of Earth’s habitable volume and thus their influence on past, present and global climate is poorly understood. It is known, however, that the microbial degradation of organic carbon in marine sediments plays a major role in controlling levels of oxygen and CO₂ in the atmosphere on long time scales (Rothman, 2002; Berner, 2006) and on the amount of CH₄ that is stored in near-shore sediments (Burwicz et al., 2011). It has been estimated, in fact, that more CH₄ has been produced by methanogens degrading petroleum reservoirs than there is primary CH₄ produced from catagenesis (Milkov, 2011). On a shorter time-scale, the microbial processing of organic carbon in the upper tens of centimeters of marine sediments leads to dynamic Fe, Mn and S cycles that influence ocean chemistry (e.g., Berner, 1980; Middelburg, 1989; Boudreau and Ruddick, 1991; Canfield, 1993; Tromp et al., 1995; Jørgensen and Kasten, 2006; Thullner et al., 2009). Throughout the sediment column, the (selective) microbial degradation of organic matter can impact the various sets of isotopic and biomarker data that are used to interpret paleoenvironmental records (Zonneveld et al., 2010). As ocean chemistry is altered by global climate change and anthropogenic activity alters marine microbial communities (Capone and Hutchins, 2013; Nogales et al., 2013), it is unclear if or how the rates of diagenetic processes will respond to climate change on geologically short timescales (< 1000 yrs). Also, as more subsurface environments are used to store nuclear waste and as potential repositories for CO₂, it is critical to know how these organisms will respond to such incursions into their habitats (Colwell and D’Hondt, 2013). In addition to their roles in geochemical cycles, the relatively recent acknowledgment that microorganisms exist throughout the subseafloor (Edwards et al., 2011; Orcutt et al., 2011; Edwards et al., 2012a; Edwards et al., 2012b; Jungbluth et al., 2013; Orcutt et al., 2013a; Robador et al., 2015) also brings up questions about the extent and limits of life on Earth and beyond.
Although the role of microbial activity in sediments was long thought to be confined to the sediment-seawater interface, SWI, near coastal margins, a number of sediment cores retrieved during ODP/IODP expeditions have revealed viable microorganisms far from coasts and hundreds of meters below the SWI (Parkes et al., 2000; Kallmeyer et al., 2012; Orcutt et al., 2014). The microbial cell count data that were available by the late 1990s were used to estimate that up to one third of the Earth’s living biomass resides in ocean sediments (~3.6 x 10^30 cells) (Whitman et al., 1998). With the addition of cell count data representing more marine habitats, the amount of biomass thought to be in marine sediments has decreased substantially: 2.9 x 10^29 cells, 4.1 petagrams C, 0.6% of Earth’s living biomass (Kallmeyer et al., 2012). Whatever the size of the marine sediment biosphere, the larger question for understanding its impact of global biogeochemical cycles is what the microorganisms are doing, how fast are they doing it and what if any influence do they have on diagenesis throughout the depths of ocean sediments (Orcutt et al., 2013a).

It is particularly important for understanding the carbon cycle to quantify what microorganisms are doing in sediments since there is evidence that they are more active in sediments than in the overlying water column with respect to organic matter (Arnosti, 2015). Furthermore, since broad extremes in physical and chemical conditions can be found in the vast subseafloor, this environment is a likely candidate for delineating at least some of the limits of life. For instance, extremes in pressure, energy availability, isolation, physical space, and temperature can all be found in marine sediments in various combinations.

In order to begin to be able to quantify the impact of microbial activity on the biogeochemistry of marine sediments and how climate change might alter this role, it is crucial to develop a better quantitative description of their habitat in terms of the main controls on microbial activity such as temperature and energy availability. Towards this end several global data sets including bathymetry, heat flow, bottom water temperature, sediment thickness and particulate organic carbon deposition have been combined with modeling efforts to provide three-dimensional maps of the distribution of organic matter, porosity and temperature in global marine sediments. In addition, these data are used to
constrain how much organic matter resides and has been degraded in marine sediments deposited since the beginning of the Quaternary (0 – 2.6 Ma), which include the most microbially active portions of marine sediments. Taken together, this global-scale quantitative description of the physiochemical properties marine sediments can be used to constrain the activity level of microorganisms in marine sediments and to better understand their physiochemical history with implications for paleoclimate studies and the limits of life.

2. SIZE

Marine sediments are the unconsolidated rock particles, marine organisms, volcanic material, authigenic precipitates, cosmogenic deposits and organic carbon that constitute the uppermost layer of most oceanic crust, and blanket nearly 31% of the continental crust that lies under seawater (Cogley, 1984). By covering $3.6 \times 10^9$ km$^2$ (Eakins and Sharman, 2010), they comprise one of the largest features of Earth’s surface and therefore one of its largest habitats and carbon reservoirs. The delivery rate of sediment to the seafloor under different water depths are listed in Table 1. Here, it can be seen that nearly 72% of the annual deposition of marine sediment is delivered to water less than 200 m deep, at a rate of $≈519$ g m$^{-2}$ y$^{-1}$. By contrast, ocean floor sediments under more than 3000 m of water receive a total of $32.6$ g m$^{-2}$ y$^{-1}$, despite covering 75% of the ocean floor. The result of this differential delivery of sediments is illustrated in Figure 1. Here, a global sediment thickness map, presented on a 0.25 x 0.25 degree grid and generated from data taken from (Divins, 2003) and (Laske and Masters, 1997), shows that the sedimentation rates presented in Table 1 have persisted long enough for thousands of meters of sediments to be deposited on continental margins. It can be seen in Fig. 1 that in numerous locations, the yellow, orange and red colors, that sediment thickness exceeds 5000 m. The royal- and dark-blue colors in Fig. 1 show that throughout broad expanses of the ocean, sediment thickness is less than 1000 m. In a number of locations, such as the Bay of Bengal, the Gulf of Mexico and Arctic regions, sediments thicker than 10,000 m can be found. The deepest sediment, at 18,126 m, is about 60 km northwest of Trinidad and Tobago.
Table 1. Surface area and sediment accumulation rates of selected depth intervals of the global ocean

<table>
<thead>
<tr>
<th>Seafloor area</th>
<th>Sediment accumulation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>water depth (m)</td>
<td>⁴(km²)</td>
</tr>
<tr>
<td>0-200</td>
<td>271.23</td>
</tr>
<tr>
<td>200-1000</td>
<td>160.12</td>
</tr>
<tr>
<td>1000-2000</td>
<td>158.44</td>
</tr>
<tr>
<td>2000-3000</td>
<td>307.62</td>
</tr>
<tr>
<td>3000-4000</td>
<td>758.24</td>
</tr>
<tr>
<td>4000-5000</td>
<td>1147.25</td>
</tr>
<tr>
<td>5000-6000</td>
<td>767.53</td>
</tr>
<tr>
<td>6000-7000</td>
<td>44.61</td>
</tr>
<tr>
<td>7000-11000</td>
<td>5.29</td>
</tr>
<tr>
<td>Total</td>
<td>3620.33</td>
</tr>
</tbody>
</table>

⁴Menard and Smith (1966); ⁵Burwicz et al. (2011)

The thicknesses data discussed above can be combined with the surficial expanse of sediments to calculate a high-resolution volume of marine sediments, ~3.04 x 10⁸ km³ (given in Table 2). Of this total, more than 73% lies within 500 km of coast lines, ~2.22 x 10⁸ km³. It is difficult to explain the discrepancies of the global sediment volume with the source of another published value, 4.5 x 10⁸ km³ (Kennett, 1982) because the cited reference for this value is a personal communication. As a basis of comparison, the global volume of seawater is 1.335 x 10⁹ km³ (Eakins and Sharman, 2010), just 4.3 times the volume of marine sediments. Although marine sediments are highly unevenly distributed (Fig. 1), the above stated values for the surface area and volume of sediment leads to an average thickness of 840 m, 68% thicker than other commonly cited estimates (e.g., 500 m, (Fowler, 1990; Fry et al., 2008)). Determining the thickness of sediments has implications for quantifying the distribution of pore space, water, temperature and organic matter in marine systems.
Figure 1. Global map of marine sediment thickness (km) at a resolution of 0.25° x 0.25° based on the data sets from Laske and Masters (1997) and Divins (2003).

The ocean floor is partitioned into shelf, margin and abyss domains in order to specify values for several of the parameters discussed below. The location of the continental margin boundaries was adopted from (Vion and Menot, 2009): shelf environments roughly correspond to water depths < 140 m, with the exception of the Antarctic region where shelf area corresponds to water depths < 500 m; areas deeper than ~3500 m are taken to be abyssal plain. Within these definitional constraints, continental shelf is about 5.70% of ocean surface area, margins make up 10.33% and the abyssal domain constitutes the remaining 83.97%. The map shown in Figure 2 shows the locations of these domains. Although not directly comparable, the percent surface of these domains roughly aligns with those for various water depths reported in (Menard and Smith, 1966), which was generated from a different data set and is shown in Table 1.
3. Porosity

One of the defining characteristics of all known life is the requirement for water. Typically, the distribution of the Earth’s surface water is divided into major categories such as oceans, ice and snow, groundwater and lesser bodies such as permafrost, lakes and the atmosphere, e.g., (Shiklomanov, 1993) (see Table 2 for volumes of some of these bodies of water). Even though the volume of marine sediments is about 23% of the volume of global ocean water, the amount of pore water in global marine sediments is underappreciated, or more typically, ignored. For instance, in the widely cited compilation of global water reservoirs by Shiklomanov (1993), there is no mention of marine sediment pore water, yet there are entries for very small reservoirs such as swamp water \(11,470 \text{ km}^3\) and biological water \(1,120 \text{ km}^3\).
Table 2. Volumes of selected water bodies and marine sediments pore waters at various temperature intervals

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of global marine sediments</td>
<td></td>
<td>calculated here</td>
</tr>
<tr>
<td>sediment pore water</td>
<td>8.1031 x 10⁷ km³</td>
<td></td>
</tr>
<tr>
<td>Volume of oceans</td>
<td>1.335 x 10⁷ km³</td>
<td>Eakins and Sharman (2010)</td>
</tr>
<tr>
<td>Volume of Southern Ocean⁴</td>
<td>7.180 x 10⁷ km³</td>
<td>Eakins and Sharman (2010)</td>
</tr>
<tr>
<td>Volume of Arctic Ocean</td>
<td>1.875 x 10⁷ km³</td>
<td>Eakins and Sharman (2010)</td>
</tr>
<tr>
<td>Volume of groundwater</td>
<td>2.34 x 10⁷ km³</td>
<td>Shiklomanov (1993)</td>
</tr>
<tr>
<td>Volume of Lakes</td>
<td>1.764 x 10⁷ km³</td>
<td>Shiklomanov (1993)</td>
</tr>
<tr>
<td>free water in upper ocean crust</td>
<td>2.6 x 10⁷ km³</td>
<td>Johnson and Pruis (2003)</td>
</tr>
<tr>
<td>Average ocean depth</td>
<td>3688 m</td>
<td>Eakins and Sharman (2010)</td>
</tr>
<tr>
<td>Average sediment thickness</td>
<td>840 m</td>
<td>calculated here</td>
</tr>
</tbody>
</table>

Volume of ocean sediments in particular temperature ranges

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Volume</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0°C</td>
<td>4.2202 x 10⁷ km³</td>
<td>calculated here</td>
</tr>
<tr>
<td>0 - 20°C</td>
<td>9.9805 x 10⁷ km³</td>
<td>calculated here</td>
</tr>
<tr>
<td>20 - 40°C</td>
<td>7.5334 x 10⁷ km³</td>
<td>calculated here</td>
</tr>
<tr>
<td>40 - 60°C</td>
<td>4.6924 x 10⁷ km³</td>
<td>calculated here</td>
</tr>
<tr>
<td>60 - 80°C</td>
<td>2.9575 x 10⁷ km³</td>
<td>calculated here</td>
</tr>
<tr>
<td>80 - 100°C</td>
<td>1.8850 x 10⁷ km³</td>
<td>calculated here</td>
</tr>
<tr>
<td>100 - 120°C</td>
<td>1.2262 x 10⁷ km³</td>
<td>calculated here</td>
</tr>
<tr>
<td>&gt; 120°C</td>
<td>2.0666 x 10⁷ km³</td>
<td>calculated here</td>
</tr>
<tr>
<td>Total volume</td>
<td>3.0384 x 10⁷ km³</td>
<td>calculated here</td>
</tr>
</tbody>
</table>

*Includes Weddell and Ross seas without ice cover

In order to determine the amount of water in marine sediment pore spaces, and for the organic carbon modeling work discussed below, a sediment compaction model has been developed to estimate the porosity structure of marine sediments. In this model, porosity, $\phi$, is calculated as a function of depth, $z$, using a standard formulation commonly used in basin-to-global scale porosity studies (Athy, 1930):

$$\phi(z) = \phi_0 \exp(-c_z z)$$  (1)
where $\phi_0$ denotes the porosity at the SWI and $c_0$ stands for the compaction length scale, which characterizes how a given sediment type will compact under its own weight. For simplicity and clarity, values of $\phi_0$ and $c_0$ were chosen to describe the shelf, margin and abyss based on sediments that are representative of these domains (Hantschel and Kauerauf, 2009) (see Table 3). Specifically, the values of $\phi_0$ for shelf, margin and abyss, 0.45, 0.6, and 0.7, are representative of a sandstone-siltstone mixture, a siltstone-shale combinations and typical shales and biogenic-dominated sediments, respectively. Similarly, the respective values of $c_0$ adopted for the shelf, margin and abyss domains are $5 \times 10^{-4}$, $6.5 \times 10^{-4}$ and $8.5 \times 10^{-4}$ m$^{-1}$, which are typical of an organic-rich limestone-siltstone mix, a limestone-chalk with 40% calcite and shale.

Using the sediment thickness data depicted in Fig. 1 together with Eq. (1) and the values of $\phi_0$ and $c_0$ noted in Table 3, porosity profiles for the shelf, margin and abyss domains are plotted as a function of depth down to 500 m in Figure 3. The model summarized by Eq. (1) assumes that compaction increases with depth, but it should be noted that mineral grain type, temperature and the proximity of tectonic activity are variables that could cause deviation from the smoothly varying porosity depicted in Fig. 3. For instance, secondary porosity can be generated up to 2.5 km into sediments where feldspars and volcanic rocks dissolve, and where fractures form due to tectonic activity (Prothero and Schwab, 2004). In addition, although sediment accumulation rates, which include water, are greater than the upward advection of pore water due to compression, fluid seepage out of sediments can occur in areas where compaction is enhanced by tectonic activity, such as at cold seeps and mud volcanoes (Wallmann et al., 2012). From a microbiological perspective, not only is pore space changing with depth, but the geometry of pores and pore-throat size might further restrict habitable volume by limiting hydraulic connectivity or/and diffusion of electron donors/acceptrs and nutrients. Moreover, as sediments are compressed, grains might puncture cells or cause tensile failure (Rebata-Landa and Santamarina, 2006).
Table 3. Selected values of parameters used to characterize the temperature, porosity and organic matter content of continental margin, continental slope and abyss domains of global marine sediments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Shelf</th>
<th>Margin</th>
<th>Abyss</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(f_o)</td>
<td>sediment porosity at the sediment-water interface</td>
<td>0.45</td>
<td>0.6</td>
<td>0.7</td>
<td>(-)</td>
</tr>
<tr>
<td>(c_o)</td>
<td>sediment compaction length scale</td>
<td>(5 \times 10^4)</td>
<td>(6.5 \times 10^4)</td>
<td>(8.5 \times 10^4)</td>
<td>m(^{-1})</td>
</tr>
<tr>
<td>(l_s)</td>
<td>thermal conductivity of sediment grains</td>
<td>3.95</td>
<td>3.00</td>
<td>1.64</td>
<td>W m(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>(a)</td>
<td>reactive continuum age parameter</td>
<td>50</td>
<td>1000</td>
<td>5000</td>
<td>yr</td>
</tr>
<tr>
<td>(n)</td>
<td>reactive continuum distribution parameter</td>
<td>0.20</td>
<td>0.15</td>
<td>0.13</td>
<td>(-)</td>
</tr>
</tbody>
</table>

If all of the pore space calculated to exist using Eq. (1) and a three-domain model for sediment types is occupied by H\(_2\)O, then this would be equivalent to \(~8.103 \times 10^7\) km\(^3\) of water. This volume of pore water would be about 7% of the global ocean and larger than both the Southern Ocean and five times the volume of the Arctic Ocean (see Table 2). Marine sediment pore water would be three times as abundant as the free water that is thought to fill the open spaces in the global igneous ocean aquifer (Johnson and Pruis, 2003), a potentially massive microbial habitat. To our knowledge, no estimates of this quantity have been published in the literature, but the repercussions of including this body of water in the global hydrological cycle could be profound since it is compositionally distinct from ocean water, typically enriched in volatiles, trace elements, alkalinity and dissolved inorganic carbon (Deyhle and Kopf, 2001). In fact, significant quantities of sedimentary pore water are released into the ocean every year through active mud volcanoes (Milkov, 2000; Dimitrov, 2002; Kopf, 2002), which have been observed on continental shelves, continental slopes and the abyssal plains of inland seas numbering between 1,000 and 100,000 (Milkov, 2000). The wide-spread occurrence of mud volcanoes is due to numerous processes that can give rise to high flow through channels: tectonic compaction, biogenic and thermogenic methane production, seismic activity, rapid sedimentation, deep-seated thrusts, catagenesis, mineral dehydration (e.g., opal, smectite),
hydrothermal alteration of crustal rock and deformation within diapiric intrusions (Milkov, 2000; Kopf, 2002).

Figure 3. Calculated porosity as a function of sediment depth for continental shelf, continental margin and abyss domains. See Fig. 2 caption and text for definitions of these domains.

4. TEMPERATURE

Although there are many factors that determine the habitability of a given environment, one of the most commonly discussed is temperature (Takai et al., 2014). The temperature range for observed laboratory microbial growth is currently -15 to 122°C (Takai et al., 2008; Mykytczuk et al., 2013), although microorganisms can survive being flash frozen in liquid nitrogen (-196°C), are routinely revived from storage in cryogenic freezers (-150°C), have been observed to survive hours below 5 K (Lipman, 1936) and have been found living in fluids that were >250°C when sampled (Takai et al., 2004; Takai et al., 2008). Given that the temperature limit to life is unknown, a thermal description of a location does not definitively determine its habitability. However, temperature is a key variable that influences other habitability parameters such as whether or not liquid water can exist, diffusion and reaction rates, and the energetics of catabolic and anabolic reactions. It is likely that the limit to life in the deep biosphere is a combination of physical and chemical
variables. In order to determine the temperature of marine sediments as a function of depth and location, the model described below was used, rather than simply assuming a particular geothermal gradient and applying it to all the world’s sediments.

The temperature of marine sediments as a function of depth, $T_z$, was calculated using

$$ T_z = T_{SWI} + \frac{q \cdot z}{\lambda_b} $$

(2)

where $T_{SWI}$ (K) stands for the temperature at the sediment water interface, $q$ (W m$^{-2}$) represents heat flow, $\lambda_b$ (W m$^{-1}$ K$^{-1}$) refers to the thermal conductivity of the bulk sediment and $z$ stands for depth below the SWI (m). Values of $T_{SWI}$ were taken to be equivalent to bottom water temperatures that were extracted from the ORCA_R025 (Barnier, 2006) configuration for an ocean general circulation model, while those for $q$ were taken from the International Heat Flow Commission (Hamza et al., 2008). In order to represent how variable porosity and mineralogy affect the thermal conductivity of marine sediments, values of $\lambda_b$ were calculated using the geometric mean of the thermal conductivities of pore fluid and sediment grains (Fuchs et al., 2013):

$$ \lambda_b = \lambda_s^{1-\phi} \cdot \lambda_f^\phi $$

(3)

where $\lambda_s$ and $\lambda_f$ refer to the thermal conductivity of sediment grains and pore fluids, respectively, and as in Eq. (1), $\phi$ designates porosity. Values of $\lambda_s$ for shelf, margin and abyss sediments are taken to be 3.95, 3 and 1.64 W m$^{-1}$ K$^{-1}$ (Hantschel and Kauerauf, 2009), respectively, reflecting sandstone, limestone and shale sediment grain types commonly found in these settings (Einsele, 2000) and $\lambda_f$ was taken to be 0.59 W m$^{-1}$ K$^{-1}$. The resulting distribution of temperature in marine sediments is depicted in Figure 4.
Figure 4. Global Distribution of temperature in marine sediments. In each panel, the thickness of marine sediments within the indicated temperature range is given for a particular grid cell. Note that the scale, and therefore the color palette, for each panel is different, especially that for the hottest sediments (> 120°C), panel h.

Because microorganisms in extreme environments are often classified by their optimal growth temperature, e.g., psychrophile (< 15°C), mesophile (20 – 45°C), hyperthermophile (> 80°C), the results of the sediment temperature calculations are shown in a series of figures corresponding to the thickness of sediment that is within a given temperature range at a particular location. For instance, Fig. 4c shows the thickness of sediment that is between 20 and 40°C and Figure 4f shows where sediments are between 60-80°C. The
scales of most of the panels are the same indicating that at locations where sediments are thick enough, there are hundreds of meters of sediment that are in each of the 20-degree temperature bins, with the exception of the Figure 4h. In this figure, the scale indicates that there are sediments thousands of meters thick that are greater than 120°C. By integrating the thicknesses of sediments that fall in the temperature bins shown in Fig. 5, the global volumes of sediments characterized by the same temperature intervals can be computed (Table 2). As the values in Table 2 show, 32.85% of the world’s marine sediments are between 0°C, and 20°C, with another 24.75% between 20°C, and 40°C. It is noteworthy that over 42% of marine sediments are above 40°C, indicating that a large proportion of the volume of marine sediments is suitable for thermophilic organisms.

5. SEDIMENTARY ORGANIC MATTER

In addition to the physiochemical constraints discussed above, one of the most important factors determining whether a given microbial population increases, decreases or stays the same size is the amount of energy that is available to it. The rate at which energy is made available in marine sediments, the microbial power supply (see (LaRowe and Amend, 2015)), is largely controlled by the rate at which particulate organic matter, POC, is delivered to sediments, which is in turn influenced by a number of factors including the overall sedimentation rate (see Table 1). The accumulation rate of POC in marine sediments throughout the Holocene and the Pleistocene are shown in Figure 5. The maps are taken from (Wallmann et al., 2012) and were generated using data from (Seiter et al., 2004) and (Romankevich et al., 2009) and an algorithm that correlates water depth and sedimentation rate (Burwicz et al., 2011) to estimate POC accumulation in areas where no data have been reported in the literature.
As with sediment deposition (Table 1), POC deposition is focused on continental margins. It can be seen in Fig. 5 how Wallmann et al. (2012) came to estimate that 88% of organic matter, OM, is deposited within 500 km of shoreline and that the rest of the globe’s sediments only receive about 12% of the global annual flux of POC. This is why the global distribution of microbial cells have been estimated, based on cell counts, to be several orders of magnitude greater near margins than in the abyss (Kallmeyer et al., 2012). In fact, the vast majority of organic carbon that reaches the SWI is biologically oxidized to CO₂ with a relatively small number of electron acceptors (EAs) in the upper tens of centimeters of sediment. Estimates of POC mineralization rates in surface sediments range from 7 - 31 x 10^{11} kg C yr⁻¹ (Burdige, 2007), whereas the global rate of POC delivery to marine sediments is thought to be 9.3 - 32 x 10^{11} kg C yr⁻¹ (Dunne et al., 2007). Some fraction of this POC is buried deep enough that it enters the methanogenic zone, where microorganisms convert residual organic matter and fermentation products such as H₂ into methane. Wallman et al. (2012) estimate that 0.12 – 3.3 x 10^{11} kg CH₄ are produced by microorganisms in marine sediments each year, which is mostly oxidized by anaerobic methane oxidizing microorganisms, or becomes bound up in methane clathrates. Beneath the biologically mediated methanogenic zone, POC remineralization either ceases or becomes so slow that it’s imperceptible. It should be noted that at many depths, there may
be microbial communities that are energetically supported by chemolithotrophic catabolisms, and that in other locations, seawater from underlying oceanic basement rock can provide electron acceptors that fuel another zone of microbial activity (e.g., (Elderfield et al., 1999; D’Hondt et al., 2004; Orcutt et al., 2013b). However, it is the initial oxidation of organic matter that drives the vast majority of these secondary redox reactions (Berner, 1980; Canfield, 1993; Thullner et al., 2009).

Between 1.5 - 26 x 10¹¹ kg C yr⁻¹ of organic matter reaching marine sediments is neither oxidized to CO₂ or reduced to CH₄ in the biologically most active upper sediment layers (Burdige, 2007). Although there a number of factors as to why this is the case (see (Burdige, 2007), (Zonneveld et al., 2010) and (Arndt et al., 2013) for recent reviews), most of the organic compounds that escape immediate mineralization tend to be unidentifiable with current characterization techniques (Burdige 2007). This molecularly uncharacterized organic matter (MU-OM) is mostly comprised of carboxyl and aromatic groups (Hedges and Oades, 1997) that, given sufficient burial depth, will become kerogen (Burdige 2007), a variable, high-molecular weight complex organic compound that is the source of petroleum. Although MU-OM and kerogen are typically classified as recalcitrant forms of organic matter, this does not mean that they are not biologically active (Petsch et al., 2000; Henrichs, 2005; Moodley et al., 2005; Burdige, 2007), it is that they are only very slowly transformed by microorganisms.

However, our quantitative understanding of the degradation and burial of organic matter on the global scale is limited due to the difficulty to constrain both the rate of organic matter deposition and its reactivity in data-poor areas (e.g., Arndt et al., 2013). This can be seen in the ranges of global deposition, degradation and burial rates listed above that overlap considerably, indicating how poorly these numbers are known. The major reason for this is that many of these estimates are based on global relationships derived from large data compilations. For example, organic carbon deposition is often linked to satellite-derived net primary production, burial efficiency is connected to net sediment accumulation rate and organic matter degradation rates are simply correlated to water depth (see Table 3 in Burdige, 2007). They are thus not only associated with large
uncertainties, but also affected by sampling biases skewed towards biogeochemical hotspots (e.g. Henrichs, 1993). The global data sets discussed in the previous sections may help remove some of this bias and reduce uncertainty. In particular, the global map of organic carbon deposition is based on a careful compilation and extrapolation of organic carbon contents in marine sediments from (Seiter et al., 2004) and (Romankevich et al., 2009). Here, we use the global maps of OM burial rate, porosity and organic carbon deposition in combination with a modeling approach (see below) to derive three-dimensional maps of the distribution of organic matter in marine sediments. In addition, these data are used to estimate how much organic matter resides and has been degraded in marine sediments deposited since the beginning of the Quaternary (0-2.6 Ma), a period for which global organic carbon fluxes and burial rates can be estimated with an acceptable level of uncertainty.

5.1. Quantification of Organic Matter Degradation and Burial in Holocene and Pleistocene Marine Sediments

In order to assess the degradation and burial of OM deposited in marine sediments throughout the Quaternary (0-2.56 Ma) on a global scale, the depth distribution of OM is estimated by dividing the sediment into a bioturbated layer (<10 cm) and a non-bioturbated layer (> 10 cm) and applying a simple 1G-model (e.g., Berner, 1980) to describe organic matter degradation in the bioturbated zone and a reactive continuum model (RCM, Boudreau and Ruddick, 1991) in the non-bioturbated zone. In the 1G model, all sedimentary organic matter is treated as a single pool that is degraded at a constant rate following first-order kinetics. This approach is a simple linear approximation for the degradation of a complex and heterogeneous mixture of different organic matter compounds. This simplification is a reasonable approximation of the degradation dynamics in the bioturbated zone where sediments are constantly mixed by infaunal activity. The organic matter concentration at the bottom of the bioturbated zone, $OM(z_{bio})$, under steady state conditions can then be calculated by solving the advection-diffusion-reaction equation (e.g. (Boudreau, 1997)): 
\[ OM(z_{bio}) = OM_0 \cdot \exp \left( \frac{\omega - \sqrt{\omega^2 + 4D_b k}}{2D_b} \cdot z \right) \]  \hspace{1cm} (4)

where \( OM_0 \) denotes content of organic matter at the sediment water interface, \( \omega \) refers to the burial rate, \( D_b \) corresponds to the bioturbation coefficient and \( k \) designates the first-order rate constant of organic matter degradation in the bioturbated layer.

Organic matter degradation below the bioturbated zone (\( > 10\text{cm} \)) is described by the RCM. The RCM assumes a continuous distribution of organic matter compounds over a range of reactivities. This avoids the need to partition the bulk material into a limited, but unknown, number of discrete compound classes, and therefore reduces the number of parameters that must be constrained. Within the RCM, the overall rate of organic matter degradation, \( R_{tot} \), for a continuous distribution of organic compounds is given by the integral:

\[ R_{tot} = -\int_0^\infty k \cdot om(k, t) dk \]  \hspace{1cm} (5)

where \( om(k, t) \) denotes a function that determines the concentration of organic matter having a degradability between \( k \) and \( k + dk \) at time \( t \), with \( k \) being analogous to a rate constant. The initial distribution, \( om(k, 0) \), may take different mathematical forms, but cannot be inferred by observations. Here, a Gamma function is used, as proposed by Boudreau and Ruddick (1991), following (Aris, 1968) and (Ho and Aris, 1987). Although their choice was partly guided by mathematical expediency, the Gamma function has the advantage of capturing the organic matter degradation dynamics observed in nature. Under these assumptions, the evolution of the bulk organic matter concentration as a function of depth, \( OM(z) \), is given by (Boudreau and Ruddick, 1991):

\[ OM(z) = OM(z_{bio}) \cdot \left( \frac{a}{a + age(z)} \right)^y \]  \hspace{1cm} (6)
where $a$ and $v$ represent reactive continuum model parameters (Boudreau and Ruddick, 1991; Arndt et al., 2013), $OM(z_{bio})$ stands for the organic carbon content at the bottom of the bioturbated zone (10 cm) derived from Eq. (4) and $age(z)$ refers to the age of the sediment layer at depth $z$. Values of $age(z)$ can be calculated on the basis of burial rates, $\omega (z)$, and porosity depth profiles $\phi (z)$. Assuming an exponentially decreasing porosity, Eq. (1), and steady-state compaction, the burial velocity, $\omega$ at depth $z$ is then:

$$\omega(z) = \left( \frac{1 - \phi_n}{1 - \phi(z)} \right) \omega_n$$

(7)

where $\phi_n$ and $\omega_n$ correspond to the porosity and burial velocity, respectively, at depths where compaction is negligible. The free, positive parameters $a$ and $v$ completely determine the shape of the initial distribution of organic matter compounds over the range of $k$ values and, thus, its overall reactivity. High $v$ and low $a$ values indicate a mixture of organics dominated by labile compounds, which are typically degraded rapidly. Low $v$ and high $a$ values, on the other hand, indicate a larger fraction of refractory compounds that degrade slowly. The parameter $a$ controls the lifetime of the most reactive compounds. Low $a$ values result in a rapid loss of the most reactive types, resulting in an increasing probability that the remaining organic compounds are less reactive. Therefore, for a constant value of $v$, low $a$ values indicate a higher degradability at the sediment–water interface and a faster decrease in OM concentration with depth. High $a$ values, on the other hand, reflect a longer lifetime of the most reactive types and lead to a slower shift of the probability distribution to less reactive types as degradation proceeds. For a constant $v$ value, high $a$ values lead to a lower degradability at the sediment–water interface, but a slower decrease of degradability with sediment depth.

The age of a given sediment layer at depth $z$ below the bioturbated zone, $age(z)$, is given by (e.g., Berner, 1980):
Appendix 4

\[ \text{age}(z) = \int_0^z \omega^{-1} \, dz \]  
\[ \text{(8)} \]

Substituting Eq. (7) into Eq. (8) results in

\[ \text{age}(z) = \frac{1}{(1 - \phi_\infty) \omega_\infty} \int_0^z (1 - \phi) \, dz \]  
\[ \text{(9)} \]

which, upon integration, leads to

\[ \text{age}(z) = \frac{z + \frac{\phi(0)}{c_0} \cdot (e^{-\omega_0 \cdot z}) - 1}{\omega(0) \cdot (1 - \phi(0))} \]  
\[ \text{(10)} \]

where \( \phi(0) \) and \( \omega(0) \) indicate the porosity and burial rate at the SWI, respectively.

The depth distribution of organic matter in marine sediments deposited since the beginning of the Quaternary can thus be calculated if the burial rate, porosity, bulk organic matter concentration at the SWI, \( OM_\infty \) and the distribution of organic compounds across the reactivity range at the sediment-water interface is known and/or specified (parameters in Eq. (5-10)). Here, we assume the constant organic carbon accumulation rates for the Holocene and Pleistocene shown in Fig. 5.

Holocene and Pleistocene organic matter contents at the sediment water interface, \( OM_\infty \) as well as sedimentation rates are based on (Wallmann et al., 2012) who used data from (Seiter et al., 2004) and (Romankevich et al., 2009) and an algorithm that correlates water depth and sedimentation rate (Burwicz et al., 2011). Porosity profiles are calculated according to Eq. (1) and the parameters detailed in Section 3. The organic matter reactivity parameters of the 1G-model, \( k \), and the RCM, \( a \) and \( \nu \) are generally determined by finding a best fit to observed OM and pore-water profiles at specific sites (e.g., Arndt et al., 2013).

There is no general framework that can be used to estimate these parameters on a global scale. Here, we assume that the bulk organic matter reactivity in the bioturbated zone is
linked to the continuous distribution of organic compound reactivities in the non-bioturbated zone by

\[ k = \nu / \alpha \]  

Following this convention, OM degradation in the bioturbated zone is equivalent to a RCM assuming an \( age(z) = 0 \) for \( z < z_{bio} \). The best known effort to constrain values of \( \nu \), based on an analysis of eight sediment cores from very different environments, concluded that the majority of the sediments are dominated by refractory components, as reflected by low \( \nu \) parameters, between 0.1 and 0.2, while the rest are characterized by higher \( \nu \) parameters, between 0.8 and 1.0 (Boudreau and Ruddick, 1991). Nevertheless, the authors point out that more data would be needed to confirm such a trend and to determine its underlying causes. Because the \( \alpha \) parameter is conceptually related to the average age of the organic matter at the sediment water interface, its value should correlate with factors that control the transit time of organic matter from the euphotic layer to the seafloor. In general, this is the case: \( \alpha \) increases with increasing water depths and decreasing deposition rates, although it should be emphasized that the dataset is still limited and variability remains significant, especially at low deposition rates. For instance, published values of \( \alpha \) vary over several orders of magnitude from 1-100 yrs for shelf environments and up to 10,000 yrs for deep sediments (Arndt et al., 2013). In summary, values of the \( \alpha \) and \( \nu \) parameters are not known \textit{a priori}, and must be estimated based on the type of material being deposited on the seafloor.

Following the porosity and temperature models, Sections 3 and 4, values of \( \alpha \) and \( \nu \) are specified for three types of oceanic sediment: shelf, slope and abyss. Although this is a rather simplistic assumption, it effectively resolves differences in the first-order characteristics that describe each of these environments, including the predominant type of organic matter, transit time through the water column and pre-aging effects. Using a recent review of marine sediment organic matter degradation models published in the literature (Arndt et al., 2013), a plausible set of baseline and high and low sets of \( \alpha \) and \( \nu \) values for
each oceanic province has been adopted. Baseline values reflect typically observed values for such environments, while high and low values span the entire range of observed values (e.g. Boudreau and Ruddick, 1991; Arndt et al., 2013). Values of these parameters for all three scenarios are listed in Table 3.

5.2.3-D GLOBAL DISTRIBUTION OF ORGANIC MATTER IN MARINE SEDIMENTS
Using the model summarized in Section 5.1, the porosity model described in Section 3, the Holocene and Pleistocene organic carbon accumulation rates (Fig. 5), Holocene and Pleistocene sedimentation defined by Wallmann et al., (2012) and the values of \( a \) and \( \nu \) given in Table 3, the global distribution of organic matter in marine sediments can be computed down to the depth for which sedimentation rates are known. As a demonstration of this capability, the fraction of organic matter remaining in Holocene and Pleistocene sediments is shown in Fig. 6. Three scenarios are considered in this figure corresponding to the three sets of values of the reactive continuum model parameters discussed in Section 5.1: a baseline case that reflects the best estimates of the \( a \) and \( \nu \) parameters, and low and high values of these parameters reflecting the range of organic matter degradabilities observed in marine sediments. In addition, the fraction of OM remaining in sediments at the base of the bioturbated zone, 10 cm, is shown for the same three cases.

More than \( \sim 90\% \) of the OM deposited in marine sediments is buried under the top 10 cm of marine sediments for both the baseline and low-reactivity scenarios considered. This can be seen by the red and dark red colors in panels a and b in Fig. 6, which depicts the fraction of OM remaining in global sediments at the base of the bioturbated zone relative to the amount that reached the SWI. However, if it is assumed that OM is more reactive than the baseline scenario, then the fraction of organic matter that gets buried beneath the top ten cm of sediment decreases significantly, to about 20% at numerous shelf environments (blue colors in Fig. 6c). In particular, OM is mostly degraded by 10 cm in the high latitudes of northern hemisphere shelf settings. Like the baseline and low-reactivity scenarios, a
significant fraction (~80%) of OM in the margin and abyss domains sediments escapes the bioturbated zone (bright red color in Fig. 6c).

Figure 6. The fraction of total organic carbon, TOC, that exists at the bottom of the (a-c) bioturbated zone (10 cm below the sediment-water interface), Holocene (d-f) and Pleistocene (g-i) sediment layers relative to the amount of organic matter deposited (see Fig. 5). For each sediment depth, three scenarios are shown reflecting baseline (a,d and g), low-reactivity (b, e and h) and high reactivity (c, f and i) organic matter degradation conditions.

The fraction of OM that remains unmineralized at the bottom of the Holocene (11,700 yrs) reveals more complex spatial patterns than those at the bottom of the bioturbated layer (Figs. 6d-f). In Fig. 6d, it can be seen that in many shelf sediments, about 40% of OM is buried beneath sediments that are 11,700 year old, that many slope sediments still retain ~60% of the OM deposited there and that further from land there is a splotchy pattern revealing regions where either >80 % or >90% of Holocene organic matter has been degraded in the baseline scenario. In the low-reactivity scenario, Fig. 6e, about 60% of OM in shelf sediments has survived the Holocene (yellow colors) whereas most sediments show
that little, <15%, of the OM has been degraded. As expected from the higher reactivities in the third scenario, as little of 10% of organic matter has been buried beneath Holocene-aged sediments near-shore (dark blue colors in Fig. 6f), large swaths of the ocean sediments retain about 40% of OM to through this age (light blue colors in Fig. 6f), and numerous patches of sediments preserve >80% of the OM deposited through the Holocene (red colors in Fig. 6f).

The fraction of organic carbon deposited over the last 2.59 million years that has survived degradation is shown in panels g-i in Fig. 6 for the three reactivity scenarios described above. One of the most striking – and expected – features of the maps shown in Fig. 6 for sediments at the bottom of the Pleistocene is that a much larger fraction of organic matter has been degraded. As in the Holocene (Fig. 6d-f), a smaller fraction of OM has survived near coastal margins than in the open ocean sediments. However, the gap between the amount that still exists in Pleistocene sediments is much smaller than those at the bottom of the Holocene. That is, the ratio of OM that has survived burial to the bottom of sediments 2.59 Myrs old in the baseline scenario is dominated by light and aqua blues, corresponding to 70% and 60% of the OM at these locations, have been degraded. However, it is noteworthy that in many locations, including sediments underlying the North and South Pacific Gyres, that the vast majority of OM deposited in sediments have not been degraded throughout the timespan of the Pleistocene. In the low-reactivity version of this simulation, Fig. 6h, this is even more-so the case. Furthermore, even in the high-reactivity scenario, large portions of the organic matter deposited in sediments at the beginning of the Pleistocene still exists in these sediments (red colors in Fig. 6i).

The results depicted in Fig. 6 provide a quantitative description of where a significant portion of Earth’s organic carbon is, and upon integration, reveal the rates of organic carbon degradation and burial in sediments of different ages on a global scale. For instance, the rates of OM degradation in Holocene and Pleistocene sediments for the baseline scenario are 329.5 and 10.9 Tg C yr⁻¹, with respective burial efficiencies, BE, of 0.48 and 0.46, where \( BE = \frac{(OM\_deposition - OM\_degradation)}{OM\_deposition} \).
The amount of organic matter that still exists at the bottom of the bioturbated, Holocene and Pleistocene sediment layers shown in Fig. 6 give a temporal sense of the geographical distribution of organic matter. In order to complete the spatial analysis of Holocene and Pleistocene organic matter, the sedimentation rates taken from Wallmann et al. (2012) have been used to illustrate the depth to which Holocene and Pleistocene sediments are located in Fig. 7.

![Figure 7](image)

Figure 7. Total volumes of bioturbated, Holocene and Pleistocene sediments and how these volumes are partitioned onto the shelf, slope and abyss domains (a). Maximum depths to which b) Holocene and c) Pleistocene sediments reach (note different scale bars).

In Fig 7b, it can be seen that Holocene sediments extend to nearly 15 meters thick (red colors) in many coastal locations, particularly in high northern latitudes, the eastern side of south America, between Southeast Asia and Indonesia, the East China Sea and the Arafura Sea. Most of the rest of the ocean’s Holocene sediments are < 1 m thick (dark blue colors in Fig. 7b). Of course, the depth to which Pleistocene sediments reach is far greater. This is shown in Fig. 7c. Here, using a different color scale, Pleistocene sediments are shown to be up to 400 m thick (deep red colors), mostly in Arctic areas. A considerable proportion of
marine sediments that are less than 2.6 Ma are between 100 – 150 m thick (lighter blue colors in Fig. 7c), while large areas in the abyssal domain are less than a few meter thick (dark blue colors).

The sizes of the bioturbated, Holocene and Pleistocene sediment layers, as well as their relative distribution in the shelf, slope and abyss domains are shown in Fig.7a. These values are given in units of cm$^3$ because microbial biomass is often reported in units of cell cm$^{-3}$. The bioturbated layer, though only 10cm thick, is global in coverage. As a result, the total volume of this layer is about 3.6 x 10$^{19}$ cm$^3$, with the vast bulk of this environment located in the abyss. However, far more organic matter delivery and degradation is happening in the bioturbated layer on continental shelves (Fig. 6a-c). The Holocene layer, by comparison, is only about an order of magnitude more voluminous, at ~4.4 x 10$^{20}$ cm$^3$.

Given the much higher sedimentation rates near coastal margins, the majority of this volume is located in the shelf domain. Most of the Pleistocene sediments, on the other hand, are located in the abyss domain with a miniscule proportion on shelves. Interestingly, despite the fact that the Pleistocene lasted ~220 times longer that the Holocene, Pleistocene aged sediments only occupy about 62 times the volume (2.7 x 10$^{22}$ cm$^3$) of Holocene sediments. This is partly attributable to lower sedimentation rates before the Holocene and the compaction of sediments that has taken place in the deeper Pleistocene sediments. The significance of the location of sediments in the Holocene and Pleistocene (Fig. 7), the proportions of organic matter still existing in sediments of these ages (Fig. 6), and the results presented earlier in this communication are discussed in the following section with respect to the distribution, activity levels, history and extent of microbial life in marine sediments, and their impact of diagenesis.

6. DISCUSSION

Marine sediments have long been appreciated as a repository of biogeochemical data that can be used to understand geologic history. In fact, many of Earth’s major climatological and environmental transformation in the Phanerozoic eon have been delineated in marine sediments due to observed changes in levels of organic matter preservation and/or the
isotopic manifestation of this (Berner, 2004). The amount of organic matter preserved in marine sediments, however, is due to an unknown combination of processes occurring in the water column and in the sediments. One of the keys to understanding at least how the sedimentary environment contributes to the preservation of OM is determining how the microorganisms in sediments respond to changing conditions. That is, marine sediments must be quantitatively described as a habitat for microorganisms in order to assess how global scale climate changes are recorded in marine sediments and how they will continue to do so. In attempt to describe marine sediments as a global ecosystem, with relevance for understanding geologic history and the nature of the deep biosphere, several of the large scale properties of marine sediments on a global scale have been determined in this study. The relevance of these physiochemical properties to the microbial ecology of marine sediments is the topic of the next several subsections.

6.1 PORE WATER

The survival of microorganisms in sediments that are millions of years old and/or tens to hundreds of meters beneath the sediment-water interface brings up some interesting questions concerning why organisms would have evolved to exist under such conditions only to face certain death/extinction from thermal stress, starvation, tensile failure or subduction. However, the vast body of pore water, estimated in this study to be $8.103 \times 10^7$ km$^3$ that exists throughout unconsolidated sediments, is a potentially mobile phase that can transport microorganisms, along with volatiles and trace elements, both laterally and vertically through marine sediments. One such manifestation of this transport at the sediment water interface is mud volcanoes.

Although estimates of the amount of fluid, and therefore the number of microorganisms, issuing from mud volcanoes is not known, the volume of pore fluid expelled from accretionary sedimentary wedges due to compaction (Bray and Karig, 1985) can be used to estimate the number of microbes that are transported from the deep marine biosphere into the overlying ocean at subduction zones. The volume of water expelled from subduction zone sediments has been estimated at between $7 - 100$ m$^3$/yr per meter of subduction
trench (Kastner et al., 1991; Le Pichon et al., 1991). Given that there is about 44,450 km of active subduction zones (Jarrard, 2003), this would result in between 0.3 and 4 km$^3$ of water per year, some fraction of which is due to the mineralogical dewatering of smectite (Jarrard, 2003). If the fluids emerging from accretionary wedges contained about $10^5$ cells per ml, this would mean that something like $10^{18}$ microorganisms from deep marine sediments are being transported above the SWI into the water column each year. This number is likely a gross underestimate because it does not include mud volcanoes that are caused by forces other than tectonic compression at subduction zones. Furthermore, this estimate does not take into account the observation that mud volcano fluids are rich in volatiles that could be used to support large populations of microorganisms (i.e., $> 10^5$ cells/ ml). Taken together, the number of microorganisms transported from marine sediments to the ocean floor could be several orders of magnitude higher than $10^{18}$ per year. Even if a relatively small flux of fluid from sediments is advected into the ocean, these flow paths represent a conduit connecting the deep biosphere of once isolated sedimentary microorganisms into other sediment horizons or even back into the ocean water column. Any viable organisms that are moved by this mechanism would most likely have already adapted to cope with extremely low levels of energy, high pressure, potentially high temperatures and the physical gauntlet of advective transport. Microorganisms that have survived the selective evolutionary pressure of extremes that are typical of the deep biosphere would be rewarded in a Darwinian sense if the mobilized microorganisms could establish themselves in the ocean water column, or in surface sediments. The tectonically-induced flux of deep sedimentary fluids into the water column provides justification for why such long-term survival skills should exist in nature.

6.2 Temperature

As with any of the limits to life, temperature must be placed in context of the other variables that describe an environment. For instance, although Methanopyrus kandleri strain 116 grew in a laboratory at 122 °C (Takai et al., 2008), it did so in a setting totally dedicated to this purpose: it was grown in an apparatus replete with nutrients and energy at
high pressures and faced no stresses (beyond temperature) such as water scarcity, environmental toxins, extremes in pH and competition from other species. If any of these non-thermal variables are varied, the maximum growth temperature of this organisms would likely change (Edgcumb et al., 2004; Lloyd et al., 2005). For this reason, it is misleading to use the temperature calculations presented in Fig. 4 and Table 2 alone to delineate where life can’t exist. Further substantiating this point, it has been noted that there seems to be a lack of microbial activity above 80°C in low permeability rock (Connan, 1984) while ~90°C seems to be a maximum for life in oil reservoirs (Wilhelms et al., 2001; Røling et al., 2003; Head et al., 2014).

Even if the organisms buried deep in marine sediments are adapted to living at temperatures significantly greater than those that prevailed when they were deposited along with sediment, they must contend with a number of geochemical and geophysical realities associated with increasing temperatures and pressures. Lithification, which includes the dissolution and precipitation of mineral grains, can decrease porosity and permeability over a range of depths while altering pore fluid chemistry. For instance, pressure alone can begin the process of transforming fine grained sediment layers into shales and other muddy rocks (Prothero and Schwab, 2004) that can decrease porosity and permeability, and carbonate diagenesis can occur at all pressures and temperatures. As temperatures approach 100 °C, some clay minerals begin undergoing a crystallographic reorganization into different clay types (Prothero and Schwab, 2004), further modifying the habitat.

From a catalytic perspective, rates of abiotic redox reactions generally speed up as temperature increases, thus depriving organisms of the disequilibrium that is needed to gain energy. In addition, maintenance energies tend to be larger as temperature increases (Price and Sowers, 2004), especially if whole proteins must be turned over in order to subvert the negative side effects of amino acid racemization (Onstott et al., 2014). As a result of the increased energetic and physiochemical stresses accompanying higher temperatures in marine sediments, it is unlikely that microorganisms can grow, or even maintain themselves, in sediments as hot as Methanopyrus kandleri strain 116. In fact, the
temperature limit for life in sediments may be much lower than this. However, there is an upside to living in deeply buried sediments for organotrophs: the conversion of kerogen and similar compounds into petroleum, catagenesis, could provide a source of labile organic matter in sediments (Parkes et al., 2000) at temperatures as low as 50 °C (Tissot and Welte, 1984). That is, the complex organic matter that has survived deep burial might be abiotically converted into low-molecular weight organic compounds that can be consumed by heterotrophs and fermenters if these compounds are transported to locations where microbial life is viable. On the other hand, organics in some diagenetic environments can also be oxidized to CO₂ by sulfate abiotically at temperature > ~100°C, through a process known as thermochemical sulfate reduction (Machel, 2001).

6.3 QUATERNARY ORGANIC MATTER

The delivery rates and distribution of organic matter shown in Figs. 5 & 6 are a proxy for microbial biomass and activity levels in Holocene- and Pleistocene-aged marine sediments. That is, the rates of OM degradation shown in Fig. 6 are effectively displaying the rates of microbial activity since all of this organic matter is too shallow to be hot enough to be abiotically transformed (Tissot and Welte 1984). Comparison of the distribution of temperature (Fig. 4) with the depth to which Holocene and Pleistocene sediments reach (Fig. 7), show that although the depth below the SWI that both these sediments reach varies significantly across the globe, virtually all of them are below 40°C.

The maps showing the depositional rates of organic matter in the Holocene and Pleistocene, Fig. 5, are a strong indicator of where microorganisms should be distributed as a function of latitude and longitude. The maps displayed in Fig. 6, showing the proportion of deposited organic that has survived microbial degradation, give an indication of how active microorganisms are across global marine environments. Clearly, places where very little OM has been buried, such as on continental shelves and margins, microorganisms have been more active (consequently, there is little OM left-over beneath these horizons to fuel additional microbial activity). This may by indicative of faster catabolic rates or larger numbers of organisms or both. However, given the distribution of known marine sediment
cell counts (Kallmeyer et al., 2012; D’Hondt et al., 2015), it seems that at the very least, this means that there are more cells in settings where organic matter degradation is more intense. In regions where microorganisms are oxidizing organic matter with electron acceptors other than O₂, secondary redox species could be further fueling metabolic activity. For example, organisms using Mn- and Fe-oxides and sulfate as oxidants can produce Mn²⁺, Fe²⁺ and various reduced sulfur species such as H₂S that can in turn serve as electron donors for chemolithotrophs living in sediments. Additionally, reduced nitrogen species, from respired organic matter or nitrate reduction, could be serving a similar purpose. Several recent studies have attempted to quantify which electron acceptors are being used in sediments. For examples, D’Hondt et al. 2015 and (Bowles et al., 2014) have mapped likely areas of O₂ and sulfate reduction, respectively, coupled to organic matter degradation in global marine sediments. (Thullner et al., 2009) looked at a broad set of likely electron acceptors concluding that sulfate reduction dominates OM degradation globally, with important contributions by oxygen, nitrate and Fe-oxide reducers.

The discussion of organic matter in marine sediments thus far has focused on environments for which sedimentation and organic matter deposition rates are reasonably well-known, through the duration of the Quaternary Period. As a result, only potential microbial activity has only been discussed in about 2.7 x 10²² cm³ (Fig. 7) of the 3.04 x 10²³ cm³ of global marine sediments, about ~ 9% of the total. If it’s assumed that there is little to no life in sediments hotter than 80°C (see above), about 17% of the global total (see Table 2), then there is still 2.25 x 10²³ cm³ of marine sediments that have not been discussed with respect to the amount of microbial biomass that is there or the rates at which microorganisms are active despite the fact that microbial cell have been found in sediments far older than the Quaternary (D’Hondt et al., 2004; Kallmeyer et al., 2012) that seem to be active (Schippers et al., 2005; Morono et al., 2011; Engelhardt et al., 2014). Although all three of the Pleistocene scenarios considered in this study (Fig. 6g-i) show that a significant amount of organic matter has been buried beneath 2.59 Myr-old sediments, the distribution and rates of organic matter degradation beneath these depths cannot be estimated using the model described in this study without additional information.
Appendix 4

cconcerning sedimentation and organic matter deposition rates extending throughout the Jurassic, to account for the oldest extant marine sediments. Despite these limitations, other lines of evidence can be used to infer the microbial potential in sediments older than the Quaternary.

6.4 Before the Pleistocene

Sediments older than the Pleistocene contain a fraction of the organic matter that has been deposited and buried over the past ca. 200 Ma - the interval for which ancient oceanic crust and sediments still exist. In addition to the trace amounts of OM found in some sediments that are tens of millions of years old (e.g., D’Hondt et al., 2015; Roy et al., 2012), sediment cores have been obtained through the DSDP/ODP/IODP and other ocean drilling programs that reveal large amounts of organic matter tens to hundreds of meters beneath the SWI that could still provide a suitable substrate for microbial activity (Krumholz et al., 1997; Coolen et al., 2002; Krumholz et al., 2002).

Over the past 200 Myrs, rates of organic matter deposition and burial have varied in response to changing climate and environmental conditions (e.g., Berner, 2004). However, there is no direct record of these variations and their reconstruction has relied on geological proxies, such as stable carbon isotopes preserved in rocks. For instance, the ratio of $^{13}$C to $^{12}$C recorded in carbonate rocks, which are assumed to record the average $\delta^{13}$C of seawater DIC, provides important insights into organic carbon burial over the Phanerozoic (Fig. 8a). Because covalent bonds involving $^{13}$C are stronger than those involving $^{12}$C, biologically mediated processes, such as photosynthesis, result in an enrichment of $^{12}$C in the product and a depletion of $^{12}$C in the reactant. Changes in $\delta^{13}$C are thus directly linked to the rate of preferential removal of isotopically light carbon from the ocean-atmosphere system: an increase in $\delta^{13}$C of seawater reflects enhanced burial of organic matter in marine sediments. The global rate of organic carbon burial in sediments of both marine and non-marine origin can be estimated on the basis of the Phanerozoic $\delta^{13}$C record (Fig. 8a) by applying mass-balance calculations and assuming appropriate values for the isotopic composition of carbon inputs and outputs (e.g., Kump and Arthur, 1999, Berner, 2004).
Fig. 8b illustrates the reconstructed organic carbon burial over the Phanerozoic eon (estimated error ±50%) based on mass balance calculations by (Berner, 2001). Reconstructed rates reveal characteristic maxima that agree with the occurrences and ages of major petroleum source rocks (Berner, 2003). For instance, the enhanced burial of organic carbon in freshwater sediments during the Carboniferous and Permian (350-250 Ma) triggered by the Devonian rise of land plants resulted in the formation of large coal basins.

![Graphs](https://example.com/graphs)

Figure 8. Isotopic fractionation of carbon, δ¹³C, as recorded in marine carbonates (a) and the corresponding inferred global organic carbon burial rate (b) throughout most of the Phanerozoic

Particularly relevant to the discussion of deep sediments is the organic carbon burial maximum in the Middle Cretaceous (90–120 Ma ago). The Cretaceous is marked by several occurrences of Oceanic Anoxic Events (OAEs) – geologically brief periods during which a large fraction of ocean bottom waters become anoxic. They are linked to
significant perturbations of the ocean carbon cycle and climate, and are often characterized by organic-rich sediments, so-called black shales. Jenkyns (2010) classifies four global-scale OAEs during the Mesozoic (T-OAE, OAE 1a, OAE 1b and C/T OAE), two others (OAE 1c and OAE 1d) as being candidates for near-global events and a number of other OAEs that lead to high regional OM concentrations in sedimentary rocks. One such example is a section of Cretaceous-aged sediments located in an area of the equatorial Atlantic known as the Demerara Rise. Drill cores from ODP Leg 207 Sites 1257, 1258, 1259 and 1260 reveal shales that typically contain between 2 and 15 wt% OM in layers ranging from 56 to 94 meters thick (ShipboardScientificParty, 2004). Methane concentrations in and immediately above these organic-rich layers reach several millimolar while NH$_4^+$ concentrations gradually decrease from about 1.5 mM in the shales to nearly 0 at the sediment water interface, indicating the production of reduced nitrogen at depth and its diffusion and consumption by microorganisms higher in the sediment columns. Sulfate concentrations exhibit the opposite trend, slowly decreasing from ocean-like levels to undetectable near the tops of the organic-rich layers. Modeling work has demonstrated that the these deep organic-rich strata likely host organisms that convert the complex OM in these shales into CH$_4$ which is subsequently consumed by anaerobic methane oxidizing, AOM, microbial consortia using SO$_4^{2-}$ as the oxidant (Arndt et al., 2006). Although cell counts are not available from ODP Leg 207, it is likely that microbial cell numbers are larger in and above these OM-rich layers in the Demerara Rise than in the hundreds of meters separating these layers from the SWI, in which the OM content is far lower. Supporting this notion, cell counts carried out in Peru Margin sediments associated with ODP Leg 201, site 1229, show maximal cell numbers ~90 m below the SWI, nearly two orders of magnitude higher than those counted in the shallowest sediments at this location. This is most likely due to a deep convergence of methane and sulfate, the latter of which is diffusing upwards from a deep brine (Jørgensen et al., 2003).

Although evidence of these OAEs have been found on land and through ocean drilling, and the global amount of carbon locked up in marine sediments due to these events can be roughly estimated on the basis of $^{13}$C values and mass balance calculations, there remain
large uncertainties regarding the duration of OAEs, the global heterogeneity of OM content in OAE sediments of the same age and the number and extent of regional OAEs (Jenkyns, 2010). Furthermore, since so many different factors influence the preservation of OM in the geologic record (Arndt et al., 2013), it is difficult to predict how local variations in such variables translate into deep OM contents and reactivities on a global scale. Nonetheless, deep, thick, organic-rich layers occur in marine sediments that could support large numbers of microorganisms that would otherwise not be counted in global estimates since it is often assumed that the number of cells in marine sediments decrease with depth according to a power law (Kallmeyer et al., 2012). The use of the reactive continuum model described above to create profiles of organic matter in marine sediments, and therefore a proxy for microbial abundance and/or activity, clearly misses such deep, OM-rich sedimentary layers such as the one found in the Demerara Rise. In addition to the deep, thick, OM–rich sedimentary layers associated with OAEs, there is another source of deep carbon that might be available for microbial life: catagenetic hydrocarbons.

Although the rate at which old, deeply buried organic matter is metabolized by microorganisms in marine sediments becomes extremely slow with depth (Middelburg, 1989), as it is exposed to sufficient pressure and temperature, complex organics such as kerogen can be converted abiotically into petroleum through a process known as catagenesis. Although it is thought that the principle zone of oil formation in organic-bearing sediments occurs from ~ 50-160°C, with pressure playing a lesser role, hydrocarbons and methane can be generated from complex organic matter at lower temperatures (Tissot and Welte, 1984; Hunt, 1996). As noted above, nearly 27% of marine sediments are above 60°C, and that even if sediments do not contain enough organic matter to be commercial sources of petroleum (TOC > 0.5% by weight), the complex organic matter in them can still be converted to microbially edible hydrocarbons through abiotic processes. Some fraction of small-molecular weight hydrocarbons and CH₄ produced in abiotic sedimentary basins could be expelled and migrate to regions that are more conducive for life. Both petroleum and natural gas can migrate hundreds of km from
their source rock (Selley, 1998), and there are certainly thermophilic microorganisms capable of oxidizing common products of catagenesis such as alkanes and benzyl-compounds (Teske et al., 2014). In addition, water, CO₂ and H₂S can also be produced in large amounts during the catagenesis of Type II kerogens (Tissot and Welte, 1984), further fueling microbial activities with carbon, and electron acceptors and donors. Furthermore, as noted above, it has been estimated that more CH₄ has been produced by methanogens degrading petroleum reservoirs than there is primary CH₄ produced from catagenesis (Milkov, 2011). In total, 1.97 – 3.94 x 10¹³ kg of free CH₄ is estimated to be in place from the microbial degradation of petroleum (Milkov, 2011). Taken together, catagenesis could be fueling microbial communities deep in marine sediments of unknown size.

7. CONCLUDING REMARKS

In the course of this study, a number of global-scale properties of the marine sediment ecosystem have been revised or determined including its size, the amount of water residing in it and the distribution of temperature and organic matter in three dimensions. Specific results include a 0.25° x 0.25° resolution map of marine sediment thickness, (based on the data sets from Laske and Masters, 1997 and Divins, 2003) a revised total volume 32% smaller than other estimates (3.0767 x 10⁸ km³) and an average thickness of 840 m. In addition, the volume of free water calculated to reside in marine sedimentary pore water (8.1031 x 10⁷ km³) exceeds that of the Southern Ocean, equivalent to about 7% of the world’s oceans. To our knowledge, no such estimates exist in the literature. In addition, global-scale maps depicting the temperature of sediment columns have been generating revealing that nearly one third of the world’s marine sediments are between 0°C, and 20°C and that 42% of marine sediments are above 40°C. The model set up to carry out these calculations can be used to quantify the thermal history of sediments, with important ramification for the rates of reactions altering proxies used for interpreting geologic history. Finally, a reactive continuum model quantifying rates of organic matter degradation has been applied on a global scale to assess the three dimensional distribution of organic matter in marine sediments stretching back throughout the Quaternary (2.588
Ma). Because the degradation of organic matter alters the chemistry of pore waters, quantifying the amount of sedimentary alteration that has occurred helps determine the impact of diagenesis of marine sediments.

In addition to revealing the history of organic matter degradation, temperature and other variables that influence the diagenesis of marine sediments, the model results discussed above can be used to interpret ongoing investigations into the size, structure and activity levels of microorganisms in the deep biosphere. In fact, since microorganisms in these environments face many of the variables that can limit life, such as temperature, energy, water, nutrient and space limitations, often in combination, some of the most fundamental questions about the limits to life can be addressed by studying the microbiology of marine sediments. For example, it is entirely plausible that the numbers of microorganisms and their rates of catabolism would closely correspond to where rates of organic matter degradation are highest, as shown in Fig. 6. As this model is applied to deeper sediments, in conjunction with global-scale data on the occurrence of organic-rich horizons, a more complete description of the nature of the deep biosphere is possible. Similarly, the thermal calculations represented by the maps in Fig. 4 can be used to delineate zones which are particularly hostile to microorganisms. Taken together, quantifying the amount of pore space, the temperature and the amount of organic present in a particular parcel of marine sediments can be used to delineate the biotic fringe. A better quantitative understanding of their environment not only allows for predictions concerning microbial activity levels and numbers, but also in looking beyond the Earth for life in other low-energy environments.

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Appendix 4


281
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CURRICULUM VITAE

Ewa Burwicz is born in Łódź, Poland, in 1985. In 2004, she started a full-time Master Studies in Geology at the Geological Institute, Jagiellonian University in Cracow and, in parallel, Geophysics studies at the AGH University of Science and Technologies in Cracow. In the years 2004 – 2009, Ewa Burwicz has been approved for an individual (personalized) system of studies with the focus on Petrology, Mineralogy and Geochemistry under distinctive supervision of prof. dr hab. Marek Michalik. In the years 2006 – 2009, she was awarded with a scientific scholarship from the Dean of Biology and Earth Sciences Faculty of the Jagiellonian University. In the year 2007, she submitted her BSc thesis in Geology entitled “Capacity of H2O in nominally anhydrous minerals (upper mantle)" supervised by prof. dr hab. Marek Michalik and received an overall 5.0 grade (in a best-worst scale from 5.0 to 2.0). In the years 2003, she became a member of the Academic Association of Students of Geology at the Jagiellonian University and held the function of 2nd Chairman of the Association in the years 2004 – 2005.

In 2008, she continued her Master of Science degree program as a guest student at the GEOMAR Helmholtz Centre for Ocean Research Kiel (previously IFM-Geomar), Christian-Albrechts University of Kiel, Germany with a supervision of prof. dr. rer. nat. Lars Rüpke and prof. dr. rer. nat. Klaus Wallmann. She accomplished her studies and received MSc degree in Geology with a final score of 5.0 (in a best-worst scale from 5.0 to 2.0) at 8th December 2009 at the Institute of Geological Sciences of Jagiellonian University, Cracow by defending the Thesis entitled “New global estimates of marine gas hydrate accumulations based on reaction- transport modeling". MSc Thesis of Ewa Burwicz is available at the thesis repository of the Jagiellonian University Library with an open access (https://www.apd.uj.edu.pl/index.php). In the year 2010, she has started her PhD program at the GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany in the research division of Magmatic and Hydrothermal Systems and research area FB4 Dynamics of the Ocean Floor with a supervision of prof. dr. rer. nat. Lars Rüpke and prof. dr. rer. nat. Klaus Wallmann where she was continuing her studies on numerical modeling of marine gas hydrate deposits. In 2012, she has additionally joined research area FB2 Marine Biogeochemistry within the research division of Marine Geosystems in the frame of a joint industry-research project investigating the abundance and perspective recovery of gas hydrate deposits in the Gulf of Mexico.

During the years 2011 – 2015, she has published, submitted or co-authored 7 peer-reviewed scientific papers, 4 conference proceedings papers and 16 of conference contributions (detailed list to be found at: www.ewaburwicz.com). In the years 2009 – 2015, she has attended several major scientific conferences (2010, 2013: EGU in Vienna, Austria; 2012: GeoMod in Lausanne, Switzerland; 2013: AGU in San Francisco, USA) including specialized conferences with a focus on gas hydrate research (2011: International Conference on Gas Hydrate- ICGH7 in Edinburg, Scotland; 2014: ICGH8 in Beijing, China; 2012: Gas in Marine Sediments-GIMS11 in Nice, France with an invited talk; 2014: GIMS12 in Taipei, Taiwan receiving The Best Student Oral Paper Award Honorable Mention) and summer school program (2011: ECORD Summer School on “Subseafloor Fluid Flow and Gas Hydrates” in Bremen, Germany). Ewa Burwicz is a member of the Academic Association of Students of Geology at the Jagiellonian University, the Polish Mineralogical Society, and the Student Section of the Polish Chemical Society.