CHARACTERIZING THE ACCUMULATION AND DISTRIBUTION OF GAS HYDRATE IN MARINE SEDIMENTS USING NUMERICAL MODELS AND SEISMIC DATA

A Thesis
Presented to
The Academic Faculty

by

Jillian Nicole Nimblett

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in the School of
Earth and Atmospheric Sciences

Georgia Institute of Technology
July 2003
To My Family
ACKNOWLEDGEMENTS

The research in this thesis was mostly sponsored by National Science Foundation grant OCE-9730846 to C. Ruppel and R. P. Lowell. The School of Earth and Atmospheric Sciences, Georgia Institute of Technology also provided financial support through graduate student assistantships and teaching assistantships. An ACS -PRF grant awarded to C. Ruppel, and a NSF subcontract grant OCE-9910566 to D. Lizzarralde also provided additional support. Supplementary support from the Georgia Tech Focused Research Program for Gas Hydrates and NSF grant OCE-0118071 to C. Ruppel and D. Lizzarralde also contributed to this work.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS ...................................................................................... iv

LIST OF TABLES ............................................................................................... x

LIST OF FIGURES ............................................................................................ xi

SUMMARY .......................................................................................................... xv

CHAPTER I: Introduction ................................................................................... 1

1.1. Introduction ............................................................................................... 1

1.2. Motivation: Global significance ................................................................. 1

1.3. Motivation: Scientific interest ..................................................................... 2

1.4. Objectives .................................................................................................. 3

1.5. Methods ..................................................................................................... 4

1.5.1. Numerical analysis ............................................................................... 4

1.5.2. Seismic Data acquisition, processing and analysis ............................ 5

1.5.3. Tomographic analysis and effective medium modeling .................... 5

1.6. Innovation .................................................................................................. 6

1.7. Contributions ............................................................................................ 7

1.8. Organization ............................................................................................. 8

CHAPTER II: Background .................................................................................. 11

2.1. Introduction ............................................................................................... 11

2.2. Properties of Gas Hydrates ...................................................................... 11
2.3. Gas Hydrate Reservoirs .............................................................................. 15
  2.3.1. Gas Hydrate phase equilibria ................................................................. 16
  2.3.2. In Situ Methane Production .................................................................. 20
  2.3.3. Mechanism of formation of Methane Hydrate in the Gas Hydrate Zone .................................................................................. 20
  2.3.4. Gas Hydrate occurrence in sediment ..................................................... 22
2.4. Size of this Natural Gas Resource .............................................................. 23
2.5. Detection of Gas Hydrate in Marine reservoirs ............................................ 24
  2.5.1. Seismic methods ..................................................................................... 25
  2.5.2. Wireline Logging ................................................................................... 26
  2.5.3. Geochemical methods ........................................................................... 26
  2.5.4. Detection limits and constraints ............................................................. 27
2.6. Focus Site – The Blake Ridge Gas Hydrate Reservoir ................................. 28
  2.6.1. Gas Hydrate occurrence on the Blake Ridge ......................................... 29
  2.6.2. Seismic velocities of the Blake Ridge sediments ................................... 32

CHAPTER III: Permeability Evolution During the Formation of Gas Hydrates in Marine Sediments .................................................................. 35
  3.1 Introduction ................................................................................................. 35
  3.2. Previous studies ......................................................................................... 38
    3.2.1. Permeability of seafloor systems ......................................................... 38
    3.2.2. Models of Gas Hydrate Reservoirs ..................................................... 41
  3.3. Numerical model ....................................................................................... 43
    3.3.1. Role of solubility ................................................................................. 44
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.2.</td>
<td>Discrete Fracture model</td>
<td>45</td>
</tr>
<tr>
<td>3.3.3.</td>
<td>Porous medium</td>
<td>46</td>
</tr>
<tr>
<td>5.4.</td>
<td>Model domain, implementation, and assumptions</td>
<td>47</td>
</tr>
<tr>
<td>3.5.</td>
<td>Model parameters</td>
<td>51</td>
</tr>
<tr>
<td>3.6.</td>
<td>Results</td>
<td>53</td>
</tr>
<tr>
<td>3.6.1.</td>
<td>Permeability evolution</td>
<td>53</td>
</tr>
<tr>
<td>3.6.2.</td>
<td>Shutdown time for fluid flow</td>
<td>56</td>
</tr>
<tr>
<td>3.6.3.</td>
<td>Variations in pore diameter and fracture aperture</td>
<td>59</td>
</tr>
<tr>
<td>3.6.4.</td>
<td>Variations in initial fluid flux</td>
<td>61</td>
</tr>
<tr>
<td>3.6.5.</td>
<td>Variations in initial energy flux</td>
<td>63</td>
</tr>
<tr>
<td>3.6.6.</td>
<td>Variations in seafloor conditions (water depth and bottom water temperature)</td>
<td>66</td>
</tr>
<tr>
<td>3.6.7.</td>
<td>Alternate permeability-porosity formulation</td>
<td>66</td>
</tr>
<tr>
<td>3.7.</td>
<td>Discussion</td>
<td>69</td>
</tr>
<tr>
<td>3.7.1.</td>
<td>Comparison to field constraints</td>
<td>69</td>
</tr>
<tr>
<td>3.7.2.</td>
<td>Modification of hydraulic regimes by gas hydrate formation</td>
<td>72</td>
</tr>
<tr>
<td>3.7.3.</td>
<td>Permeability seals at the BSR</td>
<td>75</td>
</tr>
<tr>
<td>3.7.4.</td>
<td>Renewability of gas hydrate deposits</td>
<td>76</td>
</tr>
<tr>
<td>3.8.</td>
<td>Conclusions</td>
<td>79</td>
</tr>
</tbody>
</table>

**CHAPTER IV: Gas Hydrate Accumulation and Distribution in Continental Margin Reservoirs**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1.</td>
<td>Introduction</td>
<td>83</td>
</tr>
<tr>
<td>4.2.</td>
<td>Background</td>
<td>84</td>
</tr>
</tbody>
</table>
4.3. Gas Hydrate Provinces ................................................................. 87
  4.3.1. Nankai Trough ........................................................................ 87
  4.3.2. The Costa Rican Margin .......................................................... 90
  4.3.3. The Peruvian Margin .............................................................. 92
  4.3.4. The Gulf of Mexico ............................................................... 94
4.4. Method of Analysis .................................................................... 97
4.5. Results ...................................................................................... 100
  4.5.1. Nankai Trough ....................................................................... 100
  4.5.2. The Costa Rican Margin ........................................................ 104
  4.5.3. The Peruvian Margin .............................................................. 109
  4.5.4. The Gulf of Mexico ............................................................... 111
4.6. Discussion and Conclusions ....................................................... 113

CHAPTER V: Seismic Imaging of a faulted hydrate reservoir ............ 116
5.1. Introduction ............................................................................... 116
5.2. Background ............................................................................... 117
  5.2.1. Previous Seismic Velocity studies of Blake Ridge
         Gas hydrate reservoir ............................................................. 117
  5.2.2. Estimates of hydrate concentration from seismic data .......... 119
  5.2.3. Estimates of hydrate concentration from downhole logs ...... 120
  5.2.4. Estimating the elastic properties of gas hydrate-bearing
         sediments ........................................................................... 120
5.3. Study site .................................................................................. 121
5.4. Data acquisition ......................................................................... 124
<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>Hydrate crystal structures</td>
<td>13</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Properties of methane gas hydrate and ice</td>
<td>15</td>
</tr>
<tr>
<td>Table 2.3</td>
<td>Observed occurrence of gas hydrate in marine sediments</td>
<td>22</td>
</tr>
<tr>
<td>Table 2.4</td>
<td>Estimates of the volume of methane in worldwide hydrate deposits</td>
<td>24</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Typical model parameters (Blake Ridge)</td>
<td>51</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>Clogging time as a function of initial pore size</td>
<td>61</td>
</tr>
<tr>
<td>Table 3.3</td>
<td>Clogging time as a function of various initial fluid fluxes</td>
<td>63</td>
</tr>
<tr>
<td>Table 3.4</td>
<td>Clogging time as a function of background geothermal gradients</td>
<td>65</td>
</tr>
<tr>
<td>Table 3.5</td>
<td>Clogging time as a function of seafloor and bottom water pressures</td>
<td>66</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Gas hydrate occurrence in the Nankai Trough</td>
<td>90</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>Gas hydrate occurrence in the Costa Rican Margin</td>
<td>92</td>
</tr>
<tr>
<td>Table 4.3</td>
<td>Gas hydrate occurrence in the Peruvian Margin</td>
<td>94</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>Gas hydrate occurrence in the Gulf of Mexico</td>
<td>97</td>
</tr>
<tr>
<td>Table 4.5</td>
<td>Model Parameters for various sites</td>
<td>100</td>
</tr>
<tr>
<td>Table 4.6</td>
<td>Additional model parameters for Nankai Trough</td>
<td>104</td>
</tr>
<tr>
<td>Table 4.7</td>
<td>Additional model parameters for Costa Rica</td>
<td>109</td>
</tr>
<tr>
<td>Table 4.8</td>
<td>Average gas hydrate concentrations for all Sites</td>
<td>115</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>Determination of best traveltime picks</td>
<td>138</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2.1. Worldwide distribution of gas hydrate ......................................................... 17
Figure 2.2. Methane gas hydrate phase equilibrium curves .............................................. 18
Figure 2.3. Physiographic map of the Blake Ridge .......................................................... 30
Figure 2.4. Chlorinity profiles and electrical resistivity
from cores collected at Sites 994, 995 and 997 ............................................................... 31
Figure 2.5. Seismic velocity profiles at Site 994, 995 and 997 .............................................. 33
Figure 2.6. Seismic section of the Blake Ridge gas hydrate reservoir ............................... 34
Figure 3.1 Blake Ridge sediments observed in MCS data ................................................ 37
Figure 3.2 Schematic representation of the GHZ ............................................................... 39
Figure 3.3 Relative positions of the GHZ ................................................................. 42
Figure 3.4 Evolution of permeability for porous and fracture flow ................................. 54
Figure 3.5 Evolution of hydraulic parameters in a fracture ........................................... 57
Figure 3.6 Evolution of hydraulic parameters in a porous medium ............................... 58
Figure 3.7 Clogging time for fracture and porous medium ............................................. 60
Figure 3.8 Permeability evolution in porous media and fracture as a function
of initial fluid flux .............................................................................................................. 62
Figure 3.9 Clogging time for fracture and porous medium as a function of
grothermal gradient ......................................................................................................... 64
Figure 3.10 Permeability evolution for various porosity-permeability
relationships ...................................................................................................................... 68
Figure 5.6a  Initial traveltime picks plotted on CDP gather 28180..........................132
Figure 5.6b  Initial traveltime picks plotted on CDP gather 28180 (magnified).................133
Figure 5.7  Initial 1D velocity model obtained from traveltimes data.........................136
Figure 5.8a  Best traveltime picks plotted on CDP gather 28180..............................139
Figure 5.8b  Best traveltime picks plotted on CDP gather 28180 (magnified).................140
Figure 5.9  1D velocity model obtained from best traveltime data............................141
Figure 5.10  Streamer depth as a function of shot and offset in the water column..........143
Figure 5.11  Relative position if streamer behind ship........................................144
Figure 5.12  Final 1D velocity model obtained from best traveltime data....................146
Figure 5.13  Travel time residuals for gather 28180............................................147
Figure 5.14  Traveltime residuals of data set.....................................................149
Figure 5.15a  Flattened CDP gathers of anomalous residuals...................................150
Figure 5.15b  Flattened CDP gathers of anomalous residuals...................................152
Figure 5.15c  Flattened CDP gathers of anomalous residuals...................................153
Figure 5.15d  Flattened CDP gathers of anomalous residuals...................................154
Figure 5.16  Starting velocity model used in the tomographic inversion.......................159
Figure 5.17  Traveltime residuals of data set with respect to starting
velocity model.................................................................161
Figure 5.18  Best traveltime residuals of data set obtained in the inversion..............162
Figure 5.19  Results of the tomographic inversion................................................164
Figure 5.20  Velocity profile across faults in the GHZ............................................165
Figure 5.21  Velocity profile across faults in the GHZ ........................................167
Figure 5.22  Percent change in hydrate concentration across a fault..........................169
Figure 5.23  Profile of hydrate saturation as a function of depth in the GHZ .................170
SUMMARY

Despite the increasing availability of geophysical, geochemical, and biological data that characterize in situ properties of gas hydrate reservoirs, the fundamental physical processes associated with gas hydrate formation, accumulation, distribution and dissociation in porous marine sediments remain poorly understood. This study focuses on characterizing the spatial and temporal distribution of gas hydrate in marine sediments through the application of numerical modeling and seismic data analysis. More specific objectives include: (1) exploring the impact of hydraulic parameters on permeability evolution during hydrate formation, (2) assessing the impact of the physical properties of sediments in gas hydrate accumulation, (3) quantifying hydrate concentrations in naturally occurring oceanic reservoirs and the timescales for accumulation, (4) seismic characterization of a gas hydrate reservoir, and (5) tomographic analysis of multichannel seismic data that constrain the local variations in gas hydrate concentration. The results constrain the hydraulic parameters pertinent to the hydrodynamics of gas hydrate reservoirs and provide insight about the physical properties of gas hydrate-bearing sediments relevant for estimating hydrate concentration in porous assemblages.

The work presented in this dissertation has been largely motivated by observational and theoretical studies that demonstrate that fluxes of gas, energy, and fluid (water with dissolved gas) control the distribution of gas hydrate and free gas in gas hydrate reservoirs. However, theoretical studies have so far not focused on the effect of sediment properties (e.g., permeability) on these fluxes during the formation of gas.
hydrate deposits. Using a transient, one-dimensional, two-phase (gas hydrate and fluid) numerical model based on a coupled conservation approach, we examine permeability clogging during gas hydrate formation in endmember porous media and fractures initially lacking hydrate and determine the resulting changes in fluid and advective energy flux. Gas hydrate accumulates most rapidly at depth in both systems, a result consistent with borehole logging and seismic studies on the Blake Ridge. Consideration of the ratio of surface area to fluid volume explains model results that imply more rapid permeability reduction in the porous media system and more uniform hydrate formation as a function of depth in the fracture system. Depending on fluid flux, fracture aperture or pore sizes, and other factors, the time scale for permeability clogging due to the accumulation of gas hydrate ranges from thousands to millions of years. Regenerating gas hydrate to a concentration of 10 to 15% of pore space in marine settings with fluid flux rates characteristic of Hydrate Ridge or Blake Ridge requires $10^3$ to $10^5$ years, meaning that hydrate deposits in these settings cannot be viewed as a naturally renewable resource. These results also imply that significant time is required to re-establish gas hydrate deposits after large-scale dissociation events associated with global scale climate change.

Application of the numerical model to the gas hydrate zone of four other continental margin reservoirs (Nankai Trough, Costa Rican Margin, Peruvian Margin, Gulf of Mexico) indicates that while the timescales for hydrate accumulation are highly site dependent, generating hydrate deposits that are consistent with geophysical and geochemical analyses generally requires thousands to hundreds of thousands of years. In addition, the numerical model, when integrated with the results of geophysical and
geochemical data provides a useful tool in constraining the hydraulic parameters of gas hydrate reservoirs. We estimate that fluid flux of 20 mm yr\(^{-1}\) at Sites 1178 and 808 in the Nankai Trough are required to yield hydrate concentrations that are comparable with observed concentrations on the basis of chlorinity data. The results of the numerical model also demonstrate that producing thick concentrated hydrate deposits is not solely a function of a highly advective flow regime but is also dependent on the physical characteristics of the reservoir. For example, hydrate deposits formed in deep-water environments (e.g. Site 1040, Costa Rican Margin) are additionally influenced by the increased solubility of methane as a function of in situ pressure in the sediments. We estimate average hydrate concentrations in the porous sediments of four continental margin reservoirs ranging from 5% to 35% and associated accumulation time scales of ~10\(^2\) – 10\(^6\) years.

As the results of the numerical analysis suggest, increased fluid and methane flux along permeable pathways through the gas hydrate zone, such as faults, may evolve into localized regions of concentrated hydrate. Background hydrate concentrations in the gas hydrate at the Blake Ridge are known to be ~4% - 7% by volume. At Site 997 (ODP Leg 164), a localized concentration of hydrate of nearly 100% (a hydrate plug) was recovered and believed to be associated with a fault. Seismic lines show that the Blake Ridge is pervasively cut by faults extending through the gas hydrate zone, and thus significant concentrations of hydrate may be present within these faults. The seismic velocity of methane gas hydrate is ~3.3 km s\(^{-1}\) (compared with ~1.7 km s\(^{-1}\) sedimentary velocity), and so significant local concentrations of hydrate can be detected seismically.
given data of sufficient resolution. Knowledge of the volumes of hydrate along and near faults may alter estimates for total hydrate present within this and other reservoirs and may influence parameterizations of fluid flux through these systems.

We conduct a seismic velocity analysis of the sediments in the vicinity of Site 997 in which picks of reflection traveltimes for the seafloor and the BSR (bottom-simulation reflector) from 600 CDP gathers (6.125-m spacing) were fit with 1D velocity models to develop a starting model for tomographic inversion. Residuals of these 1-D models are small, on the order 2 ms - 3 ms, but correlated. The patterns of the residuals are suggestive of localized velocity anomalies extending through the gas hydrate zone. Results of a reflection tomography analysis based on 6-km multi-channel seismic streamer data spanning a 3.7-km region across Site 997 are suggestive of velocity anomalies on the order of 0.03 km s⁻¹ that may be due to the presence of concentrated hydrate along faults.
CHAPTER I
INTRODUCTION

1.1. Introduction

One of the foremost challenges facing gas hydrate researchers today is the development of predictive models that quantify and describe the dynamics of the oceanic gas hydrate system in response to variations in the hydraulic and physical properties in marine settings. A necessary prerequisite to development of these predictive models is improved characterization of the physical, chemical and biological processes important in gas hydrate areas and the spatial and temporal scales over which they occur. Improving our understanding of the gas hydrate system therefore requires the application of diverse methods of analysis.

This dissertation uses numerical modeling, tomographic inversions, and field-based data to study particularly the spatial but also the temporal distribution of gas hydrate in porous marine sediments and to explore how the presence of hydrate affects the properties of the reservoir.

1.2. Motivation: Global significance

Scientists have studied gas hydrates for over a century, initially as a laboratory curiosity then as an offshore drilling and pipeline hazard. More recently, interest in gas hydrates has been motivated by the role they may play in natural processes such as climate change and submarine slope failure. The resource potential of gas hydrates is discussed in greater detail in Chapter 2. Under the National Methane Hydrate R&D Act
of 2000, several areas of research have been identified for exploration by academic and industry oriented institutions. Some of these include: (1) developing technologies to assess the distribution of methane hydrate resources, (2) conducting research to determine the role of methane hydrate in the natural environment and devising means of mitigating any negative environmental impact, (3) investigating the chemical and physical properties of methane hydrate through laboratory and field based studies, (4) developing technologies for the efficient production and transportation of methane hydrate for commercial use. The work presented in this dissertation may contribute to the advancement of our ability to assess the resource potential of methane gas hydrate stored in marine deposits.

1.3. Motivation: Scientific interests

Knowledge of the fundamental physical processes associated with gas hydrate formation, accumulation, distribution and dissociation in porous marine sediments is critical to properly characterizing these deposits. While diverse techniques have been applied to constrain the in situ properties of gas hydrate reservoirs, many questions remain unanswered. Laboratory experiments to simulate the formation of gas hydrate in high-pressure vessels do not adequately replicate in-situ conditions nor do they provide a true representation of the mechanisms involved in gas hydrate formation. While seismic data yield a static picture of the state of gas hydrate reservoirs, the results are often times averaged over large spatial scales (Katzman et al, 1994; Korenaga et al, 1996). Thus, local variations are not adequately captured in conventional marine data. In addition, it is difficult to separate the effects due to the presence of gas hydrate alone from the
combined effects of sediment and gas hydrate in the near seafloor marine sediments. Theoretical studies may use analytical models to describe the accumulation of gas hydrate in marine sediments, thereby revealing important information applicable to the dynamics of gas hydrate reservoirs. A major shortcoming of such models is their steady state nature and their inability to duplicate the evolving gas hydrate system. The existing analytical models are therefore of limited utility in addressing problems related to the dynamic gas hydrate system in marine sediments (Davie and Buffett, 2000; Nimblett and Ruppel, 2003).

To expand the existing knowledge base of gas hydrate systems, it is necessary to (1) conduct fine scale seismic studies that account for sediment heterogeneities, (2) incorporate time dependence in numerical models of the gas hydrate formation process, and (3) implement realistic model parameters based on well constrained in situ sediment properties of marine gas hydrate reservoirs. This dissertation examines such fundamental questions as:

1. Where and in what relative concentration does gas hydrate form in marine sediments?
2. What factors affect the spatial distribution of gas hydrate in sediments?
3. How do variables such as sediment properties and in situ flux rates affect the rate of gas hydrate formation and concentration?

1.4. Objectives

The overarching goal of this dissertation is to combine modeling and seismic data analysis to respectively predict and measure the distribution of gas hydrate in marine sediments. More specific objectives that ultimately contribute to the overall framework
include:

1. Development of a numerical model to investigate the evolution of permeability associated with gas hydrate formation in porous marine sediments.
2. Evaluation of the factors controlling the accumulation and distribution of gas hydrate in marine reservoirs.
3. Assessment of the effect of physical properties of the sediments on gas hydrate formation.
4. Comparative analyses of gas hydrate formation in various geologic and hydrologic settings.
5. Seismic characterization of a faulted gas hydrate reservoir.
6. Tomographic imaging of the seismic velocities associated with local variations in hydrate concentration in a gas hydrate reservoir.

1.5. Methods

This work represents the synthesis of various principles, among these are: conservation laws, fluid dynamics, flow and transport in porous media, classical thermodynamics, reflection seismology and tomographic inversion. The application of these principles is described in the following subsections.

1.5.1. Numerical analysis

A major objective of this study was to implement the numerical model described in (1) above to describe the effects of permeability clogging on the hydrodynamic regime of the gas hydrate reservoir. This required the application of (1) the coupled equations of
mass and energy for the two-phase system of hydrate and fluid (dissolved methane in seawater), (2) a thermodynamic formulation of the solubility of methane in seawater as a function of temperature and pressure, (3) the conservation of momentum, expressed as Darcy’s Law, and (4) geometrical models of porosity-permeability relationships. The model was applied to a range of gas hydrate provinces for which many of the key parameters, such as fluid flux, seafloor temperature and pressure and geothermal gradient were measured. The results for our base case, the Blake Ridge, are presented in Chapter 3 and a comparative study of four continental hydrate reservoirs is presented in Chapter 4.

1.5.2. Seismic data acquisition, processing and analysis

The data used in the seismic study were acquired on the Blake Ridge aboard the R/V Ewing in September and October 2000. Our focus area, a transect coincident with Site 997 of the Ocean Drilling Program, was chosen because of the presence of laterally distributed stratigraphic heterogeneities and the abundance of well constrained and diverse data obtained on ODP Leg 164. The Ewing 2000 data were initially stacked shipboard using the versatile seismic data processor, SioSeis. Our shore-based analysis continued with a rigorous velocity analysis in which travel time data were obtained over very small lateral scales ~ 6.25 m and inverted for a velocity depth structure (Chapter 5).

1.5.3. Tomographic analysis and effective medium modeling

One of the objectives of the seismic study was to develop a smooth 2D velocity model, or tomographic image, of the hydrate-bearing sediments at Site 997. Given the large data set acquired, the development of the smooth 2D velocity model required the
use of a robust tomographic inversion scheme, such as the model developed by Van Avendonk et al. (1998). Post stack migration was conducted using SioSeis and the model parameters obtained in the inversion. Finally, a weighted equation that relates the amount of hydrate concentrated in pore space to increased seismic velocities in unconsolidated sediments (Lee, 2000) was employed to obtain the concentration of gas hydrate (Chapter 5).

1.6. Innovation

Several elements differentiate this study from previous studies. First, whereas previous models (Rempel and Buffett, 1997; Xu and Ruppel, 1999) of the marine gas hydrate system have focused on static gas hydrate systems and their response to instantaneous perturbations, in this analysis we develop a fully time dependent model to describe the formation of gas hydrate in porous marine sediments. Incorporating a formulation of the coupled mass, momentum, and energy conservation equations we are able to use parameters characteristic of real hydrate reservoirs to study the theoretical aspects of gas hydrate formation and distribution in natural settings. The results have significant implications for resource characterization and estimating the renewability of these deposits.

Second, the numerical model is the first of its kind to fully account for variations in the thermal and physical regime at discrete depths in the gas hydrate zone. This allows us to examine the evolution of the gas hydrate reservoir and in particular explore the role of fluxes, assess the impact of permeability clogging and examine the dynamic interplay
between variations in temperature and pressure and their dependencies (e.g. methane solubility) on the formation of hydrate in porous media.

Third, this study integrates two independent research disciplines: (1) numerical modeling that quantifies the accumulation and distribution of methane gas hydrate formation under variable *in situ* conditions such as temperature and pressure, fluid flux and sediment permeability and (2) seismic velocity analysis that quantifies variations in hydrate concentrations linked to lithologic features and variable fluid flux. Comparison of the results allows us to assess the validity of anecdotal evidence that suggests that more concentrated hydrate is associated with regions of increased fluid flux such as high permeability conduits (Brooks et al., 1986; Wood and Ruppel, 2000; Nimblett and Ruppel, 2003).

Finally, the seismic component of this study represents one of the most detailed seismic investigations of its kind. Our velocity analysis is able to account for lateral variations on the scale of tens of meters in contrast to previous studies that average velocities over hundreds to thousands of meters (Korenaga et al., 1994; Holbrook et al., 1996; Gorman et al., 2002; Hornbach et al., 2003). This type of analysis may serve as a useful prototype in the development of geophysical techniques to estimate the resource potential of deep-seated gas hydrate reservoirs.

1.7. Contributions

Some of the major contributions of this dissertation toward the advancement of our understanding of the dynamics of gas hydrate systems are:
• To investigate the effect of permeability clogging in the gas hydrate zone and in particular permeability sealing at the BSR and explore the implications for the hydraulic and thermal regime of the gas hydrate zone.

• To provide a description of the evolving hydrodynamic state of the gas hydrate reservoir in one dimension during hydrate formation through the application of a coupled conservation approach.

• To quantify the accumulated concentration of methane gas hydrate in the gas hydrate zone with time as hydrate formation occurs and discusses the implications for the renewability of gas hydrate deposits and regeneration times.

• To implement a robust thermodynamic formulation that allows us to account for changes in methane saturation as temperatures and pressures fluctuate.

• To present one of the most detailed seismic velocity analyses of a section of the Blake Ridge gas hydrate zone.

• To constrain local variations in seismic velocities correlated to increased hydrate concentrations associated with high permeability pathways.

• To integrate the results of seismic velocity analysis and numerical work that imply an association between increased hydrate concentration and regions of rapid fluid flux.

1.8. Organization

This dissertation consists of 6 chapters that include introductory and background material, the results of numerical and seismic studies, and concluding remarks. Chapter 2
provides an overall background on gas hydrates and outlines some of their fundamental physical characteristics and relevant societal and scientific significance. Chapter 2 also includes background information specific to our focus study site and the research objectives that constitute part of a larger study of a gas hydrate system discussed in Chapter 3.

Chapter 3 focuses on the numerical modeling of the Blake Ridge gas hydrate reservoir. The model is parameterized with well-constrained physical parameters obtained in previous investigations of the Blake Ridge system (Paull et al., 1996). We investigate the time scales over which hydrate accumulates, related permeability clogging, and the impact of various hydraulic and physical conditions on the distribution and concentration of gas hydrate in the reservoir. As a continuation of the discussion of the dynamics of gas hydrate formation in porous sediments initiated in Chapter 3, Chapter 4 contains a comparative analysis of the evolution of the gas hydrate zone in various settings. Specifically, the analysis in Chapter 4 investigates the different physical characteristics of hydrate formation in four well studied gas hydrate regions: Nankai Trough, Japan, The Peruvian continental margin, The Costa Rican margin and Gulf of Mexico.

Chapter 5 focuses on the seismic velocity analysis of the Blake Ridge faulted gas hydrate reservoir. We describe some of the fundamental elements of seismic reflection tomography analyses and provide details of our data set and model parameterization. We integrate the results of numerical studies to explain observed phenomena in the seismic data. In addition, we apply a model (Lee, 2000) to constrain hydrate concentration in the gas hydrate zone. Finally, Chapter 6 contains a synopsis of the major results and
conclusions of this research, and provides recommendations for further research.
CHAPTER II
BACKGROUND

2.1. Introduction

This dissertation describes the accumulation and distribution of gas hydrate in marine sediments based on the application of numerical models and analysis of multi-channel seismic data. The objectives of this study are two-fold: (1) to properly characterize the dynamics of the gas hydrate system and (2) to relate variations in local concentration of hydrate in real gas hydrate reservoirs to changes in the hydraulic regime. This requires the integration of geochemical, geophysical and hydrologic principles. This chapter provides background on gas hydrates in general, introduces the mechanistic aspects of the submarine hydrate system, and concludes with a review of the physical properties and characteristics of the Blake Ridge gas hydrate reservoir, the primary site for application of the model developed in Chapter 3 and for interpretation of high-quality seismic data described in Chapter 5.

2.2. Properties of Gas Hydrates

Gas hydrates, first noticed by the petrochemical industry when they were discovered as blockages in natural gas pipelines (Hammerschmidt, 1934), also occur naturally as ice-like compounds that form when water molecules cluster around small gaseous (guest) molecules (e.g. methane, ethane, propane, hydrogen sulfide, and carbon dioxide) at temperatures and pressures common in marine sediments on many continental margins. The water molecules are held together by hydrogen bonds and form a rigid,
orderly, cage-like structure encapsulating molecules of natural gas within its cavities. Clathrate hydrates form in one of three types of crystal structures: Structure I occurs as a cubic structure hosting molecules as large as C₄ (methane) and C₂ (ethane) hydrocarbons; Structure II exists as a diamond lattice in a cubic framework and hosts molecules smaller than C₆ (butane) Structure H hydrates have a hexagonal framework and can support molecules as larger than C₆ (Sloan, 1998).

The hydrate structures may be further differentiated according to the size and number of cavities available for occupation by a gas molecule. Structure I and II gas hydrates, the most common types, possess both large and small cavities. Large cavities are filled more often than small ones, and this preferential occupation is predetermined by the size and shape of the guest molecule. Due to its size, one molecule of methane gas can occupy either of the two cavities of a Structure I or Structure II hydrate. Structure I hydrate is preferred since the presence of the methane molecule lends more to the stability of Structure I than Structure II. Furthermore, Structure I methane hydrate is more stable when methane molecules preferentially occupy the large cavities. The ideal cell formula for perfect stoichiometry of a methane hydrate crystal is given in Table 2.1. Given an ideal stoichiometry, the ratio of the number of water molecules to the number of guest molecules, the hydration number, is 5.75 for a Structure I hydrate. Naturally occurring methane hydrate crystals rarely possess this stoichiometry. For example, only a fraction of the cavities, ~95% of large and ~50% of the small are occupied in the "typical" methane hydrate molecule, resulting in a mole fraction of water > 0.85 (Sloan, 1990). Matsumoto and Borowski (2000) recorded hydration numbers of ~ 6.2 for the Structure I methane hydrates found on the Blake Ridge. A less common type of gas
hydrate, Structure H, contains cavities of three sizes; large, medium and small, and cages of two sizes must be occupied for the molecule to be stable.

**Table 2.1. Hydrate crystal structures, adapted from Sloan (1990).**

<table>
<thead>
<tr>
<th></th>
<th>Structure I</th>
<th>Structure II</th>
<th>Structure H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of guest molecules</td>
<td>&lt; 6Å</td>
<td>(6 to 7Å)</td>
<td>(7 to 9Å)</td>
</tr>
<tr>
<td>No. Cavities/Unit cell</td>
<td>2 small</td>
<td>16 small</td>
<td>1 small, 2 medium</td>
</tr>
<tr>
<td>X - large; Y - medium; Z - small</td>
<td>6 large</td>
<td>8 large</td>
<td>large</td>
</tr>
<tr>
<td>Ideal unit cell formula</td>
<td>6X·22Z·46H₂O</td>
<td>8X·16Z·134H₂O</td>
<td>3X·2Y·12Z·34H₂O</td>
</tr>
</tbody>
</table>

In many of the best-studied gas hydrate provinces, Structure I methane hydrate occurs most commonly. However, thermogenic basins (e.g., the Gulf of Mexico) also have widespread Structure II and occasional Structure H hydrates (Brooks et al., 1986; Sassen and MacDonald, 1994; Sassen et al., 1999). Most of this dissertation focuses on the study of methane-only or predominantly methane systems like the one on the Blake Ridge.

Hydrate structures are mainly composed of water molecules that form cages around less abundant gas molecules with which they interact only through weak van der Waals forces. This structure bears some similarity to that of water ice, and water ice is sometimes studied as a possible analog for the mechanical and thermal properties of hydrate. The properties of water ice and Structure I methane hydrate are summarized in Table 2.2. A key similarity, not mentioned in the table is that the presence of hydrate in porous sediments, like ice, increases the strength of the sediment matrix (Durham et al., 2003; Winters et al., 2001; Winters et al., 2002). Additionally, laboratory research and theoretical studies have recently demonstrated that hydrate formation in porous sediments

13
may occur either along grain boundaries as a cementing material (Ecker et al. 1998) or in the pore space away from grain boundaries (Clennell et al., 1999; Winters et al., 2001; Winters et al., 2002). The presence of hydrate either as a grain "coating" material or pore fluid component strengthens the sediments it forms in, by increasing grain-to-grain cohesion or formation strength of the matrix (frame) respectively. Guerin et al.'s (1999) modeling showed that increased hydrate concentration (as a grain cementing material) increased the bulk moduli of the sediments. Durham et al.'s (2003) triaxial deformation experiments on pure hydrate demonstrated that methane hydrate is > 20x stronger than ice. Dillon et al.'s (2003) work on Northern Gulf of Mexico gas hydrate sediment samples using GHASTLI showed that during undrained shear tests, dilation resulted in negative pore pressures. Gas hydrate formation in porous sediments may therefore inhibit natural processes such as compaction because hydrate is not as easily deformed as sediment grains and will also limit pore fluid expulsion. Dissociation of hydrate into a gas-liquid mixture in deep-seated reservoirs may produce zones of decreased shear strength in which the sediments may become fluidized and unconsolidated or overpressured due to gas build up. Natural triggers such as gravitational loading and seismic activity may weaken layered sediments containing gas-charged zones and promote slope failure (Kayen and Lee, 1991).

The acoustic velocities of methane hydrate and ice are larger than the velocities recorded for marine sediments (~ 1.7 km/s). The velocity contrast may enable the seismic detection of methane hydrate in sediments (Gorman et al., 2005; Hombach et al, 2003). Another important similarity is that, like the melting of ice, the dissociation of methane gas hydrate is an endothermic process that requires the input of heat. Increased
bottom water temperatures may initiate hydrate dissociation and trigger the dissociation of methane and its release into the ocean. If this gas were to reach the atmosphere, methane (a greenhouse gas) might exacerbate global warming and initiate a feedback loop leading to greater warming of ocean water and dissociation of gas hydrate (Dickens et al., 1997; Kennett (2003).

While there are important similarities between water ice and hydrate, the thermal conductivity of ice is more than 4 times larger than that of methane hydrate (de Martin et al., 1999). The disparity is due to the the scattering of phonons (which transmit energy) because of a resonant coupling of the translational and rotational motion of guest molecules and the anharmonic vibration of water molecules about a fixed position (Sloan, 1998). This has important implications for assessing the thermal evolution of and the impact of temperature changes on gas hydrate reservoirs as hydrate formation progresses.

**Table 2.2. Properties of methane gas hydrate and ice.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Ice</th>
<th>CH₄ hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermal properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat capacity (J K⁻¹ kg⁻¹)</td>
<td>2.097 @ 270 K</td>
<td>2.07 @ 270 K</td>
</tr>
<tr>
<td>Heat of dissociation (kJ kg⁻¹)</td>
<td>333.5 @ 273 K</td>
<td>338.7 @ 273 K</td>
</tr>
<tr>
<td>Thermal conductivity (W m⁻¹ K⁻¹)</td>
<td>2.2 @ 263 K</td>
<td>0.5 @ 263 K</td>
</tr>
<tr>
<td><strong>Physical properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk Compressibility (Pa)</td>
<td>12 x 10⁻¹¹ @ 273 K</td>
<td>~14 x 10⁻¹¹ @ 273 K</td>
</tr>
<tr>
<td>Density (kg m⁻³)</td>
<td>917 @ 273 K</td>
<td>910 @ 273 K</td>
</tr>
<tr>
<td>Compressional velocity (m s⁻¹)</td>
<td>~3800 @ 273 K</td>
<td>3369 @ 273 K</td>
</tr>
</tbody>
</table>

### 2.3. Gas hydrate reservoirs

In the focus areas for this thesis, naturally occurring gas hydrate is mainly found as structure I methane hydrate with trace amounts of CO₂, H₂S and higher hydrocarbons.
present (Kvenvolden and Lorenson, 2001). Gas hydrate occurrences have been
documented at over fifty locations worldwide (Figure 2.1). In permafrost environments,
hydrates may occur at depths of 150 to 2000 m in the sedimentary section. Marine
deposits concentrated in organic-rich sediments on continental margins contain most of
the world's gas hydrate.

2.3.1. Gas hydrate phase equilibria

From a thermodynamic perspective, \textit{in situ} pressure and temperature (P-T) are the
two most dominant factors governing the formation and dissociation of gas hydrate in
marine sediments, and these are to first order governed by seafloor temperature,
geothermal gradient, fluid flux rates, and hydrostatic pressure. Figure 2.2 shows the
pressure-temperature regime under which hydrate is stable in oceanic and permafrost
environments for the methane system in pure water. To the left of the stability boundary,
hydrate is stable and coexists with aqueous phase methane. At higher temperatures,
aqueous phase methane coexists with methane gas. It should be noted that the phase
equilibrium curve only delineates the P-T conditions under which gas hydrate may
theoretically exist. Other factors control whether gas hydrate will actually form in a
given region that lies within the stability field.

Research has also demonstrated that the stability conditions of gas hydrates in
marine sediments are also affected by secondary factors such as salinity, physical
properties of sediments, mineralogy of host sediments and gas composition (Sloan, 1998;
Figure 2.1
Figure 2.1. Worldwide distribution of observed or inferred gas hydrate occurrences (modified from Kvenvolden, 1993)
Figure 2.2. (a) Methane gas hydrate phase equilibrium curves in (a) Continental reservoir and (b) Oceanic reservoir (modified from Collett, 2001).
Dickens and Quinby-Hunt, 1997; Zatsepina and Buffett, 1997; Clennell et al., 1999). These secondary factors play a critical role in governing the local extent of the gas hydrate zone (GHZ). For example, increased salinity lowers the activity of water and depresses dissociation temperatures, shifting the stability curve to the left, elevating the base of the GHZ (Handa, 1990; Dickens and Quinby-Hunt, 1997). Capillary pressures, which are really an expression of the excess internal energy of a small crystal when confined to a small pore space, also shifts the stability curve to the left, elevating the base of the GHZ (Clennell et al., 1995; Clennell et al., 1999; Henry et al., 1999). This phenomenon has been invoked as one possible explanation for anomalously low temperatures at the base of the GHZ (Ruppel, 1997). Sediment host properties may also affect phase equilibria. For example, the presence of substrates such as clays, which have large interfacial surface areas (third surfaces), may inhibit gas hydrate stability (Cha et al., 1988). The third surface may alter the liquid-solid area over which the hydrate phase transformation occurs. Furthermore, sediments may lower the free energy of water within pores, thereby increasing the interactions between water and mineral substrates at the walls. Water near the pore walls remains bound to the mineral surface while water away from the boundary is free to form hydrate. As more hydrate forms in pore space more energy is required to draw water away from pore walls for hydrate formation (Clennell et al., 1999). Decreased temperatures, which result in a shift of the stability boundary to the left, provide the excess energy needed for further hydrate formation. Additionally the presence of gases such as CO₂ and C₂H₆ may lend additional stability to the Structure I methane hydrate crystal, shifting the curve to the right, thus potentially lowering the base of the GHZ (Sloan, 1998; Kvenvolden, 1993).
2.3.2. In Situ Methane production

Methane hydrate in marine sediments may include either biogenic or thermogenic gas. Thermogenic methane, along with quantities of ethane and propane, is produced by a catagenic process in which buried organic material is decomposed at increased temperatures and pressures (Sloan, 1998). These processes take place at depths in excess of 1000 m in the sediment column (Kvenvolden and Lorenson, 2000). Thermogenic methane must migrate upwards through great distances via faults and mud volcanoes to reach the gas hydrate zone (Brooks et al., 1986).

Biogenic methane is a byproduct of the breakdown of organic matter by microbial organisms (Whiticar, 1999). The Blake Ridge gas hydrates are largely formed from biogenically derived methane (Paull et al., 1996). Evidence for this is provided by analysis of: (1) the ratio of methane to ethane + propane \((C_1/(C_2+C_3))\); a high ratio indicates biogenic production whereas a low ratio is indicative of thermogenic methane; and (2) the \(^{13}C\) ratio that relates \(^{13}C\) to \(^{12}C\) in the sample to that in the Pee Dee Belemnite standard. Carbon isotopes are fractionated during the reduction of \(CO_2\) by microbial organisms to produce \(CH_4\). The \(^{13}C\) ratio is therefore higher for microbiologically derived \(CH_4\) and lower for thermogenically generated \(CH_4\).

2.3.3. Mechanism of Gas Hydrate Formation

Methane produced either thermogenically or biogenically beneath the base of the gas hydrate stability zone can migrate into the stability zone as free gas or in aqueous solution. While gas hydrate has been observed to form from methane in either one of these phases (Brewer et al., 1997), equilibrium thermodynamics suggests that the presence of
free gas is not required to produce hydrate (Zatsepina and Buffett, 1997). There are currently three proposed mechanisms for the formation of gas hydrate in marine sediments: (1) hydrate may form directly from biogenically derived methane in situ, (2) hydrate may form from free gas (biogenically or thermogenically derived or both) either migrating upwards into the gas hydrate stability zone or recycled from free gas derived from the dissociation of hydrate at the base of the gas hydrate stability zone driven by subsidence, and (3) hydrate may form from the migration of dissolved gas (biogenically or thermogenically derived or both) in seawater migrating upwards through the gas hydrate zone.

Of the scenarios mentioned above, there are two reasons that make (3) the likely mechanism of formation of gas hydrate in marine sediments. First, hydrate formation from methane created in situ requires a higher rate of methane production than has yet been recorded in microbial systems from microorganisms (Hyndman and Davis, 1992; Paull et al., 1996). Second, results of equilibrium thermodynamics studies are not consistent with the formation of hydrate from the free gas phase (Zatsepina and Buffett, 1997). Nonetheless, gas hydrate has been observed to form from free gas in laboratory (Tohidi et al., 2001) and seafloor experiments (Brewer et al., 1997). The mechanism of hydrate formation we adopt in this study is precipitation from gas saturated pore water migrating into the gas hydrate stability zone (Hyndman and Davis, 1992; Zatsepina and Buffett, 1997). If the concentration of methane migrating into the gas hydrate stability zone is high enough (i.e., it exceeds its local solubility in seawater), then the dissolved gas will combine with pore water to form gas hydrate (Hyndman and Davis, 1992). Further evidence for the formation of hydrate from aqueous phase methane was recorded in a study by Booth et al.,
(1996) in which they demonstrated that 70% of all recovered samples of gas hydrate were found in sediments conditions consistent with the two-phase (high pressure, low temperature) region of methane hydrate stability. This does not imply however that only two phases were present in the GHZ.

2.3.4. Gas Hydrate occurrence in sediment

Booth et al. (1996) demonstrated that hydrate formation in coarse-grained sediments generally resulted in segregated structures such as lenses, nodules or pellets, whereas accumulation in fine-grained sediments usually occurred in disseminated form. Other studies have provided similar evidence (Table 2.3).

<table>
<thead>
<tr>
<th>Location</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blake Ridge</td>
<td>Heterogeneous sediments containing hydrate nodules, possible fracture fillings and layers embedded in clay</td>
</tr>
<tr>
<td>Cascadia Margin</td>
<td>Small pellets disseminated in silty clays and massive hydrate near surface</td>
</tr>
<tr>
<td>Costa Rica</td>
<td>Massive hydrate in fractured clays and siltstones. Thin sheets in fractures. Hydrite cement in ash layers</td>
</tr>
<tr>
<td>Gulf of Mexico</td>
<td>Scattered crystals of mm to cm diameter associated with sandy layers</td>
</tr>
</tbody>
</table>

Sources: Tich et al. (1985); Kopf et al. (1995); Bolton et al. (2000); Fauld et al. (1996)

These observations suggest that there may be a correlation between the formation of more concentrated hydrate with accumulation in more coarse lithologies.

Additionally, Brooks et al. (1984) observed that biogenically derived hydrate occurred in disseminated form in the Gulf of Mexico sediments and that thermogenic hydrate was found in massive deposits. The latter observation indicates that massive hydrate may be associated with high permeability pathways since thermogenic gas must
migrate through great distances to get to the gas hydrate zone. Hydrate formation in sediments therefore depends not only on the availability of methane gas but also on sediment lithology and structure. Estimates of hydrate concentration in sediments and consequently the size of the global reservoir must take into account such variables.

2.4. Size of the Natural Gas Resource

One cubic meter of pure methane hydrate can contain as much as 164 cubic meters of methane gas at standard temperature and pressure (Sloan, 1998). For this reason gas hydrates are sometimes considered to a source of untapped energy, and much research has been focused on (1) the recovery of methane gas from its clathrate structure (Selim and Sloan, 1989; Yousif et al., 1991), and (2) quantifying the amount of methane sequestered in gas hydrate deposits worldwide (Kvenvolden, 1993; Gorzitz and Fung, 1994; Harvey and Huang, 1995; Holbrook et al., 1996; Dickens et al., 1997; Collett, 2001; Riedel et al., 2001). The most recent estimate of the total amount of methane sequestered in hydrate reservoirs is \( \sim 2.0 \times 10^{16} \text{ m}^3 \) (Collett, 2001). This value is two orders of magnitude larger than the amount in conventional natural gas reservoirs.

Depending on the estimation technique, methane content in worldwide gas hydrate deposits ranges from \( \sim 2.0 \times 10^{16} \text{ m}^3 \) to \( \sim 14 \times 10^{16} \text{ m}^3 \) (Kvenvolden and Lorenson, 2000) (Table 2.4). Kvenvolden’s (1993) estimate is based on observations of BSRs on marine seismic records over the globe and conservative estimates of the lateral extent of the gas hydrate zone and hydrate concentration. Holbrook’s estimate is based on more precise estimates of hydrate concentrations and deposits in the Blake Ridge reservoir from seismic data, but is extrapolated for a conservative worldwide average.
Gornitz and Fung (1994) and Harvey and Huang (1995) obtain their estimates from general circulation models that include input parameters such as thermal gradients, porosities, phase equilibria, and in situ methane production. Finally, Dickens' (1997) estimate is based on measurements of the volume of methane degassing from hydrate cores brought to the surface while maintained at in situ conditions.

The motivation for considering gas hydrate as a potential energy resource is based on the fact that natural gas consumption is expected to increase by as much as 40% over the next twenty years (Collett, 2001). Such an increase could significantly drain the estimated 1400 trillion cubic feet supply of conventional natural gas resources (Collett, 2001). For gas hydrates to be developed as a resource, techniques to (1) remotely detect the presence of gas hydrates in their natural environment, (2) accurately quantify the global inventory of methane gas sequestered in gas hydrate reservoirs, and (3) efficiently extract methane gas from marine and permafrost environments for public consumption will be required (Collett, 2001).

Table 2.4. Estimates of the volume of methane gas trapped in oceanic deposits worldwide, adapted from Kvenvolden and Lorensen (2000).

<table>
<thead>
<tr>
<th>Volume(m³)</th>
<th>Reference</th>
<th>Estimation technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8 x 10⁶</td>
<td>Kvenvolden (1993)</td>
<td>Seismic data</td>
</tr>
<tr>
<td>2.6 - 14 x 10⁶</td>
<td>Gornitz and Fung (1994)</td>
<td>Modeling</td>
</tr>
<tr>
<td>4.5 x 10⁶</td>
<td>Harvey and Huang (1995)</td>
<td>Modeling</td>
</tr>
<tr>
<td>5.5 x 10⁷</td>
<td>Holbrook et al. (1996)</td>
<td>Seismic data</td>
</tr>
<tr>
<td>1.8 x 10⁹</td>
<td>Dickens et al. (1997)</td>
<td>Pressure core sampling</td>
</tr>
</tbody>
</table>

2.5. Detection of Gas Hydrate in Marine Reservoirs

Geophysical, geological and geochemical techniques have been employed to identify the occurrence of gas hydrate in marine sediments. Geophysical evidence has
been provided in the form of seismic and well logging data. Geological evidence usually takes the form of sediment and mud properties and gas hydrate samples from recovered cores. Finally, geochemical methods depend on analysis of pore water chemistry and gas compositions. A more detailed summary is provided below.

2.5.1. Seismic methods

For over 20 years, the presence of gas hydrate in marine sediments has been inferred using geophysical techniques. The presence of the bottom simulating reflector (BSR) in marine seismic records has traditionally been considered evidence for the occurrence of gas hydrate (Tucholke et al., 1977). The BSR is a high amplitude event characterized by a negative reflection coefficient and marks the phase transition between gas hydrate above and underlying free gas at the base of the gas hydrate stability zone (BGHS). A defining characteristic of the BSR is that it cuts across stratigraphy, and the reflector often loosely mimics seafloor topography. While the presence of the BSR is indicative of the presence of gas hydrate, the absence of a BSR does not always imply the absence of hydrate. Hydrate occurrences have been repeatedly observed in the absence of a BSR, for example in the Gulf of Mexico and at Site 994, ODP Leg 164 (Paull et al., 1996) indicating that the BSR is not a necessary feature of gas hydrate in marine sediments. It has been theorized that the BSR is formed only when the base of the gas hydrate zone and the base of gas hydrate stability are coincident (Xu and Ruppel, 1999). Furthermore, seismic analysis of the BSR can only yield information that is limited to sediments in the near vicinity of the BSR (Holbrook et al., 2002). Estimates of the size of worldwide deposits of methane gas hydrate based on the occurrence of the BSR in
seismic section and limited knowledge of concentrations may therefore be erroneous. More recently, the presence of bright spots, enhanced seismic reflection from high velocity regions (Gorman et al., 2002; Hornbach et al., 2003), and the occurrence of amplitude blanking, a phenomenon exhibited in seismic data as suppressed reflectance caused by a reduction in impedance contrast between more and less porous sediments (Dillon et al., 1993; Lee and Dillon, 2001; Holbrook et al., 2002), have been adopted as a geophysical marker for the presence of gas hydrate in marine sediments.

2.5.2. Wireline logging

Wireline logging is also a useful tool in detecting oceanic as well as permafrost gas hydrate (Collett, 1983, 1993). Neutron spectroscopy logs measure the number of neutrons emitted from collisions with hydrogen molecules, and therefore reveals the amount of hydrogen in pore space. The amount of hydrogen can then be related to the amount of water and hydrocarbons (Collett, 2001b) present in drilling muds containing pore fluids and other constituents from gas hydrate dissociation. Sonic velocity logs register increased compressional velocities due to the presence of rigid hydrate in pore space, and resistivity logs provide information about the level of pore water saturation and salinity in sediments. Measurements of pore water saturation and salinity can yield direct estimates of hydrate concentration in sediments since hydrate dissociation freshens pore waters and decreases salinity (increasing resistivity), whereas ion exclusion during hydrate formation increases salinity (decreasing resistivity).

2.5.3. Geochemical methods
Geochemical evidence for the presence of gas hydrate has been mainly provided on the basis chloride (Cl) anomalies. The formation of gas hydrate in marine sediments 'removes' water and gas molecules from pore fluids but excludes ions such as Cl. Ions form colomic bonds with water resulting in an increase in effective radii, which causes them to be both too large and too polar for cage occupancy (Sloan, 1998). Consequently, pore waters in the vicinity of gas hydrate deposits may be enriched in Cl ions with respect to background seawater chlorinity values (Ussler and Paull, 2001), although recent studies in the Gulf of Mexico indicate no such relationship (Santamarina, pers. comm.). Furthermore, when gas hydrate dissociates, it releases water depleted in Cl ions into the pores, resulting in pore water freshening (Hesse and Harrison, 1981). A decrease in Cl concentration upon dissociation is therefore a direct measure of the bulk volume of the sediment matrix occupied by gas hydrate. In addition to pore water chloride anomalies the presence of gas hydrate has also been inferred on the basis of 18O isotope. Water δ18O is fractionated on hydrate. 18O is more concentrated in the hydrate cages relative to that in the pore water. Therefore enrichment in the 18O in pore fluids may be indicative of gas hydrate dissociation (Kvenvolden and Kastner, 1990).

2.5.4. Detection limits and constraints

While seismic, logging and chemical data provide a reliable means of estimating hydrate concentrations in marine deposits, there are a few difficulties that must be addressed in order to accurately interpret the data. For example, in the analysis of logging and chemical data, imprecise estimates of background values of sediment porosity, in situ salinity and empirical constants can lead to incorrect predictions of
hydrate concentrations. In particular, in the case of chloride anomalies, these excursions may also be due to clay mineral authigenesis in the sediments (Kastner et al., 1998).

The successful interpretation of seismic data for gas hydrate concentrations also relies on accurate estimates of background sediment properties (e.g. porosity), and an understanding of the elastic properties of the media. Additionally, seismic models must also account for the presence of more than one matrix component in their respective proportions (i.e. hydrate, sediment and fluid). The Blake Ridge is such a well-studied region that background sediment properties are well defined, elastic properties have been estimated, and models relating hydrate concentration in pore space to seismic velocity developed making it a benchmark for focused studies of gas hydrate formation in marine sediments.

2.6. Focus Site – The Blake Ridge Gas Hydrate Reservoir

The Blake Ridge is a sedimentary feature that formed on the transitional continental to oceanic crust off the Eastern margin of the United States during the late Oligocene to early Miocene (Mountain and Tucholke, 1985). Named for its positive topography, the Blake Ridge was deposited by currents flowing longitudinally along the Atlantic margin and carrying sediments eroded off the Blake Plateau. Lithologically, Blake Ridge sediments represent Miocene to Pleistocene hemipelagic muds and silty clays. More specifically they are composed of nanofossil-rich clays and claystones, opaline silica and moderate carbonate. Sediment porosity averages 55 to 60% and particle sizes range from $10^{-6}$ to $10^{-9}$ m (Clennell et al., 1999; Ginsburg et al., 2000) for silty clays to $10^{-7}$ m for diatoms (Kraemer et al., 2000).
The sediments form a homogeneous stratigraphic sequence both vertically and laterally, which allows us to image discontinuities related to the presence of concentrated hydrate seismically and provides the opportunity to conduct a comparative analysis of lateral variations in sediment properties caused by increased hydrate concentrations associated with lithologic features. Furthermore, the Blake Ridge lies in a tectonically inactive region on a passive margin (Figure 2.3), making the area an important type section for a relatively steady-state hydrate reservoir.

2.6.1. Gas Hydrate occurrence on the Blake Ridge

Apart from direct observations of gas hydrate from cores obtained from drill holes at Sites 994 and 997, geochemical and logging analyses indicate that gas hydrate is present in disseminated deposits in the Blake Ridge sediments between 190 and 450 mbsf across the transect including Sites 994, 995 and 997 (Figure 2.4). Chemical and physical analyses also indicate that nearly 100% of the hydrate samples recovered on ODP Leg 164 are Structure I methane hydrate (Matsumoto and Borowski, 2000).

Analyses of seismic sections also indicate that the BGHZ and the free gas zone are coincident at Site 997 (strong BSR reflections), but not at Site 994 (no detectable BSR). This observation is explained by modeling studies (Xu and Ruppel, 1999; Wood and Ruppel, 2000) that reveal coincidence of the top of the free gas zone, the BGHZ, and the BGHS at sites with methane flux in excess of a critical value (e.g., Site 997) but separation between the zone of hydrate occurrence and the top of the free gas zone at locations of subcritical methane flux (e.g., Site 994). Furthermore, hydrate has been
Figure 2.3. Physiographic map of the southeastern continental margin of the United States. The region over which hydrate is estimated to be present on the basis of a BSR is lightly shaded, Leg 164 drill sites re-plotted as circles.
Figure 2.4. (a) Chlorinity profiles for pore water collected from cores at Sites 994, 995 and 997 (b) Electrical resistivity data from the respective sites (modified from Paull et al., 1996).
observed in disseminated form at Site 994 (sub-critical methane flux), whereas more concentrated forms were observed at high flux sites Sites 995 and 997.

2.6.3. Seismic velocities of the Blake Ridge sediments

Seismic velocities ranging from 1550 km s⁻¹ at 150 mbsf to 1750 km s⁻¹ and 1850 km s⁻¹ km at 450 mbsf have been observed in the porous sediments at Sites 994, 995 and 997 ODP Leg 164 (Figure 2.5) on the basis of vertical seismic profiling (VSP) data. Based on a model relating seismic velocities to hydrate content the observed velocities have been determined to be consistent with hydrate concentrations of ~ 4% to 7% by volume (Holbrook et al., 1996). Seismic sections reveal that the entire region is pervasively faulted, with faults sometimes penetrating the BSR and extending to depths as shallow as 10 m. The faults have an average dip of 55° (Figure 2.6) and could represent high flux migration pathways along which concentrated hydrate may form. ODP Leg 164 drilled through one of these faults at Site 997, and Wood and Ruppel (2000) interpret seismic and thermal data and discuss the implications of massive hydrate found at this site.
Figure 2.5. Seismic velocity profiles for the Blake Ridge determined from inversion VSP traveltine data (Shipboard Scientific Party (1996)).
Figure 2.6. Seismic section of the Blake Ridge gas hydrate reservoir crossing Leg 164 drill sites.
CHAPTER III
PERMEABILITY EVOLUTION DURING THE FORMATION OF GAS HYDRATE IN MARINE SEDIMENTS

3.1. Introduction

Methane gas hydrates are solid, ice-like compounds of water and methane stable at temperatures and pressures characteristic of marine continental margins and permafrost regions. Much of the research on gas hydrates has focused on characterizing the location of these deposits and estimating the amount of sequestered carbon or methane. More recently, attention has turned to understanding the dynamics of gas hydrate reservoirs and the mechanisms for formation of the deposits [Rempel and Buffett, 1997; Xu and Ruppel, 1999; Reppel and Kinoshita, 2000; Davie and Buffett, 2001]. A key outcome of some of these studies has been the realization that fluid (water + dissolved methane), methane, and energy fluxes largely control the distribution of free gas (excess gas above saturation) and gas hydrate in simple, homogeneous systems.

Anecdotal evidence has long suggested a spatial association between gas hydrate deposits and zones of rapid flux of gas and fluids [e.g., Ginsburg and Sobolev, 1997; Hyndman and Davis, 1992]. Particularly in active margin settings, hydrologic systems that produce focusing of gas and gas-charged water are a defining characteristic at locations where gas hydrate is concentrated [Davis et al., 1995; Tryon et al., 1999; Trehu et al., 1999]. Similarly, faults bounding salt diapirs provide conduits for fluids, gas, and heat and lead to the formation of seafloor gas hydrate mounds in some parts of the Gulf.

---

1 The contents of this chapter represent a slightly modified version of a manuscript currently in press in the Journal of Geophysical Research and are copyrighted by the American Geophysical Union.
of Mexico [Brooks et al., 1984; MacDonald et al., 1994]. On the Blake Ridge, a passive margin sediment drift deposit, focused flux concentrates gas hydrate in shallow sediments and at the seafloor at Ocean Drilling Program (ODP) Site 996 [Pauil et al., 1996; Van Dover et al., in press]. More widespread advective flux [Wood and Ruppel, 2000] may occur in the system of pervasive, fine-scale, high-angle (~55° dips) faults (Figure 3.1) visible in single channel seismic data [Holbrook et al., 1996] and higher resolution multichannel [Holbrook et al., 2002] and deep-tow data [Rowe and Gettrust, 1993]. The faults extend from ~200 m below the bottom simulating reflector (BSR, nominal depth of 450 m below seafloor or mbsf) to within tens of meters of the seafloor and may provide pathways for gas migration from below the BSR into the overlying gas hydrate stability zone [Garman et al., 2002].

In recent years, the results of theoretical models that couple energy, momentum, and mass conservation have supported the idea that advection, unlike diffusion, favors the concentration of gas hydrate and the formation of thick gas hydrate zones [Xu and Ruppel, 1999]. Although such theoretical models have provided the physical basis for understanding the simple hydrodynamics of marine gas hydrate systems, a fundamental shortcoming of these models is their reliance on steady-state, analytical formulations and their assumption of homogeneous sediment properties. In addition, the models provide little insight into the mechanistic aspects of gas hydrate formation as a transient process. In this paper, we investigate the evolution of gas hydrate zones in fractured and porous media and explore the implications of permeability reduction for the trapping of gas, alteration of hydrodynamic regimes, and regeneration of gas hydrate deposits.
Figure 3.1. Blake Ridge sediments observed in (a) a high-frequency multi-channel seismic section, recorded by the Naval Research Laboratory (NRL) using a deep-towed acoustics/geophysics (DTAGS) system and (b) a single channel seismic section (courtesy of W.S. Holbrook). The lines zirk steeply-dipping (55°) faults having ~20 m offsets and extending from just below seafloor through the BSR.
3.2. Previous Studies

Although previous research has not explicitly explored the link between the evolution of permeability in marine sediments and the hydrodynamics of gas hydrate systems, two classes of studies lay a critical foundation for this research. The first category of studies concerns the interaction of fluids with pore space and fractures in rocks and sediments (permeability evolution). The second class of studies focuses on models for the dynamics of marine gas hydrate systems.

3.2.1. Permeability of Seafloor Systems

In most sedimentary systems, fluid transport occurs through a heterogeneous permeability network that can be represented as a combination of fractures and a porous medium, shown schematically in Figure 3.2. Microscopically, the permeability of the medium is controlled by the degree of connectivity of pore space, pore size distribution, fracture width, and pore diameter. Describing hydrodynamic systems in marine sediments therefore requires a formulation that links pore-scale characteristics to permeability variations.

In this paper, we examine gas hydrate formation and resulting permeability evolution in two endmember models. For the first model, flow is confined to a discrete fracture [Snow, 1968; Steefel et al., 1994; Steefel et al., 1998], and permeability is proportional to the square of the fracture aperture. In the second model, flow occurs in a porous medium [Bear, 1972], and permeability is proportional to the square of the pore diameter. In contrast to the work of Barenblatt and Zheltov [1960], who study
Figure 3.2. Schematic representation of the structure of marine sediments. At the far left, the top of the gas hydrate stability zone (TGHZ) lies at some depth within the sediments, and the base of the gas hydrate zone (BGHZ) only coincides with the BSR where there is sufficient free gas in the system (see Figure 3; Xu and Ruppel, 1999). The enlarged views illustrate the fractures within a porous media and illustrate the physical meaning of some of the parameters used to describe the endmember models formulated in this study.
permeability evolution by coupling fluid flow between porous and fractured parts of a medium, we consider flow in fractures and porous media separately.

To some extent, the formation of gas hydrate from dissolved gas in porous media can be considered analogous to mineral precipitation of dissolved species in pores and fractures. Existing laboratory and analytical studies of precipitation of dissolved species focus on chemical diagenetic systems [Aharonov et al., 1998; Tenthorey et al., 1998; Aharonov et al., 1997; Bolton et al., 1996; Bolton et al., 1997] and mass transfer formulations [Wood and Hewett, 1982; Lowell et al. 1993]. Of particular relevance is the research of Bolton et al. [1997], who use a numerical model to describe the dissolution and precipitation of quartz in a porous medium and to track the evolution of permeability and porosity in a forced flux environment. A key difference between our gas hydrate model and the quartz precipitation model of Bolton et al. [1997] is their inclusion of reaction kinetics, which is not considered here. We provide a justification for this assumption in a later section.

Permeability reduction models based on mass transfer approaches have been applied to problems as diverse as silica cementation of sandstones [Wood and Hewett, 1982] and silica precipitation in hydrothermal upflow zones [Lowell et al., 1993]. Assuming chemical equilibrium and ignoring reaction kinetics, precipitation of silica in pores or fractures is modeled by considering the mass balance between the silica deposited and that concentrated in the fluxing fluid. We adopt a comparable approach and similar assumptions to describe the role of permeability evolution in altering the hydraulic regimes in gas hydrate-bearing sediments.
3.2.2. Models of Gas Hydrate Reservoirs

Existing models of the marine gas hydrate system provide the second critical building block for research on the permeability evolution of hydrate-bearing sediments. The one-dimensional, steady state models of Rempel and Buffett [1997] and Xu and Ruppel [1999] adopt simplifying assumptions that lead to analytical solutions of the coupled equations for conservation of mass, momentum, energy, and total methane (i.e., all methane present in solid, liquid, and gas phases). In this paper, we use methane to indicate the molecular compound CH₄, regardless of its phase. Free gas is the term used to denote gas in excess of saturation, particularly beneath the base of gas hydrate stability.

The results of studies such as Xu and Ruppel [1999], Ruppel and Kinoshita [2000], Wood and Ruppel [2000] underscore the role of energy, methane, and fluid flux in determining the existence of the bottom simulating reflector (BSR), the vertical extent of the gas hydrate zone (GHZ), and the thickness of zones devoid of either free gas or gas hydrate (Figure 3.3). Although such models have provided important insights into the dynamics of gas hydrate reservoirs, the steady-state nature of the models renders them inapplicable to the complete range of problems relevant for understanding these systems.

In this study, we adopt a fully dynamic approach by adding time dependence to a modified version of an existing one-dimensional model describing the accumulation of gas hydrate in the two-phase (gas hydrate and water + dissolved gas) region of the three-phase system. The model tracks the permeability changes that accompany hydrate formation and deposition and determines the consequent reduction in fluid flux. Through
Figure 3.3. The relative positions of the gas hydrate zone (GHZ), which is our model domain, the gas hydrate stability zone, and the free gas zone in a generic system in which the supply of methane is subcritical, meaning that the top of the free gas zone is not coincident with the base of the hydrate zone. For our model, the methane supply is always assumed just in excess of critical so that the base of the GHZ coincides with the base of the stability zone. The base of the stability zone occurs where the pressure-temperature stability condition (solid line) crosses the geotherm (dashed line). Temperatures are read across the top axis. The bottom axis corresponds to the methane solubility curve Msl (heavy dotted line) and the methane concentration curve M, or the mass fraction of methane in solution (solid curve). Within the stability zone, hydrate is assumed to form only when M exceeds Msl. The pressures and temperatures in the GHZ are determined from fluid and energy fluxes and the boundary conditions of seafloor temperature, pressure and depth, T0, P0, z0 respectively. Figure after Xu and Ruppel (1999).
full coupling of flow and transport, we account for transient hydraulic, thermal, and chemical gradients that develop in the gas hydrate zone during permeability changes.

3.3. Numerical Model

In this section, we describe the fundamental components of the numerical model and give the mathematical formulation for the evolution of permeability in the porous and fractured media endmembers. Methane may occur as three phases in marine sediments: gas hydrate $h$, seawater with dissolved methane $l$, and free gas $g$. Assuming equilibrium thermodynamics, the three phases can coexist only along the curve separating the gas hydrate and free gas stability fields. In nature, these three phases can coexist at the BSR, where methane may be in a continual state of transformation between the solid, liquid and gas phases. Seafloor seeps such as those associated with seafloor gas hydrate mounds (e.g., Gulf of Mexico [Macdonald et al., 1994] and Site 996 on the Blake Ridge [Van Dover et al., 2003]) represent other loci at which methane may coexist in all three phases. For the most part, though, only two phases—gas hydrate and aqueous methane—need be accounted for within the GHZ at any time [Handa, 1990; Rempel and Buffett, 1997; Xu and Ruppel, 1999], and this is the approach adopted in this study.

The formation and dissociation of gas hydrate are governed by temperature, pressure, the activity of water, and the concentration of methane. To simplify the discussion, we cast these parameters in terms of temperature, pressure, and methane solubility. Pressure and temperature conditions constrain the region of gas hydrate stability in marine sediments. Methane solubility, a strong function of pressure, temperature, and the activity of water, increases as a function of depth within the gas
hydrate stability zone and then decreases with depth in the underlying free gas zone (e.g., Duan et al., 1992; Zatsepina and Buffett, 1997), as demonstrated in Figure 3.3. In simple systems, gas hydrate can only form where the mass fraction \( M \) of methane dissolved in water exceeds its local solubility \( M_d \) (Xu and Ruppel, 1999).

3.3.1. Role of solubility

The relationship between mass fraction of methane and its solubility is fundamental to this research and is therefore explained in more detail here. Typically, the zone in which gas hydrate is stable (if it forms) extends downward from the seafloor to the depth at which the geothermal gradient intersects the phase equilibrium curve. In real settings, gas hydrate often occurs neither as shallow as the seafloor nor as deep as the base of the stability zone. Near the seafloor, three factors contribute to the exclusion of gas hydrate in systems in which water is not a limiting component. First, the low concentration of methane at conditions characteristic of the most shallow sediment pore water and bottom water (i.e., fluids are undersaturated with respect to methane) means that any gas hydrate that forms and is in contact with undersaturated fluids will dissolve relatively rapidly. Deposits formed at or near the seafloor under such conditions can only be maintained if they are constantly replenished from below by new supplies of methane or are armored from dissolution in the overlying seawater by such physical barriers as petroleum coatings. Second, chemical processes (e.g., sulfate reduction and anaerobic methane oxidation) in the shallow sediments on many continental margins lead to the consumption of methane, except in high flux settings. Third, in many cases, methane fluxing upward through the sediments is mostly consumed by hydrate formation at depths
tens to more than a hundred meters below the seafloor, depending on the setting. If in situ methane production at shallower depths does not yield enough methane to locally saturate pore fluid, no hydrate will form and only a dissolved gas zone will lie between the seafloor and the top of the gas hydrate.

Near the base of the gas hydrate stability zone, other factors contribute to the absence of gas hydrate under some circumstances. Here, methane solubility is higher, and gas hydrate only forms when aqueous methane is supplied in excess of its solubility. Xu and Ruppel [1999] define a critical methane flux required for gas hydrate to form as deep as the base of the stability zone, and this flux is also a condition for the existence of a bottom simulating reflector (BSR) in simple systems.

3.3.2. Discrete fracture model

Assuming laminar flow, the flux (mass flux per unit area per unit time) $q_f$ through a vertical smooth-walled, parallel fracture of aperture $d$ can be described by Darcy’s Law [Snow, 1968; Phillips, 1991], which we here give in scalar form owing to the one-dimensional nature of the model:

$$ q_f = -\frac{d^2 \rho}{12 \mu_l} \frac{dp}{dz} + \rho_l g, $$

(1)

where $p$ is pressure, $g$ denotes gravitational acceleration, $\rho_l$ represents the density of the liquid phase, and $\mu_l$ gives the dynamic viscosity of the liquid phase. The evolution of fracture aperture is given by the expression:

$$ d_i = d_i(1 - S_i), $$

(2)
where \( d_i \) represents the fracture aperture at time \( t \), and \( d_i \) is the initial fracture aperture. In (2), \( S_i \) is the volumetric fraction of pore space filled with hydrate at time \( t \) and is determined from the expression for methane hydrate accumulation rate [Xu and Ruppel, 1999]:

\[
\frac{\partial S_i}{\partial t} = \frac{1}{\phi_r (\rho_r M_h - \rho_h M_i)} \left[ \phi_r K_m \frac{d^2 M_a}{dz^2} - q_f \frac{dM_a}{dz} \right]
\]  

In (3) \( M_a \) represents the methane mass fraction in the solid phase, \( \rho_h \) is the density of methane hydrate, and \( K_m \) denotes the product of the dispersion-diffusion coefficient (\( D_m \)) and fluid density. Obtaining \( d \) from (2), fracture permeability is calculated using the permeability relationship for a parallel fracture with smooth walls [Snoow, 1968]:

\[
k_f = \frac{d^2}{12}
\]  

3.3.3. Porous medium

For the porous medium model, fluid flux \( q_f \) is given by:

\[
q_f = -\frac{k_m \rho_f}{\mu_f} \left[ \frac{dp}{dz} + \rho_f \frac{d\phi}{dz} \right]
\]  

where \( k_m \) represents permeability. The porosity change due to hydrate accumulation is calculated from:

\[
\phi = \phi_i (1 - S_i)
\]  

where \( \phi_i \) is the porosity at time \( t \), and \( \phi_i \) is the initial porosity. Porosity \( \phi \) is related to permeability \( k_m \) [Bear, 1972] through:

\[
k_m = \frac{\phi^3}{(1 - \phi)^2} \frac{d^2}{12} = \phi \frac{d^2}{12}
\]
where \( l \) is the representative grain diameter and \( d_m \) the pore diameter. This permeability-porosity formulation is based on an idealization of the porous medium as a homogeneous, isotropic distribution of capillary tubes of diameter \( d_m \). The average distance between the tubes is analogous to the grain diameter \( l \).

3.3.4. Model domain, implementation, and assumptions

The model domain for this study extends only from the top of the GHZ to the base of gas hydrate stability and initially contains no hydrate. This thickness of the model domain is determined \textit{a priori} by applying the steady-state \textit{Xu and Ruppel} [1999] model, which predicts the location of GHZ given fluid, methane, and energy flux conditions, as well as boundary conditions such as seafloor depth, temperature and pressure. To ensure that gas hydrate can accumulate all of the way to the base of the stability zone, we ascribe methane flux just in excess of the critical methane flux defined by \textit{Xu and Ruppel} [1999] calculated using their approach. Once the model domain has been established, we follow these steps to model the evolution of permeability in the GHZ:

1. We ascribe the initial pore diameter or fracture aperture for a porous medium or fracture flow model, respectively.

2. Depending on the thickness of the GHZ calculated \textit{a priori} and the desired resolution for the final results, the model domain is discretized into 100 to 1000 equally spaced nodal points of separation \( dz \).

3. Initially, we assign a constant fluid flux throughout the GHZ and assume that the fracture or porous medium is devoid of gas hydrate. Given initial fluid flux, the location of the GHZ in the sediment column, background permeability, and fluid
viscosity we calculate the pressure gradient required to drive flow in the GHZ from Darcy’s Law (1) for a fracture or (5) for a porous medium. The pressure gradient includes both a hydrostatic component ($\rho g$) and a component due to motion of the fluid. The hydrostatic component is several orders of magnitude larger than the component dependent on fluid flow, which is further reduced as permeability clogs, rendering the pressure gradient hydrostatic. Thus, we hold the pressure gradient constant throughout each model run for the sake of simplicity. Even non-uniform deposition of gas hydrate, which leads to non-uniform pressure gradients in the porous medium, does not give rise to large enough pressure changes to violate our assumption of a constant pressure gradient throughout the GHZ for this first-order model.

4. Pressures and temperatures in the GHZ are then determined from equations (17) and (18) of Xu and Ruppel [1999].

5. To describe initial energy flux, we assume a constant, background conductive geothermal gradient and constant thermal conductivity and superpose advective thermal perturbations associated with fluid flow. Total energy changes with time to account not only for a reduction in fluid flux accompanying hydrate deposition (reduces the advective thermal perturbation) but also for the exothermic heat of hydrate formation.

6. We then calculate methane solubility corresponding to the pressures and temperatures in the sediment from the formulation of Egeberg and Dickens [1999]. In most cases, the upward migrating fluids containing dissolved methane encounter lower pressure and temperature and thus decreased methane solubility.
In our model, these conditions of decreased methane solubility encountered by a rising package of fluid drive the formation of hydrate.

7. Values of the volume saturation of methane hydrate $S_4$ are then obtained at nodal points along the fractures or in pore space by numerically integrating expression (3). Once formed, hydrate is not transported in the fluxing fluid [Clennell et al., 1999; Tohidi et al., 2001] and instead remains immobile, altering local porosity and thus permeability conditions.

8. The new porosity is calculated from (2) or (6), and the corresponding change in permeability is determined from (4) or (7), respectively.

9. Using Darcy’s Law in the appropriate form (either (1) or (5)), the flow field is then updated based on the new permeabilities. Calculations of pressures and temperatures are made again (Step 4). As the permeability of the system decreases, fluid flux and the advective component of the energy flux are further reduced, leading to new temperature, and solubility conditions. The model thus provides a dynamic feedback between permeability changes and related changes in the hydraulic and thermal state of the system.

To simplify the model, we do not include reaction kinetics, an assumption justified by the short growth times of methane hydrate relative to the characteristic time scales for chemical and thermal transport [Rempel and Buffett, 1997]. We also ignore the effects of sediment host properties on phase equilibria. One such effect is related to the presence of clay particles, which have alternately been shown to inhibit gas hydrate through third surface effects [Cha et al., 1988] or to have no impact on stability [Kotkasie et al., 1990; Englezos and Hall, 1994]. Another sediment-related effect is
capillary forces. Empirical and theoretical research has also shown that capillary forces in fine-grained sediments can strongly inhibit gas hydrate stability [e.g., Handa and Stupin, 1992; Zahrzewski and Handa, 1993; Clennell et al., 1995; Clennell et al., 1999; Henry et al., 1999]. Although capillary forces could be incorporated in the model, we ignore this effect for this first generation study. We also assume a constant thickness model domain (GHZ) instead of allowing the base of the GHZ to deepen relative to the seafloor as vertical advection shuts down, lowering temperatures. With an initial GHZ thickness of approximately ~500 m and parameters for our base case (Table 3.1), such cooling effects would cause a new hydrate-bearing zone of maximum thickness 36 m to be added to the base of the GHZ. Finally, the model developed here assumes that water is never limiting in the system. In real settings, methane might remain as free gas within the hydrate stability zone if sufficient water is lacking to form hydrate. In our model, we assume that enough water will always be present to form hydrate at any depth at which methane concentration exceeds its solubility.
### Table 3.1. Typical parameters (applicable to the Blake Ridge system) used in simulations.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Physical Meaning</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$</td>
<td>gravitational acceleration</td>
<td>9.81 m s$^{-2}$</td>
</tr>
<tr>
<td>$T_0$</td>
<td>temperature at seafloor</td>
<td>3.0 °C</td>
</tr>
<tr>
<td>$\phi$</td>
<td>porosity</td>
<td>0.60</td>
</tr>
<tr>
<td>$z_d$</td>
<td>depth below sea level</td>
<td>2800 m</td>
</tr>
<tr>
<td>$D_m$</td>
<td>diffusion-dispersion coefficient</td>
<td>$1.0 \times 10^{-3}$ kg m$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$q_f$</td>
<td>fluid flux</td>
<td>$10^7$ kg m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$q_c$</td>
<td>energy flux</td>
<td>$40 \times 10^3$ kg m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$q_m$</td>
<td>methane flux</td>
<td>$2 \times 10^4$ kg m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>thermal conductivity</td>
<td>1.0 W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\rho_o$</td>
<td>density of liquid phase</td>
<td>1024 kg m$^{-3}$</td>
</tr>
<tr>
<td>$C_l$</td>
<td>specific heat capacity of liquid phase</td>
<td>$4.18$ kJ kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\mu_l$</td>
<td>dynamic viscosity of liquid phase</td>
<td>$8.87 \times 10^3$ kg m$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\rho_h$</td>
<td>density of methane hydrate</td>
<td>$930$ kg m$^{-3}$</td>
</tr>
</tbody>
</table>

#### 3.3.5. Model parameters

The model developed here is generalized enough to be applied to a broad range of gas hydrate provinces. To provide an example application, we here focus on the well-studied Blake Ridge gas hydrate province for which many of the key parameters were measured or inferred (Table 3.1) during ODP Leg 164 and associated studies [Paull et al., 1996]. As noted earlier, the model domain includes only the thickness of the GHZ. Initial pore diameters are assumed to be of the same order of magnitude as the grain diameters ($10^3$ to $10^4$ m) estimated for Blake Ridge sediments [Cleenwenn et al., 1999; Ginsburg et al., 2000]. Although studies have shown that these sediments consist of a mixture of particles ranging from fine silty clays ($10^9$ m) to diatoms ($10^3$ m) [Kraemer et al., 2000], we ignore such heterogeneities for this model and assume that a single size of spherical particles makes up the sediments. Constraining the width of typical fractures is more difficult, particularly given that the lateral resolution of the deep towed...
multichannel seismic data [Rowe and Gettrust, 1993] is at best ~21 ns. Lacking precise information about the width of faults, we instead adopt an approach that permits direct comparison between the results of the porous and fractured media endmember models by assigning fracture apertures equal to pore diameters.

Fluid flow in natural systems is controlled by gradients in pressure, temperature, or chemical composition, with compaction-driven dewatering being one of the most common driving forces in marine sedimentary environments. Simple one-dimensional calculations to constrain dewatering-induced fluid flux (e.g., after Pedersen et al., 1997) for the Blake Ridge yield rates an order of magnitude less than those determined by chemical and thermal studies [Egeberg and Dickens, 1999; Ruppel, 1997]. In this study, we ascribe an initial, constant upward fluid flux ranging from $10^4$ to $10^6$ kg m$^{-2}$ s$^{-1}$ (0.3 mm yr$^{-1}$ to 60 mm yr$^{-1}$) throughout the model domain, without considering the mechanism for driving the upward flux. The lower endmember is consistent with advective flux estimated from chemical analyses conducted on Leg 164 pore waters by Egeberg and Dickens [1999]. The upper bound is more than an order of magnitude greater than the maximum value estimated by Ruppel [1997] based on down-hole temperature gradients measured on Leg 164. These flux values would be conservative for focused flow in active margin (e.g., Cascadia margin) settings, where rates of $10^2$ to $10^3$ mm yr$^{-1}$ have been reported [Tryon et al., 1999]. Near the end of this study, we consider a simulation with fluid flux of $3 \times 10^6$ kg m$^{-2}$ s$^{-1}$ (180 mm yr$^{-1}$) with parameters applicable to Hydrate Ridge on the Cascadia margin.
3.4. Results

The numerical model permits investigation of a number of issues related to the evolution of gas hydrate deposits in porous marine sediments. In particular, we explore (a) the evolution of permeability during hydrate formation; (b) the impact of hydrate formation on flow pathways; (c) the role of pore and grain diameters and fracture sizes in controlling the amount and rate of hydrate accumulation; (d) the impact of fluid and energy flux variations; and (e) the effect of seabed pressure, and bottom water temperature (BWT) on the rate of permeability clogging. We also examine how the adoption of other permeability-porosity relationships may change the interpretations of our results.

4.4.1. Permeability Evolution

Permeability reduction in sediments may be accomplished by decreasing porosity or constricting migration pathways without a decrease in porosity [Alfaranov et al., 1997]. Here we attribute all permeability reduction to a decrease in the porosity of the sediments as gas hydrate clogs the system. For the same initial fluid flux, comparison of the porous media and fracture flow results (Figure 3.4) reveals that hydrate formation and permeability reduction occur more rapidly in the porous media model than in the fractured model. In both models, permeability decreases most rapidly at the onset of hydrate accumulation, and the rate of permeability reduction then decreases with time as the supply of advecting fluids diminishes. As shown in Figure 3.4, permeability is reduced by almost 2 orders of magnitude in the porous flow model during the first 10 M.y., and there is an additional order of magnitude reduction in the next 50 M.y. For the
Figure 3.4. Evolution of permeability for (a) the porous flow model and (b) the fracture flow model. The dotted, dashed, and solid curves represent the permeability at the base, middle, and top of the GHZ, respectively. The curves correspond to initial fracture and pore diameters of 1 μm with fluid flux of 1 x 10^{-7} kg m^{-2} s^{-1} and geothermal gradient of 34°C km^{-1}. The heavy solid line in each plot represents the bulk permeability at which clogging occurs in the porous (3.88 x 10^{-12} m²) and fracture flow (4.1 x 10^{-16} m²) cases. Clogging occurs at 55 Ma in the porous case and at 58 Ma in the fracture case when we apply the base permeability-porosity relationship.
fracture flow model, permeability decreases by only a single order of magnitude in the first 10 M.y., and another 50 M.y. is required for a reduction by another order of magnitude. These results should not be interpreted as implying that flow systems are maintained or that fractures and porous networks remain available for hydrate deposition over such long time periods. Instead, these theoretical results merely highlight the time necessary to reduce permeability by forming hydrate from dissolved methane in a system that initially contains no gas hydrate. Because the initial system lacks hydrate, these results have important implications for the time required to establish a hydrate reservoir in a sedimentary section.

The differences between the rates of permeability reduction for the endmember models may be attributed to the effect exercised on the precipitation process by the surface area to volume ratio, \( R_{SV} \), or, stated differently, the amount of matrix surface area in contact with a particular volume of fluid. Pores of a given diameter have more surface area available for reaction with a certain volume of fluid (high \( R_{SV} \)) than a fracture of comparable aperture. Consequently, the porous medium (high \( R_{SV} \)) becomes clogged faster than the fractured medium (low \( R_{SV} \)). Furthermore, large pores or apertures have low \( R_{SV} \) and therefore exchange mass less readily than regions with high \( R_{SV} \) [Bolton et al., 1996].

In both the porous and fractured models, the deposition of gas hydrate produces a non-uniform permeability field with permeability decreasing with depth. With time, hydrate continues to form only at depths at which fluid flux is sufficient to maintain a supply of dissolved methane from rising fluids. Thus, the distribution of gas hydrate and consequently the degree of permeability reduction become more uniform with time.
3.4.2. Shutdown Time for Fluid Flow

The simulations are run until fluid flow is shut off at the base of the gas hydrate zone due to permeability clogging. The shutdown time could be defined on the basis of a molecular size criterion in which the flow pathways are considered closed when fluxing components are too large for the dimensions of pores or fractures (1.4 Å for water and 4.36 Å for methane). More realistically, shutdown would occur before the pathways reach ~7.0 Å, the diameter of a methane molecule surrounded by a water shell [Koh et al., 2000]. With this value of \( d_{\text{clog}} \), the clogging permeability \( k_{\text{clog}} \) is given by

\[
k_{\text{clog}} = d^{3}_{\text{clog}}/12 \text{ for the discrete fracture case and } \phi_{\text{clog}}d^{3}_{\text{clog}}/12 \text{ for the porous medium,}
\]

where \( \phi_{\text{clog}} = d_{\text{clog}}/(1 + d_{\text{clog}}) \).

Figures 3.5 and 3.6 illustrate the decrease of fracture aperture and porosity in the endmember models during hydrate accumulation. The corresponding reduction in fluid flux lowers the advective flux and thus the temperatures in the sediments. These changes in turn reduce methane solubility and consequently the amount of gas hydrate precipitated from solution. Based on the molecular size criterion, fluid migration is shut down at 58 M.y. in the fracture and at 55 M.y. in the porous medium. Not surprisingly, the fracture mode sustains greater fluid flux than the porous medium since \( R_{\text{fr}} \) does not decrease as rapidly with time. We emphasize again that the clogging times reported here are significantly higher than the times required to merely establish a gas hydrate deposit in a sedimentary section originally lacking in gas hydrate.
Figure 3.5. Evolution of hydraulic parameters in a fracture within the GHZ. Dotted, dash, and solid curves correspond to the bottom, middle, and top of the GHZ, respectively. (a) Normalized fluid flux as a function of time, with schematic diagrams showing the accumulation of hydrate and the corresponding feedback on flux regimes during evolution of the system. We note here that the fluxes at the top middle and base of the GHZ are not representative of the true velocity of the fluid on a point-to-point basis. Rather, the fluid flux at any point in the GHZ is the cumulative flux inclusive of the volume of fluid flowing through the system from the BGHZ to that point. (b) Fracture aperture as a function of time in the GHZ, with inset illustrating the non-uniform deposition of gas hydrate along the fracture. The curves correspond to an initial fracture diameter of 1mm, fluid flux of $1 \times 10^{-7}$ kg m$^{-2}$ s$^{-1}$, and geothermal gradient of 34 °C km$^{-1}$. 

57
Figure 3.6. Similar to Figure 3.5 and using all the same parameters, except for a porous medium. (a) Normalized fluid flux. (b) Porosity. Inset: Schematic representations of the state of the porous medium at different stages of gas hydrate accumulation, with darker regions indicating lower permeability.
3.4.3. Variations in Pore Diameter and Fracture Aperture

We also examined permeability clogging associated with varying pore diameter and fracture aperture with initial fluid flux of $10^{-3}$ kg m$^{-2}$ s$^{-1}$ and conductive thermal gradient of 34$^\circ$C km$^{-1}$. The results of these model runs (Table 3.2 and Figure 3.7) indicate that a 10-fold increase in fracture width from 0.1 $\mu$m to 1 $\mu$m lengthens clogging time from 1.34 M.y. to 58 M.y. For a similar change in pore diameter, we observe an increase of 0.42 M.y. to 55 M.y. in the time required to reach shutdown permeability in the porous medium. Most importantly, for pore diameters or fracture apertures greater than 1 $\mu$m, the fracture clogs faster than the porous medium.

The physical explanation for these results is once again based on a consideration of the solid matrix to fluid volume ratio $R_{\text{SF}}$. For larger pore diameters or fracture apertures, $R_{\text{SF}}$ is smaller, resulting in decreased fluid-solid matrix interaction and slower rates of permeability reduction. At any time, the sustained higher fluid fluxes in the fracture flow case results in larger supply of dissolved methane relative to the porous model. Consequently a fracture with aperture 10 $\mu$m clogs faster (249 M.y.) than a porous medium of equal pore dimensions (438 M.y.). After point B on Figure 3.7 the advective flux in the GHZ becomes so small that diffusion dominates. Since formation of hydrate by diffusional processes is so slow, hydrate production appears to have stopped in the model. While sediments characterized by smaller pores clog faster, it should be noted that small pores could lead to increased capillary pressures, an effect not included in our models. High capillary pressures inhibit gas hydrate formation from dissolved methane [Clennell et al., 1999], the only means of hydrate formation considered in the model. In terms of the true multiphase system, capillary pressures play
Figure 3.7. Clogging time for fracture (solid line) and porous medium (dashed line) models. The curves correspond to initial fluid flux of $10^{-7} \text{ kg m}^{-2} \text{ s}^{-1}$ and geothermal gradient of 34 °C km$^{-1}$. For the complete range of fracture apertures and pore diameters tested here, we obtain clogging times ranging from 1.34 M.y. to 249 M.y. for the fracture model and 0.42 M.y to 438 M.y. for the porous model. A fracture of width greater than 1 μm (beyond point A) will clog faster than pores of the same diameter. Beyond point B fluid flow in the fracture and porous medium becomes so slow (diffusion-dominated) that hydrate formation appears to stop.
a role in inhibiting the formation of gas bubbles, a factor that could affect the amount of hydrate formed from the free gas phase [Clennell et al., 2000].

Table 3.2. Clogging time as a function of initial pore size or fracture aperture for initial fluid flux of $10^8$ kg m$^{-2}$ s$^{-1}$ and geothermal gradient of 34 °C km$^{-1}$ using the base case porosity-permeability relationship.

<table>
<thead>
<tr>
<th>d (µm)</th>
<th>Clogging Time for Porous</th>
<th>Clogging Time for Fracture</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.42</td>
<td>1.34</td>
</tr>
<tr>
<td>1</td>
<td>55</td>
<td>58</td>
</tr>
<tr>
<td>10</td>
<td>438</td>
<td>249</td>
</tr>
<tr>
<td>100</td>
<td>&gt; 438</td>
<td>&gt; 249</td>
</tr>
<tr>
<td>1000</td>
<td>&gt; 438</td>
<td>&gt; 249</td>
</tr>
</tbody>
</table>

3.4.4. Variations in Initial Fluid Flux

Previous theoretical studies have shown that advective flux is probably required to produce appreciable quantities of gas hydrate in natural systems [Xu and Ruppel, 1999], a conclusion that confirms anecdotal evidence from a variety of gas hydrate provinces. Most importantly, increased advective flux supplies a greater amount of dissolved methane for hydrate formation. For specific fracture apertures and pore diameters, we test the sensitivity of the model to variations in initial fluid flux. Figure 3.8 and Table 3.3 show that clogging occurs more rapidly for increased initial fluid flux in both the porous and fracture flow cases. A five-fold increase in fluid flux from $3 \times 10^8$ kg m$^{-2}$ s$^{-1}$ to $15 \times 10^8$ kg m$^{-2}$ s$^{-1}$ results in a reduction in clogging times from 680 M.y. to 29 M.y. in the fracture flow case and from 365 M.y. to 29 M.y. in the porous flow case. In the case of the high flux endmember, clogging for the fracture and porous flow cases are nearly the same. Although initial hydrate formation is more rapid in the porous model, higher rates of dissolved methane supply can be maintained longer in the fracture flow model.
Figure 3.8. Comparison of the permeability evolution in a (a) porous medium and (b) fracture at various depths in the GHZ for different initial fluid fluxes. The curves represent permeability at the base of the GHZ as a function of time, and $k_{clog}$ denotes the clogging permeability based on the molecular size criterion. Initial conditions are fluid flux ranging from $10^{-9}$ kg m$^{-2}$ s$^{-1}$ to $1.5 \times 10^{-7}$ kg m$^{-2}$ s$^{-1}$, fracture aperture and pore diameter of 1.0 µm, and conductive thermal gradient of 34 °C km$^{-1}$. 
Table 3.3. Clogging time as a function of various initial fluid fluxes for an initial pore size or fracture aperture of 1 μm and geothermal gradient of 34 °C km⁻¹. Except as noted, all calculations use the base porosity-permeability relationship.

<table>
<thead>
<tr>
<th>Fluid flux</th>
<th>Clogging Time for Porous Medium</th>
<th>Clogging Time for Fracture</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>365</td>
<td>680</td>
</tr>
<tr>
<td>5</td>
<td>152</td>
<td>194</td>
</tr>
<tr>
<td>7</td>
<td>94</td>
<td>103.5</td>
</tr>
<tr>
<td>10</td>
<td>55.3</td>
<td>58.3</td>
</tr>
<tr>
<td>15</td>
<td>28.5</td>
<td>28.4</td>
</tr>
<tr>
<td>100</td>
<td>6.0</td>
<td>5.7</td>
</tr>
<tr>
<td>300 (a)</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>300 (b)</td>
<td>0.4</td>
<td>2.4</td>
</tr>
<tr>
<td>300 (c)</td>
<td>0.6</td>
<td>2.4</td>
</tr>
</tbody>
</table>

(a) The model run was carried out for seafloor depth of 1000m at Hydrate Ridge, Cascadia
(b) Same as (a) but for Kozeny-Carman porosity-permeability relationship
(c) Same as (a) but for Brinkman porosity-permeability relationship

3.4.5. Variations in Initial Energy Flux

The balance among heat advected into the GHZ via fluid migration, heat conducted out of the medium, and heat supplied by the exothermic process of methane hydrate formation is reflected in the energy balance equation, which describes total energy flux \( q_e \). Energy flux is therefore critical in determining the temperatures in the GHZ, which in turn affect the solubility of methane and thus the amount of dissolved methane available for hydrate formation.

For constant fluid flux and pore and fracture diameter, we explore the effects of changing the initial energy flux by varying the background geothermal gradient. Figure 3.9 and Table 3.4 illustrate that clogging occurs more rapidly for increased geothermal gradients in both the fracture and porous flow cases. This result is easily explained by the increased solubility and therefore increased availability of dissolved...
Figure 3.9. Clogging time as a function of geothermal gradient for the fracture (dashed) and porous medium (solid) models. The curves correspond to initial fracture width and pore diameter of 1.0 μm for gradients ranging from 20 °C km^{-1} to 40 °C km^{-1} and values of fluid flux specified in Table 3.4.
methane at higher temperatures. In the porous model we observe clogging times of 228 M.y. to 30 M.y. for background conductive thermal gradients of 20°C km⁻¹ to 40°C km⁻¹, respectively. For the same increase in temperature gradient, clogging time for the fracture case is reduced from 240 M.y. to 32 M.y.

Table 3.4. Clogging time for various background geothermal gradients and an initial pore size or fracture aperture of 1 μm, initial fluid flux of 10⁻⁷ kg m⁻² s⁻¹, and the base porosity-permeability relationship.

<table>
<thead>
<tr>
<th>Geothermal Gradient (°C m⁻¹)</th>
<th>Clogging Time for Porous Medium (M.y.)</th>
<th>Clogging Time for Fracture (M.y.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>228</td>
<td>240</td>
</tr>
<tr>
<td>0.034</td>
<td>55</td>
<td>58</td>
</tr>
<tr>
<td>0.03</td>
<td>82</td>
<td>86</td>
</tr>
<tr>
<td>0.04</td>
<td>30</td>
<td>31.6</td>
</tr>
</tbody>
</table>

3.4.6. Variations in Seafloor Conditions (Water Depth and Bottom Water Temperature)

As noted earlier, the thickness and location of the hydrate stability zone are dictated by pressure and temperature, which also strongly influence methane solubility. Thus, changing the depth of the seafloor (hydrostatic pressure) or bottom water temperatures (BWT) affect the evolution of the gas hydrate system. While we did explore the impact of BWT and seafloor depth on permeability clogging, the results, which are summarized in Table 3.5, can be qualitatively determined by calculation of the methane solubility curve at the appropriate pressure and temperature conditions. Where the solubility of methane is higher, as for increased BWT (for constant water depth) or greater water depth (for constant BWT), the rate of permeability clogging increases.
Table 3.5. Clogging time as a function of seafloor pressure and bottom water temperatures for initial pore size or fracture aperture of 1 μm, geothermal gradient of 34 °C km⁻¹, initial fluid of 10³ kg m⁻² s⁻¹, and the base porosity-permeability relationship.

<table>
<thead>
<tr>
<th>Seafloor Pressure (MPa)</th>
<th>Bottom water temperature (°C)</th>
<th>Clogging Time for Porous Medium (M.y.)</th>
<th>Clogging Time for Fracture (M.y.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>3</td>
<td>48</td>
<td>49.8</td>
</tr>
<tr>
<td>28</td>
<td>3</td>
<td>55</td>
<td>58</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>84</td>
<td>92</td>
</tr>
<tr>
<td>28</td>
<td>0</td>
<td>59</td>
<td>62</td>
</tr>
<tr>
<td>28</td>
<td>7</td>
<td>50.4</td>
<td>55.2</td>
</tr>
</tbody>
</table>

3.4.7. Alternate Permeability-Porosity Formulations

For porous media flow, the fundamental parameter constrained in our models is porosity, not permeability. The determinations of permeability therefore depend inextricably on the porosity-permeability relationship we adopt. Equation (7) provides a simple relationship between permeability and porosity based on pore geometry described by a capillary tube model. Another widely-accepted empirical relationship is the Kozny-Carman model, which idealizes the porous medium as a bundle of capillary tubes [Bear, 1972] with permeability \( k_p \) of

\[
k_p = \frac{\phi^4}{5S_p^2(1-\phi)^2}.
\]

(8)

where \( S_p \) represents the specific surface area of solid exposed to fluid. For an average distance between tubes \( l \), \( S_p = 6l \). In the alternate Brinkman model [Dullien, 1991], flow occurs around an assemblage of spheres, and permeability \( k_p \) is linked to the drag of fluid on the pore walls:

\[
k_p = \frac{l^2}{72}
\left[ 3 + \frac{4}{(1-\phi)^3} \left( \frac{8}{(1-\phi)^3} \right)^{1/3} \right].
\]

(9)
Regardless of the permeability-porosity model we adopt, we obtain the expected results of decreased permeability reduction with time during hydrate accumulation and more rapid permeability reduction at the base of the GHZ than at the top. Based on the proportionality between permeability and the pore geometry (expressions (7), (8) and (9)), permeability and therefore clogging time for small pore sizes will be large (55 M.y. in our example; Figure 3.10) in the base model \( k = \phi \varepsilon^2 \) and significantly lower (5 M.y.) in the Kozeny-Carman model \( k = \phi^2 \varepsilon^2 \). For the particular combination of parameters used here, clogging time for the more complicated Brinkman case is 6 M.y., close to that of the Kozeny-Carman model. The results presented throughout this paper represent conservative estimates of clogging times, and we provide a direct comparison of the impact of other permeability-porosity relationships for parameters characteristic of a real setting in Table 3.3.
Figure 3.10. Comparison of the evolution of permeability in a porous medium at the base of the GHZ for different porosity-permeability models. Dotted, dashed, and solid curves represent permeabilities in the Brinkman, base model, and Kozeny-Carman, respectively. Initial conditions are given in Table 3.1.
3.5. Discussion

The modeling results have implications for the interpretation of field observations, the evolution of hydrodynamic regimes in gas hydrate provinces, permeability sealing at the BSR, clogging times for marine sediments in gas hydrate provinces, and the regeneration and potential renewability of gas hydrate deposits. Owing to the availability of both remotely sensed data (e.g., seismic data) and direct observations from drilling, we here apply the model to the interpretation of the Blake Ridge gas hydrate province. As noted earlier, the model also provides generic insights and has the flexibility to be applied to most gas hydrate provinces.

3.5.1. Comparison to Field Constraints

Nearly any sedimentary system can be viewed as a combination of fractured and porous media components, and the homogeneous hydrate-bearing sediments of the Blake Ridge have long been known to be characterized by just such a juxtaposition of fractured and porous sediments [Rowe and Gettrust, 1993]. Downhole logs reveal increasing gas hydrate concentrations with depth at Site 997, with up to 2.5% of porosity filled with hydrate near the top of the GHZ and 10% to 15% of the pore space filled with hydrate deep in the GHZ [Lee, 2000]. When such concentrations are attained near the base of the GHZ in our dynamic models, hydrate occupies 2% to 5% of available pore space at the top of the GHZ for parameters specified in Table 3.1 (Figure 3.11). While our results bracket the observation, we may overpredict hydrate concentration at the TGHZ due to our assumption that advecting fluids are always locally saturated with methane.

Similarly, by assuming an initial uniform porosity of 60% with depth in the GHZ, we
underestimate the percentage of pore space available for hydrate formation near the top of the gas hydrate zone (closer to 70% according to Paul et al. [1996]) and therefore estimate higher hydrate concentrations than would otherwise be obtained.

Sufficient concentrations of gas hydrate strengthen the sediment aggregate [W. Durham et al., 2003], change the bulk moduli, and consequently increase seismic velocities [Ecker et al., 1998; Dvorkin et al., 1993; Helgerud et al., 1999]. On the Blake Rìge, seismic velocities increase with depth through the GHZ [Katzma et al., 1994; Holbrook et al., 1996; Korenaga et al., 1997]. This observation may reflect the accumulation of gas hydrate as well as increasing sediment density during compaction (porosity reduction from ~70% at the seafloor to ~55% at the BSR; Paul et al., [1996]). Direct comparison of seismic data to our numerical results on hydrate accumulation is complicated because seismic data integrate over bulk sediment properties (e.g. variable porosity with depth), including both fractures and porous media. However, our results may provide a starting point for explaining the observed variations in seismic velocity.

The sensitivity of the rate of hydrate formation to initial pore diameters and fracture apertures underscores the importance of lithological characterization of hydrate-bearing sediments for refining predictive studies. In contrast to our model system, which has uniform initial pore size, real systems have a wide range of pore diameters. Whether hydrate formation in bulk sediment will be controlled by the largest pores or fractures or by the mean size remains a question for future study, perhaps using a stochastic description for sediment heterogeneity.
Figure 3.11. Comparison of the percentage of pore space filled with methane hydrate over time at the base (dotted curves), middle (dashed curves) and top (solid curves) of the gas hydrate zone in two distinct gas hydrate provinces: (a) Blake Ridge and; (b) Hydrate Ridge, Cascadia margin. Gas hydrate fills 10% of pore space deep within the GHZ at 0.47 M.y. at the Blake Ridge and at 0.019 M.y. at Hydrate Ridge. At these times hydrate concentrations near the top of the GHZ are ~2% for the Blake Ridge and ~5% for Hydrate Ridge.
3.5.2. Modification of Hydraulic Regimes by Gas Hydrate Formation

Although we do not consider the driving forces for fluid flow, several factors independent of hydrate reservoir dynamics favor preferential flow through fractures. Not only are pressure gradients along open fractures less than those in porous media, but capillary pressures and tortuosity inhibit flow in unfractured fine-grained sediments. In gas hydrate systems, additional factors favor focused flow and the concentration of hydrate in fractures. First, capillary pressures within fine-grained porous media inhibit gas hydrate formation [Clennell et al., 1999]. Second, for the same initial fluid flux supplied at the base of the model systems, the porous medium experiences more rapid permeability reduction than the fracture. Thus, fractures that remain open will be the primary conduits sustaining fluid flux over longer time scales in gas hydrate systems.

Even within an unfractured, homogeneous porous medium, the rate of hydrate deposition is closely related to the vigor of the advective system, and consideration of transient effects and the dynamic feedback between permeability evolution and fluid flux are critical. In their steady state analytical model which assumes constant homogeneous permeability, Xu and Ruppel [1999] calculated that fluid flux of 0.5 mm yr\(^{-1}\) to 6 mm yr\(^{-1}\) produces hydrate accumulation rates of \(10^{15} \text{ s}^{-1}\) to \(10^{14} \text{ s}^{-1}\), respectively. In addition the Xu and Ruppel accumulation rates are fairly uniform throughout the GHZ. For the same variation in fluid flux, our transient model with evolving permeability and robust solubility formulation yields hydrate accumulation rates that are faster (\(10^{13} \text{ s}^{-1}\) to \(10^{14} \text{ s}^{-1}\)). Furthermore, in contrast to the previous steady-state model, the dynamic model predicts higher accumulation rates at the base of the GHZ than at the top even for advection at less than 1 mm yr\(^{-1}\).
The enhancement of hydrate formation at the base of the GHZ may to some extent reflect the morphology of the solubility curve. For fluid saturated with methane, the difference between the amount of methane present in solution and its local solubility is greatest just as the fluid advects upward across the base of the GHZ, potentially leading to enhanced hydrate formation at this location.

In natural systems, flow regimes in gas hydrate reservoirs are more strongly two or three-dimensional than can be represented in this first generation of models. For example, fracures that serve as conduits for focused flux may be juxtaposed with surrounding porous sediments through which diffuse advective flow systems operate. The total flow system for free gas and methane-laden fluid may include both stratigraphic (presumably porous) and tectonic (presumably fractured) pathways. Such a juxtaposition of focused flux conduits and more diffuse flow regimes should lead to significant spatial variations in hydrate concentrations, gas emission patterns, BSR character, and chemosynthetic community development, as illustrated schematically in Figure 3.12. On the Blake Ridge, Paull et al. [1996] and Holbrook [2000] have inferred increasing hydrate concentrations toward the ridge crest. While such a lateral distribution of gas hydrate might be related to updip, largely lateral migration of gas along stratigraphic boundaries, fine-scale faulting is known to be more pervasive on the ridge crest than on the flanks [Holbrook, 2001]. These relatively steep faults (dips of ~55°) provide more vertical, tectonic pathways for migration of gas and fluids and may be an important factor contributing to the concentration of gas hydrate near the crest of the Blake Ridge.
Figure 3.12. Schematic diagram after Reppel (2001) portrays the complex hydrodynamics associated with gas hydrate reservoirs. The diagram shows key relationships among flow pathways, the impact of permeability contrasts, the possible loci of focused gas venting and chemosynthetic communities, the juxtaposition of fractures and porous media, various controls on the variability of BSR depth, and other potential complications associated with heterogeneous distribution of gas and gas hydrate in real systems. This study provides constraints on permeability evolution during reservoir development in a highly simplified one-dimensional system, but a multidimensional reservoir simulation approach will ultimately be required to resolve some of the more complex aspects of gas hydrate distribution and concentration in natural settings.
3.5.3. Permeability Seals at the BSR

The model results show that, even for low advective fluxes characteristic of natural sediments, permeability becomes preferentially more clogged at the base of the GHZ relative to the top. A natural system most comparable to our model system would have gas supplied predominantly from below the GHZ, instead of through in situ gas generation by biogenic processes within the GHZ. To date, most studies of biogenic generation of methane have not produced rates high enough to render in situ production of methane the principal component of the methane budget in gas hydrate systems.

Instead, much of the gas that is incorporated into gas hydrates is likely older, recycled gas that migrated into the gas hydrate zone through stratigraphic or tectonic pathways. Such a system might develop in regions of rapid sedimentation, where the base of the GHZ is constantly moving across the phase boundary and undergoing dissociation from hydrate to free gas. Largely vertical gas flux might also predominate in tectonically active settings where faults penetrate the top of the free gas zone and provide conduits for upward migration of gas.

Particularly where gas flux is dominated by fluid pathways that tap into the free gas zone below the BSR, permeability seals may form at the base of the GHZ, eventually creating a barrier to further migration of gas both in fractured sediments and in porous media. In seafloor experiments with coarse-grained sediments, the formation of concentrated gas hydrate impedes upward migration of gas, and the pressure accumulation associated with gas accumulation beneath the permeability seal eventually lifts the overlying sediments [Brewer et al., 1997]. In fine-grained systems, permeability sealing due to gas buildup leads to hydrofracturing that may reopen pre-existing fractures.
or form new fractures [Brewer et al., 1997]. We note that complete clogging of permeability at the base of the GHZ is not required for upward migration of gas or methane-laden fluid to be hindered. Depending on grain and pore sizes in the sediment, gas can be partially self-sealed against upward migration through the formation of capillary seals [Clennell et al., 2000].

For the advective fluxes characteristic of some natural systems, the time scales for permeability clogging are on the order of several millions of years. Such clogging times are many orders of magnitude greater than those observed in open boreholes (e.g., ODP Hole 892B; Becker, pers. comm.) and much longer than the time necessary to form hydrate in free water systems at the seafloor [Brewer et al., 1997] or in the lab (propane hydrate; Helgerud, 2001). Two physical phenomena explain this disparity. First, the mechanism for nucleation and formation of gas hydrate in open water systems differs from that operating in porous media [Sloan, 1998]. In open water, gas hydrate typically forms not from methane dissolved in solution, which is the mechanism assumed in this study, but rather from free gas that either enters the system through fractures or is bubbled through by artificial means. In such systems, gas hydrate forms almost instantaneously on the bubble surface (gas-water interface), and with time hydrate nucleation progresses from the bubble’s surface to its center [Brewer et al., 1997]. Second, in seafloor experiments, laboratory vessels, and open boreholes that intersect faults, fluid flux is orders of magnitude faster than in porous marine sediments. The increased rate of gas delivery results in more rapid hydrate formation.

3.5.4. Renewability of Gas Hydrate Deposits
Methane gas hydrate has been touted as a potentially renewable energy resource [Kvenvolden, 1993], and the results presented here have implications for the regeneration time of gas hydrate deposits in marine sediments. On the Blake Ridge, vertical seismic profiles [Holbrook et al, 1996], downhole logs [Collett and Ladd, 2000], and a combination of logging and laboratory data [Lee, 2000] indicate that gas hydrate fills 2% to 3.3% of porosity at Site 994 and 5%-7% at Sites 995 and 997. Using parameters given in Table 3.1, the model predicts that accumulating gas hydrate to concentrations of 5% to 7% of porosity would require $10^5$ years (Figure 3.11). Thus, even if the hydrate accumulations on the Blake Ridge were significant and concentrated enough to be completely exploited, naturally regenerating gas hydrate to the present-day average concentrations would require too long a time for these deposits to be considered a renewable energy resource. In high flux settings (e.g., Gulf of Mexico, Oregon margin), hydrate accumulation rates will be significantly faster. For example, we calculate that gas hydrate would occupy 10% of pore space in as little as 10$^3$ years for fluid flux of 180 mm yr$^{-1}$ as reported for Hydrate Ridge by Tryon et al. [1999] (Figure 3.11).

The calculation of regeneration time also provides a constraint on the time scale for the re-establishment of gas hydrate deposits following total dissociation, which may have occurred during global climate change events like the Paleocene/Eocene Thermal Maximum (e.g., Dickens et al., 1997). Because our regeneration time calculations are initiated with an equilibrium geotherm, not a geotherm readjusting to perturbations associated with bottom water temperature changes, the results provide only an upper bound on the time for re-formation of gas hydrate in sedimentary systems. On the other hand, the assumption that gas is supplied only from below the system instead of through
in situ production within the GHZ means that the regeneration times could be underestimated. We suggest that the regeneration times determined here may serve as a rough guide to the analysis of the re-equilibration of seafloor hydrate reservoirs following complete dissociation, while at the same time underscoring the need for more detailed modeling studies of this problem.

The regeneration times calculated here should not be confused with the age of gas hydrate deposits, the age of individual zones of hydrate concentration, or the age of the gas contained within gas hydrates. Instead, these regeneration times are merely indicative of the time necessary to produce gas hydrate at the bulk concentrations noted in some field settings based on a two phase system (gas hydrate and seawater + dissolved methane) in which no hydrate is initially present and the flow system is established instantaneously at the onset of the model. In real settings, sedimentation, erosion, subsidence, uplift, and other processes (e.g., changes in bottom water temperatures) cause constant perturbations to gas hydrate deposits. If in situ production of biogenic methane within the GHZ is ignored, then these perturbations will most seriously affect the longevity of gas hydrate at the top and base of the GHZ. For slow forcing of the reservoir by sedimentary or tectonic processes, it is likely that the relative age of the gas hydrate averaged over the thickness of the GHZ remains nearly constant or increases. In isolated pockets within the GHZ or in fractures, gas hydrate could form rapidly even as the background advection through the system produces slower accumulation consistent with our modeling results.

Finally, isotopic studies that indicate the presence of 55 Ma $^{13}C$ in pore waters extracted from 1.8 to 6 Ma sediments on the Blake Ridge [Fehn et al., 2000] also do not
produce results that can be directly compared to those of the permeability clogging simulations. The isotopic results reflect the origin time of the biogenic methane gas that is fluxing into the GHZ from older, deeper sediments, but do not represent the actual age of the hydrate or the time required to form it. Modeling studies that constrain the potential age of gas hydrate deposits or the age of trapped methane will require more detailed consideration of molecular- and pore-scale processes, including methane diffusion out of the hydrate lattice, the longevity of individual hydrate molecules, and the role of structured water in re-formation of gas hydrate in perturbed systems [Stoan, 1998].

3.6. Conclusions

The primary results emerging from this dynamic model of hydrate accumulation in porous and fractured systems are:

1. Assuming the same initial properties, hydrate accumulation and permeability clogging occur at a faster rate in the porous medium than in the fractured system. While a number of factors independent of hydrate reservoir dynamics renders fractures the preferred pathways for fluid flux, the model results indicate that flow in hydrate reservoirs is likely to be sustained much longer in fractures than in the surrounding porous aggregate.

2. As a function of depth, hydrate accumulates less uniformly in fractures than in porous media. In both systems, hydrate concentrations increase as a function of depth. This effect at least partially reflects the morphology of the methane solubility curve, which changes sign and slope at the base of the GHZ. Whereas
earlier steady-state models [Xu and Suppel, 1999] produced notably increased hydrate concentrations near the base of the GHZ only for high advective flux, our transient model consistently yields higher concentrations deep in the GHZ regardless of the advection rate. Compared to the steady-state model, this transient model yields hydrate accumulation rates $10^3$ times faster for the same ascribed advection rates.

3. Reduction rates for permeability, fluid flux, and fracture aperture continue to decrease until the base of the GHZ is sealed. Sealing does not imply complete blockage of pore space by gas hydrate but rather sufficient permeability reduction to serve as a barrier to the flow of system components like methane. Although we focus on hydrate accumulation as the sealing mechanism for the base of the GHZ, we emphasize that the free gas may play an equally important role in sealing permeability [Clennell et al., 2000].

4. The model presented here is one-dimensional, with methane supplied from below at an ascribed rate. Hydrodynamic regimes in natural gas hydrate reservoirs are more two- or three-dimensional, have both vertical and lateral flow components, and may include both stratigraphic and tectonic flow pathways. Qualitatively, the increase in seismic velocity toward the crest of the Blake Ridge [Holbrook, 2001], where fine-scale faulting is more pervasive, is consistent with model results that imply greater concentration of gas hydrate for the more vigorous flux regimes characteristic of fractured systems. Concentrated gas hydrate was also observed on ODP Leg 164 where a one-dimensional feature (the borehole) intersected a
two-dimensional flow system (dipping fracture) at Site 997 [Wood and Ruppel, 2000].

5. A regeneration time of \(\sim 10^5\) years is required to produce hydrate concentrations of 10 to 15% of porosity in a natural system characterized by physical parameters that describe the Blake Ridge. Shorter regeneration times are predicted for marine hydrate provinces with more rapid fluid flux and methane supply or with significant production of methane within the GHZ. Clearly, natural systems are unlikely to regenerate gas hydrate quickly enough for these deposits to be considered a renewable resource. We underscore that the regeneration time for gas hydrate is distinct from the age of gas hydrate deposits.

Notation for Chapter III

- \(d\): pore diameter or fracture aperture (m).
- \(g\): gravitational acceleration (m s\(^{-2}\)).
- \(l\): grain diameter (m).
- \(p\): pressure (Pa).
- \(z\): depth below seafloor (m).
- \(T\): temperature (°C).
- \(\phi\): porosity.
- \(D_m\): diffusion-dispersion coefficient (m\(^2\) s\(^{-1}\)).
- \(M\): methane mass fraction (kg kg\(^{-1}\)).
- \(M_{sl}\): solubility of methane gas (kg kg\(^{-1}\)).
- \(q_r\): total mass flux rate (kg m\(^{-2}\) s\(^{-1}\)).
- \(q_m\): methane flux rate (kg m\(^{-2}\) s\(^{-1}\)).
- \(q_e\): energy flux rate (W m\(^{-2}\)).
- \(k\): permeability (m\(^2\)).
- \(\rho\): density (kg m\(^{-3}\)).
\( R_{sv} \)  surface area to fluid volume ratio.

\( S \)  volume saturation of methane hydrate.

\( S_0 \)  specific surface area (m\(^2\)).

\( \mu \)  dynamic viscosity (kg m\(^{-1}\) s\(^{-1}\)).

**Variables related to individual phases**

\( l \)  subscript denoting liquid phase.

\( g \)  subscript denoting methane free gas phase.

\( h \)  subscript denoting gas hydrate phase.

\( m \)  subscript denoting porous matrix.

\( f \)  subscript denoting fracture system.

\( \rho_i \)  density of phase \( i \) (kg m\(^{-3}\)).

\( k_i \)  permeability function for system (m\(^2\)).

\( \mu_i \)  dynamic viscosity of phase \( i \) in fluid (kg m\(^{-1}\) s\(^{-1}\)).

\( S_i \)  mass concentration (kg kg\(^{-1}\)) of phase \( i \) (kg kg\(^{-1}\)).

\( q_{fi} \)  flux rate for phase \( i \) (kg m\(^{-2}\) s\(^{-1}\)).

\( M_i \)  methane mass fraction in phase \( i \) (kg kg\(^{-1}\)).
CHAPTER IV
GAS HYDRATE ACCUMULATION AND DISTRIBUTION IN CONTINENTAL MARGIN RESERVOIRS

4.1. Introduction

The presence of gas hydrate deposits on continental margins has been directly observed or inferred using geophysical and geochemical techniques in water depths as shallow as 500 m in the continental slope of the Gulf of Mexico (Brooks et al., 1984; Mac Donald et al., 1994) and as deep as 5000 m in the Peruvian outer continental margin (Kvenvolden and Kastner, 1990). Most of these deposits have been observed at sediments depths of 100 mbsf to 400 mbsf (Kastner, 2000). Surficial hydrate has been observed in high flux environments where methane gas and methane laden fluids are advected at high flux rates to shallow sediment depths and the overlying water column; for example, in faulted regions of the Gulf of Mexico (Mac Donald et al., 1994), at the Blake Ridge Diapir (Paull et al., 1996; Van Dover et al., 2002) and at the Cascadia accretionary prism (Kastner et al., 1998; Whiticar et al., 1995).

Recent analytical and numerical studies have demonstrated that concentrated hydrate deposits are also associated with regions characterized by high advective flux rates (Xu and Ruppel, 1999; Wood and Ruppel, 2000; Nimblett and Ruppel, 2003), a result consistent with observational evidence. For example, in low flux environments, such as low permeability zones in clay-rich sediments (e.g. Costa Rica, ODP Site 1041), gas hydrate is commonly found in thin layers that parallel the sediment fabric or in thin veins of microfractures (Kimura et al., 1997). More concentrated hydrate is observed at
Site 1041 in fractured claystones where permeability is higher and fluid flux is more localized. In the relatively coarse sediments (high permeability) of the Nankai Trough, where fluid and energy fluxes are high, gas hydrate was observed to occupy ~ 100% pore space at Site 808 (Taira et al, 1991).

These results all highlight the importance of the hydraulic parameters and the physical properties of sediments in gas hydrate habitats on the concentration and distribution of gas hydrate deposits. Given the increased interest in gas hydrate as a possible source of renewable energy, proper characterization of these deposits in their respective environments is a first step toward determining whether these deposits can be viewed as a viable option for production. In this study we investigate the evolution of methane gas hydrate deposits in four continental margin reservoirs. In particular, we quantify the distribution of gas hydrate saturation over the speculated lifetime of the deposits and explore the implications for the production and renewability of these reservoirs.

4.2. Background

Results of ODP Legs 112, 131, 170, 190, and 201 and DSDP Leg 96 provide much of the background materials for this study. Gas hydrate occurrences at the Nankai Trough (Legs 131 and 190), the Costa Rican Margin (Leg 170), the Peruvian Margin (Legs 112 and 201), and the Gulf of Mexico (Leg 96) were documented based on direct observations from recovered core samples and the results of geochemical and geophysical analyses. Legs 131 and 190 were dedicated to characterizing the deformational processes and hydrogeology of the Nankai Trough Accretionary Prism.
Gas hydrates were recovered in cores at Site 808 (Taira et al., 1991) and its presence inferred at Site 1178 (Moore et al., 2001). Our knowledge of gas hydrate occurrence at the Costa Rican Margin comes from results of Leg 170 that focused on describing the mass and fluid fluxes between accreted and subducted sediments (Kimura et al., 1997), where gas hydrate samples were recovered in cores at Sites 1041 and 1040. On the Peruvian Margin gas hydrate was recovered at Sites 685 and 688 during coring on Leg 112, which was dedicated to examining the role of tectonic and oceanic processes in sedimentation and diagenesis in the forearc basin of the margin (Kvenvolden and Kastner, 1990). More recently gas hydrate samples were also collected on Leg 201 at Site 1230 (D'Hondt et al., 2003), which is co-located at Site 685. This leg focused on examining life in marine sediments. There is a relative paucity of ODP data regarding gas hydrates in the Gulf of Mexico (GOM) when compared to other known gas hydrate provinces. The only observations of gas hydrates made on an ODP voyage were on DSDP Leg 96 at Site 618 in the Green Canyon region (Paum et al., 1986). In other independent studies in the Garden Banks block, gas hydrate has been recovered in cores (Shipley et al., 1979; Brooks et al., 1986). Our study of gas hydrate in the GOM will focus on that region.

To the best of our knowledge, the only estimates of gas hydrate concentrations at the sites targeted in this study have been made on the basis of chlorinity gradients and direct observation. For example, Kvenvolden and Kastner (1990) in a rudimentary analysis calculated the pore water chloride concentration at Sites 685 and 688 on the Peruvian Margin and, on the assumption that the measured chlorinity gradients were solely due to the degree of pore water freshening from gas hydrate dissociation, postulate
that 3% to 10% of sediment volume is saturated with gas hydrate; an assumption we adopt later in this study. Milkov and Sassen (2002) report that concentrations of up to 15% of sediment volume have been observed in sediments at the Garden Banks 385.

Several other gas hydrate provinces have benefited from developing techniques to determine gas hydrate concentration. For example, based on downhole logging data gas hydrate saturation of pore space has been estimated at 25% to 30% at the Cascadia Continental Margin (Hyndman et al, 1999), at ~42.5% at the North Slope of Alaska (NW Eileen State2-well) (Collett, 2001), and 3% to 6% at the Blake Ridge (Collett and Ladd, 2000). On the Blake Ridge seismic studies also indicate that 2% to 5% of sediment pore space is saturated with gas hydrate (Holbrook et al., 1996) and analysis of in situ chlorinity profiles indicate that 4% of porosity is filled with gas hydrate (Egeberg and Dickens, 1999).

While significant advances have been made in refining the techniques to yield the most accurate estimates of hydrate concentrations in worldwide deposits, difficulties still arise in arriving at a concise result. Depending on the formulation adopted to relate the physical properties of sediments to the velocity of the formation, hydrate concentrations may vary significantly (Reister, 2003). Calculations of hydrate concentration from pore water chlorinity profiles are dependent on the background chloride concentrations assumed and proper preservation of cores (Egeberg and Dickens, 1999). The quality of well log data, uncertainties associated with downhole measurement and parameter estimation are also factors contributing to errors in estimates of hydrate concentration (Lee and Collett, 2001).
The development of predictive models that constrain hydrate concentration on the basis of variable input parameters such as the hydraulic, physical and chemical properties of the reservoir may serve as a useful tool when integrated with the results of geochemical and geophysical analyses. In this study we apply such a model to estimate the concentration of gas hydrate in four gas hydrate reservoirs for which estimates based on other techniques are lacking. The model describes the accumulation of methane gas hydrate from the two-phase system of gas hydrate and dissolved methane in seawater in porous sediments.

4.3. Gas Hydrate Provinces

In this section we provide a brief introduction to the focus sites of this study and the nature of gas hydrate deposits in these regions.

4.3.1. Nankai Trough

The Nankai Trough is located in the Sea of Japan and has developed due to the subduction of the Philippine Sea Plate beneath the SW Japan Arc (Figure 4.1), which began approximately 5 Ma (Taira et al., 1991; Moore et al., 2001). The Nankai accretionary prism was formed by the accumulation of hemipelagite and turbidite sediments scraped off the downgoing plate. Six holes were drilled on ODP Leg 190 along the Muroto Transect beginning in the trench axis and ending well into the subduction complex (Figure 4.2). While no solid gas hydrate was recovered in cores during Leg 190, its presence was inferred at Sites 1178 and 1176 based on the existence of a RS, pore water chlorinity measurements and core temperatures (Moore et al.,
Figure 4.1. Shaded relief map of the Nankai Trough. Inset is a tectonic map of the Philippine Sea region (Modified from Moore et al., 2001).
Figure 4.2. Schematic representation of the Mauvo transect showing the Leg 190 drill sites and the focus sites of this study (Modified from Morce et al. 2001).
Fragments of gas hydrate were recovered in wash core on ODP Leg 131, which also drilled at Site 808. In addition a BSR was observed ~ 20 km west of Site 808 (Teira et al., 1991). Methane is the dominant gas at the sites and is speculated to be of biogenic origin based on isotopic evidence.

In this study we focus on Site 1178, located in the landward section of the accretionary complex in an area characterized by a thick sediment cover overlying landward dipping strong reflectors and thrust faults, and Site 808 located in the toe of the prism in an area populated by small-displacement faults in which the trench wedge facies tilt seaward and the sediment section thickens landward. Further details are presented below in Table 4.1.

<table>
<thead>
<tr>
<th>Evidence of occurrence</th>
<th>Mode of occurrence</th>
<th>Lithology</th>
<th>Gas composition and origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1178</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. BSR - 400 mbsf</td>
<td>No hydrate recovered</td>
<td>Hemipelagic mud</td>
<td>Moderate CH$_4$ Thermogenic</td>
</tr>
<tr>
<td>2. CT profiles indicate hydrate (150 to 400 mbsf)</td>
<td></td>
<td>Sandy mud</td>
<td></td>
</tr>
<tr>
<td>3. Cold core temps</td>
<td></td>
<td>Silt-sized turbidites (Late Miocene to Pliocene)</td>
<td></td>
</tr>
<tr>
<td>Site 808</td>
<td>One piece in cemented sand</td>
<td>Fine-grained sand and silt sized thin turbidite layers with hemipelagic muds (Pliocene)</td>
<td>Mostly CH$_4$ Biogenic</td>
</tr>
<tr>
<td>1. BSR - 200 mbsf 20 km west</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. CI profiles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. in situ CH$_4$ conc.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sources: Moore et al. (2001); Kastner (2005); Teira et al. (1991)

4.3.2. The Costa Rican Margin

The Middle America Trench is the surface expression of the subduction of the Cocos Plate beneath the Caribbean Plate. The Costa Rican Margin sits on the southernmost region of the trench where, it is now believed, the prism is composed of slumped slope sediments rather than accreted materials from the downgoing Cocos Plate.
Figure 4.3. Contour map of a section of the Costa Rican margin. Leg 170 drill sites are plotted on the lower right inset (Modified from Silver et al., 2000).
(Morris et al., 2003). On ODP Leg 170, four holes were drilled along the Line CR-20 transect (Figure 4.3) beginning in the trench axis (Site 1039) and extending landward onto the forearc basin (Site 1041). For the purpose of this study we focus on two sites at which gas hydrates were recovered: Site 1041, located ~12 km landward of the trench axis in a sedimentary apron ~500 m ~600 m thick and Site 1040, located ~1.6 km upslope of the toe of the prism in the sediment wedge (Figure 4.4). Gas hydrate samples were observed in cores between 120 and 280 mbsf at Site 1041 in four lithologically distinct forms (Shipley et al., 1997) (Table 4.2). At Site 1040 small amounts of unevenly distributed disseminated hydrate were present between 20 mbsf and the decollement zone (360 mbsf). Biogenic methane is the dominant gas at both sites.

<table>
<thead>
<tr>
<th>Evidence of occurrence</th>
<th>Mode of occurrence</th>
<th>Lithology</th>
<th>Gas composition and origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1040</td>
<td>1. CT profiles</td>
<td>Disseminated crystals between 20 mbsf to 360 mbsf</td>
<td>Clay with silty sand Clayey diatomite with ash layers (Mid Miocene)</td>
</tr>
<tr>
<td></td>
<td>2. Core samples</td>
<td>Silstones Claystones Silty sandstone (Late Miocene)</td>
<td>Mostly CH₄ Biogenic</td>
</tr>
<tr>
<td>Site 1041</td>
<td>1. CT profiles</td>
<td>Small crystals disseminated in silstones; Massive in fractured clays; Small plates as fracture fill; Cement in as; all samples between 120 ~ 340 mbsf</td>
<td>Mostly CH₄ Biogenic</td>
</tr>
<tr>
<td></td>
<td>2. Core samples</td>
<td>Silstones Claystones Silty sandstone (Late Miocene)</td>
<td>Mostly CH₄ Biogenic</td>
</tr>
</tbody>
</table>

Source: Kimura et al. (1997)

4.3.3. The Peruvian Margin

The present-day Peruvian Margin is the result of oblique subduction of the Nazca Ridge beneath the South American Plate. The margin was non-accretionary between Eocene time to ~6 to 7 Ma. Leg 112 drilled along two corridors on the margin: Sites 685
Figure 4.4. Seismic section of the line crossing Sites 1040 and 1041 (Modified from Silver et al, 2000).
and 688 were both drilled in the lower slope of the trench on the Southern (across the Lima Basin) and Northern (off central Peru) Corridors respectively (Figure 4.5). Gas hydrates were observed in cores at both sites: as cementing material in silty muds of Pleistocene age at sediment depths of 99 mbsf and 166 mbsf at Site 685 and 141 mbsf at Site 688 (Kvenvolden and Kastner, 1990). Analysis of gas samples indicate that methane is the predominant gas (> 99%) in the fraction and the measured δ¹³C values suggest that methane is primarily of biogenic origin with possible mixing of thermogenic methane (Table 4.3).

Table 4.3. Gas hydrate occurrence in the Peruvian Margin

<table>
<thead>
<tr>
<th>Site 685</th>
<th>Evidence of occurrence</th>
<th>Mode of occurrence</th>
<th>Lithology</th>
<th>Gas composition and origin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1. CT profiles</td>
<td>Cements in mud at</td>
<td>Diatomaceous muds (Pleistocene)</td>
<td>Mostly CH₄ Biogenic</td>
</tr>
<tr>
<td></td>
<td>2. Core samples</td>
<td>99 mbsf and 166 mbsf</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. BSR at 612 mbsf</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site 688</td>
<td>1. CT profiles</td>
<td>Hydrate-mud complex at 141 mbsf</td>
<td>Diatomaceous muds (Pleistocene)</td>
<td>Mostly CH₄ Biogenic</td>
</tr>
<tr>
<td></td>
<td>2. Core samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. BSR at 473 mbsf</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Kvenvolden and Kastner (1990)

4.3.4. The Gulf of Mexico

Rifting of the North and South American Plates during the Jurassic resulted in the formation of the Gulf of Mexico (GOM) basin (Condie, 1989)(Figure 4.6). A layer of salt was subsequently deposited on crystalline basement rock and was in turn buried by Late Jurassic and Early Cretaceous shelf carbonates, and predominantly silicic clastic sediments of Upper Cretaceous to Pleistocene age (Matthews, 1984). The uppermost sedimentary layer in the GOM is now predominantly composed of shelf carbonates. Structurally, the GOM geological province in pervasively faulted as a result of

94
Figure 4.5. Contour map of the northwestern continental margin of South America (above) and the location of the focus sites 685 and 688 along the Peru Continental Margin.
Figure 4.6. Relief map of the southern US, DSDP Leg 96, Site 618 in white. JB388 is just west.
sedimentation and isostatic subsidence as well as deformation and migration of the salt layer into the upper regions of the sediment column (Rowan et al., 1999). These faults serve as high permeability pathways along which hydrocarbons migrate from deep within the sedimentary layer to the seafloor (Behrens, 1988; Reilly et al., 1996). The Garden Banks region is located in the northwestern part of the GOM in an area characterized by salt-related faulting and associated hydrocarbon seepage (Figure 4.7). Gas hydrates were recovered in sediment cores as small plates and chunks (Brooks et al., 1986; Reilly et al., 1996), and isotopic composition analyses indicate that the source gas is ~99.5% methane of biogenic origin (Brooks et al., 1986).

<table>
<thead>
<tr>
<th>Evidence of occurrence</th>
<th>Mode of occurrence</th>
<th>Lithology</th>
<th>Gas composition and origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB 388</td>
<td>1. Core samples</td>
<td>Small plates and chunks between 2.8 m and 3.8 m</td>
<td>Clayey muds (Pleistocene)</td>
</tr>
</tbody>
</table>

Source: Brooks et al. (1986)

4.4. Method of Analysis

Observational data such as those obtained on ODP legs are used to constrain the physical parameters adopted in our analysis (Table 4.5). We implement the steady-state analytical model developed by Xu and Ruppel (1999) to constrain fluid and methane flux rates where lacking. Their formulation predicts the location of the GHZ based on fluid, methane and energy conditions. In this analysis we follow the procedure outlined in Ruppel and Kinoshita (2000) for Sites 1039, 1040 and 1041, and use observables such as the location of the BSR, chloride concentrations, and in situ gas hydrate occurrence to
Figure 4.7. Location map of several gas hydrate occurrences, including GB388, in the Gulf of Mexico region (Sassen et al., 2001).
constrain the relative position of the gas hydrate zone in the sediment column and apply the Xu and Ruppel (1999) model to estimate fluxes of fluid, methane and energy that yield the same GHZ. To provide an example, we describe our method of analysis for one of the focus sites (Site 1178 in the Nankai Trough) in the next section.

Hole 1178 was drilled at ~1740 m water depth at a location with an estimated seafloor temperature of 2.5 °C. Based on measurements of in situ methane and chloride concentrations and the presence of a BSR, we conclude that the base of the gas hydrate stability zone (BGHS) is coincident with the base of the gas hydrate zone (BGHZ) at 400 mbsf and that the top of the GHZ (TGHZ) is at least 120 mbsf. Porosity estimates for the sediments range from 50% at 100 mbsf to 35% at 400 mbsf (Moore et al., 2001).

Estimates of fluid flux vary in this setting. For example, independent studies indicate that fluid venting near the frontal thrust of the Nankai accretionary prism is ~20 mm yr⁻¹ based on pop-up pore pressure measurements but may be as high as 100 mm yr⁻¹ based on the density of clam colonies (Le Pichon et al., 1992). A rough calculation of dewatering-induced fluid flux (e.g. after Pedersen et al., 1997) yields results two orders of magnitude less than that measured by pop-up pore pressure instruments. Heat flow at Site 1178 is not well constrained and may vary between 60 mW m⁻² and 130 mW m⁻² (Moore et al., 2001). Application of the analytical model using the constraints described above yields estimates of fluid, energy and methane flux consistent with a GHZ located between 120 mbsf and 400 mbsf (Table 4.5). With these estimates of energy and fluid fluxes and the location of the GHZ, we then apply the numerical model to describe the accumulation and distribution of gas hydrate with time at the site. Details of the model are presented in Chapter 3 of this dissertation.
Table 4.5. Base model parameters for the various sites examined in this study

<table>
<thead>
<tr>
<th>Sites</th>
<th>$\eta_r$ (m m$^{-2}$)</th>
<th>$\eta_v$ (m mol m$^{-2}$)</th>
<th>$\eta_m$ (mm yr$^{-1}$)</th>
<th>$Z_0$ (m)</th>
<th>$T_0$ (°C)</th>
<th>$\phi$</th>
<th>TGHZ (mbsf)</th>
<th>BGHZ (mbsf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1178</td>
<td>0.03</td>
<td>37</td>
<td>0.004</td>
<td>1750</td>
<td>2.5</td>
<td>0.5</td>
<td>118</td>
<td>390</td>
</tr>
<tr>
<td>808</td>
<td>20</td>
<td>140</td>
<td>3.7</td>
<td>4500</td>
<td>2.5</td>
<td>0.5</td>
<td>3</td>
<td>195</td>
</tr>
<tr>
<td>1040</td>
<td>5</td>
<td>22</td>
<td>0.34</td>
<td>4180</td>
<td>1.7</td>
<td>0.5</td>
<td>4</td>
<td>405</td>
</tr>
<tr>
<td>1041</td>
<td>0.04</td>
<td>18.2</td>
<td>0.003</td>
<td>3300</td>
<td>2.0</td>
<td>0.5</td>
<td>115</td>
<td>335</td>
</tr>
<tr>
<td>685</td>
<td>1</td>
<td>41</td>
<td>0.194</td>
<td>5670</td>
<td>1.5</td>
<td>0.65</td>
<td>40</td>
<td>615</td>
</tr>
<tr>
<td>688</td>
<td>1</td>
<td>45</td>
<td>0.175</td>
<td>3820</td>
<td>1.7</td>
<td>0.65</td>
<td>35</td>
<td>475</td>
</tr>
<tr>
<td>GR388</td>
<td>100</td>
<td>152</td>
<td>8.4</td>
<td>850</td>
<td>7</td>
<td>0.5</td>
<td>2</td>
<td>145</td>
</tr>
</tbody>
</table>

4.5. Results

The goal of this study is to estimate methane gas hydrate concentrations in the porous sediments of four continental margin reservoirs by applying a numerical model that tracks the accumulation and distribution of gas hydrate in the two-phase region (gas hydrate and water + dissolved gas) of the three phase system of methane gas, solid hydrate and liquid. Using the model parameters presented above we examine the evolution of porosity in the GHZ as methane hydrate saturates pore space and discuss the implications for the renewability of these deposits.

4.5.1. Nankai Trough

Although no gas hydrate was recovered at Site 1178, if we assume that the pore water freshening is due only to gas hydrate dissociation, chloride anomalies in the 120 mbsf to 400 mbsf interval indicate that gas hydrate may be present in concentrations as large as 7% (Taira et al., 2001) in the coarsest grained sediments. We adopt the parameters listed in Table (4.5) and pore diameters of 100 μm to reflect this lithology and
determine the decrease in porosity as a function of depth with time as gas hydrate formation occurs. The duration of our model simulation is constrained by the age of the sediments at Site 1178. The results are presented in Figure 4.8. We estimate that the average hydrate concentration in the GHZ is \( \sim 0.3\% \) at 10 M.y. This is an order of magnitude less than inferred on the basis of chlorinity profiles, and the disparity can most likely be attributed to the underestimation of fluid flux in the system.

If we adopt an initial fluid flux of 1 mm yr\(^{-1}\), we obtain an average hydrate concentration of 7% in \( \sim 1.6 \) M.y.; a fluid flux of 20 mm yr\(^{-1}\) yields the same concentration in 0.09 M.y. (Figure 4.9). Increasing the magnitude of the fluid flux not only increases the rate of formation of hydrate, but also alters the distribution of gas hydrate in the sediments and increases the thickness of the GHZ by shoaling the TGHZ (Table 4.6). For low advective fluxes we observe a nearly linear profile of porosity variation with depth. This is due to the interdependence of hydrate saturation, methane solubility, and temperature and fluid flux. The temperatures in the GHZ are a function of the magnitude of the advective flux; higher advection rates perturb the background thermal profile making the gradient concave upwards higher in the GHZ. This in turn alters the morphology of the solubility curve and the solubility gradients, which determine the amount of gas hydrate that will precipitate from dissolved fluid to form hydrate (Nimblett and Ruppel, 2003).
Figure 4.8. Plot of porosity as a function of depth in the GHZ at Site 1178 in 2 M.y. intervals. Inset: the evolution of porosity at 0.2 M.y. intervals.
Figure 4.9. (above) Plot of porosity as a function of depth in the GHZ at 0.2 M.y. intervals for Site 1178 with an initial fluid flux of 1 mm/yr. (below) Porosity at the base, middle and top of the gas hydrate zones as a function of time for a fluid flux of 20 mm/yr.
### Table 4.6. Additional model parameters adopted for Site 1178

<table>
<thead>
<tr>
<th>$q_r$</th>
<th>$q_e$</th>
<th>$q_w$</th>
<th>$Z_0$</th>
<th>$T_0$</th>
<th>$\phi$</th>
<th>TGHZ</th>
<th>BGHZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mm yr$^{-1}$)</td>
<td>(mW m$^{-2}$)</td>
<td>(mol m$^{-2}$ yr$^{-1}$)</td>
<td>(m)</td>
<td>(°C)</td>
<td></td>
<td>(mbsf)</td>
<td>(mbsf)</td>
</tr>
<tr>
<td>1</td>
<td>0.038</td>
<td>0.13</td>
<td>1750</td>
<td>2.5</td>
<td>0.5</td>
<td>11</td>
<td>404</td>
</tr>
<tr>
<td>20</td>
<td>0.065</td>
<td>2.6</td>
<td>1750</td>
<td>2.5</td>
<td>0.5</td>
<td>3</td>
<td>403</td>
</tr>
</tbody>
</table>

At Site 808, which is relatively close to the frontal thrust of the prism, fluid flux is expected to be greater than at Site 1178 due to (1) deformational processes that enhance the upward expulsion of pore fluids that migrate along the decollement and (2) the presence of small faults that provide conduits for these fluids. For the purpose of a comparative analysis, we adopt an initial fluid flux of 20 mm yr$^{-1}$, the upper endmember used in our analysis at Site 1178. For the parameters outlined in Table 4.5, we determine the evolution of porosity in the sediments associated with hydrate accumulation at Site 808 (Figure 4.10). The duration of our simulations is again constrained by the age of the sediments. The results indicate that hydrate formation reduces porosity from 0.5 to 0.13 at the BGHZ and 0.5 to 2.5 at the TGHZ in 2 M.y. Based on our estimates we conclude that the maximum average concentration of gas hydrate at Site 808 is ~ 30% assuming hydrate forms from dissolved methane.

#### 4.5.2. Costa Rican Margin

At Site 1040 on the Costa Rican Margin using the parameters in Table 4.5 we estimate that the average gas hydrate concentration is ~ 20% given that the sediments are ~ 15 M.y. (Figure 4.11). Our estimate of hydrate concentration is in fairly good agreement with geochemical analyses, which indicate that gas hydrate dissociation at 180
Figure 4.10. Plot of porosity as a function of depth in the GHZ at 2 M.y. intervals for Site 808 with an initial fluid flux of 20 mm/yr. Inset: porosity evolution at 0.2 M.y. intervals.
Figure 4.11. Plot of porosity at the top middle and base of the gas hydrate zone at Site 1040 for an initial fluid flux of 5 mm/yr.
mbsf is responsible for 29% dilution of seawater (Kimura et al., 1997). Our underprediction of the gas hydrate concentration may be partially explained by the fact that stratigraphic analyses indicate a possible fault between 180 mbsf and 190 mbsf based on observations of deformational bands and stratal disruptions (Kimura et al., 1997). We do not account for fluid flow along fault conduits in this study, but have previously demonstrated that more concentrated hydrate is associated with focused flow faults using the same numerical model (Nimblett and Ruppel, 2003).

At Site 1041 the fluid, energy and methane fluxes we adopt are constrained by observations of gas hydrate in cores between the intervals of 120 mbsf and 340 mbsf (Table 4.5). Based on these parameters we estimate a maximum average hydrate concentration of ~ 0.3% in the GHZ (Figure 4.12). This is significantly lower than gas hydrate concentrations inferred on the basis of geochemical data that indicates pore water freshening due to gas hydrate dissociation accounts for an estimated 34% to 36% dilution between 120 mbsf and 280 mbsf (Kimura et al., 1997). If we adopt increased fluid fluxed of 1 mm yr⁻¹ and 20 mm yr⁻¹ (Table 4.7) we obtain average hydrate concentrations of 10% and 35% respectively. The results indicate that an initial fluid flux of 20 mm yr⁻¹ yields gas hydrate concentrations most consistent with inferred concentrations based on chlorinity data. While a relatively quiescent flow regime in the sediment apron at Site 1041 is more consistent with the inferred location of the gas hydrate zone, phenomena associated with more vigorous advection of fluids such as mud diapirs, seeps and vent communities occur just landward of Site 1041 in the sediment apron, as previously noted by Ruppel and Kinoshita (2000) in their analysis of gas hydrates in this setting. Thus regions of high flux do exist in the vicinity of Site 1041. Furthermore the mode of
Figure 4.12. Plot of porosity at the top, middle and base of the gas hydrate zone for an initial fluid flux of 0.04 mm/yr in (a), 1 mm/yr in (b) and 20 mm/yr in (c) at Site 1041.
occurrence of hydrate at Site 1041 (Table 4.2) is more consistent with hydrate formation in a highly advective system.

Table 4.7. Additional model parameters adopted for Site 1041

<table>
<thead>
<tr>
<th>( q_e )</th>
<th>( q_a )</th>
<th>( Z_a )</th>
<th>( T_s )</th>
<th>( \phi )</th>
<th>( \text{GHZ} )</th>
<th>( \text{BGHZ} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{mm yr}^{-1} )</td>
<td>( \text{mW m}^{-2} )</td>
<td>( \text{mol m}^{-2} \text{yr}^{-1} )</td>
<td>( \text{m} )</td>
<td>( ^\circ \text{C} )</td>
<td>( \text{mbsf} )</td>
<td>( \text{mbsf} )</td>
</tr>
<tr>
<td>1</td>
<td>0.0182</td>
<td>0.66</td>
<td>3300</td>
<td>2.0</td>
<td>0.5</td>
<td>12</td>
</tr>
<tr>
<td>20</td>
<td>0.0666</td>
<td>2.4</td>
<td>3300</td>
<td>2.0</td>
<td>0.5</td>
<td>3</td>
</tr>
</tbody>
</table>

4.5.3. Peruvian Margin

Our study of gas hydrate concentrations on the Peruvian margin focuses on Sites 685 and 688. Both are located at the lower slope of the accretionary prism and with the exception of the depths of the BSRs, have relatively similar features, such as lithology, and fluid, energy and methane fluxes. We therefore combine our discussion of the results for these sites. At both sites, the model yields gas hydrate concentrations comparable to those estimated on the basis of pore water chloride excursions. At Sites 685 and 688 we obtain gas hydrate concentrations of ~ 7% and 14% at the BGHZ, and average concentrations of ~ 5% and 7.5% in the GHZ respectively (Figure 4.13). Kvenvolden and Kastner (1990) report pore water dilutions of ~ 3% and 13% at the bottom of the drill holes at Sites 685 (400 mbsf) and 688 (770 mbsf) respectively. They also note that pore water freshening increases with depth in the sediments. We can therefore assume that hydrate concentrations would be > 3% at the BSR at Site 685 and less than 13% at Site 685 based on the CI data if all of the pore water dilution is due to gas hydrate dissociation. Without further information on the CI profiles the only fair inferences we
Figure 4.13. Plot of porosity at the top middle and base of the gas hydrate zone for an initial fluid flux of 1 mm/yr at (a) Site 685 and (b) Site 688
can make are that the 7% hydrate concentration we predict for the BGHZ at Site 685 may lie reasonably close to the actual concentration and that in all likelihood we overpredict the concentrations at the BGHZ at 688, but are unable to say by how much. For this application, we are limited by the availability of additional data to better constrain our results.

4.5.4. Gulf of Mexico

In northwestern Gulf of Mexico gas hydrate accumulation is associated with the migration of hydrocarbons and their gases along faults and proximal to salt bodies (Sassen, 1999). At the Garden Banks site, GB 388, small chunks of gas hydrate were observed very shallow in the sedimentary column, but its presence has been inferred in large quantities based on seismic phenomena such as acoustic attenuation and signal loss in faulted sediments (Brooks et al., 1986). No BSR was observed at this site despite indications of high methane flux and vent gassing (Reilly et al., 1996). To extend the reasoning of Xu and Ruppel (1999), the lack of a BSR may be a reflection of the vigor of the advective regime in the sediments and/or the preferential migration of gas along faults rather than accumulation of gas into a free gas zone beneath the GHZ.

The Garden Banks data set is the most poorly constrained of those used in this study. We have no reliable a priori information on any of the fluxes in the GHZ. However, observations of surficial hydrate, vent gases, and chemosynthetic communities (Sassen et al., 2001) at sites in close proximity to GB388 suggest that the hydrodynamic regime there may be similar to that of a high flux region such as along the Oregon Margin. We therefore adopt a conservative estimate of fluid flux of 100 mm yr⁻¹ based on
Figure 4.14. Evolution of porosity as a function of depth in the GHZ at 0.4 My intervals. Inset porosity reduction at 0.04 M.y. intervals.
measurements by Tryon et al. (1999) at Hydrate Ridge and vary the energy and methane fluxes to yield a GHZ that extends from 2 mbsf to ∼ 150 mbsf in the sediments at GB388. Adopting this high fluid flux to reflect advective transport in the sediments, we determine that gas hydrate occupies ∼ 25% of the pore space in the GHZ (Figure 4.14). Our estimate is in excess of the observed concentration of ∼ 15% noted by (Milkov and Sassen, 2002) and implies that the fluid flux at GB388 is probably less than the 100 mm yr⁻¹ we adopt.

4.6. Discussion and Conclusions

The modeling results presented here provide an opportunity to examine the temporal and spatial evolution of gas hydrate deposits in continental margin reservoirs and enable us to investigate the effect of the local hydrodynamic conditions on the accumulation of these deposits. Incorporating the results of geochemical and geophysical data, we are able to better constrain the hydraulic parameters estimated for these reservoirs.

When coupled with geophysical and geochemical results, the numerical model provides a useful tool for constraining the hydraulic parameters of gas hydrate reservoirs. For example, we estimate that the fluid flux at Site 1178 (located in thick sediment cover thrust faults) is ∼ 20 mm yr⁻¹ based on seismic data that constrain the base of the gas hydrate zone and geochemical data that provide estimates of in situ hydrate concentrations. This a result that is further supported by measurements of vent fluids using pop-up pore pressure instruments at the seafloor (Le Pichon et al., 1992).
In general our results show good agreement with other estimates of hydrate concentrations for our focus regions. With the exception of Site 1178 at the Nankai Trough, and Sites 685 and 688 on the Peruvian Margin we obtain average hydrate concentrations in excess of 15% pore volume at four site-specific continental margin reservoirs. The overarching result is that more concentrated hydrate deposits are associated with high flux settings, as predicted from the steady-state models of Zatepina and Buffett (1997) and Xu and Ruppel (1999). However, even the low endmember advective flux regimes can produce concentrated hydrate in deep-water hydrate reservoirs. For example, we obtain an average hydrate concentration of 20% in the sediments at Site 1040 (Costa Rica) for a fluid flux of 5 mm yr\(^{-1}\). This high concentration of hydrate is due to the fact that Site 1040 was drilled at 4200 m water depth. Since solubility is a function of both temperature and pressure and the hydrate accumulation rate is dependent on solubility and its derivatives (Chapter 3), the increased pressures are enough to give rise to high concentrations of gas hydrate. Likewise, comparatively speaking, one would expect the largest hydrate concentration at GB 388 (Gulf of Mexico) because of the high advective flux rates there (100 mm yr\(^{-1}\)). However, Site 808 (Nankai Trough), with an advective flux of 20 mm yr\(^{-1}\), has a more hydrate-rich GHZ even though the two sites have comparable energy fluxes. The difference is again due to the increased pressures in the GHZ sediments at Site 808. These results hint at the complexities involved in characterizing gas hydrate deposits and highlight the role that predictive models, such as the one implemented in this study, can play in resource assessment of these deposits.
We estimate average hydrate concentrations in the GHZ of multiple sites at four continental margins. The results range from as low as 5% to a maximum of 35% (Table 4.8). While these estimates are significant enough to warrant consideration from the standpoint of resource potential and production standpoint, we note two disadvantages: (1) As modeled, these deposits are distributed throughout porous sediments; and (2) With the current model and boundary conditions, hundreds to thousands of years are required to attain significant hydrate concentrations. As noted by Collett (2001), "the role that gas hydrates will play in contributing to the world's energy requirements will ultimately depend less on the volume of gas-hydrate resources than on the cost to extract them".

### Table 4.8. Average gas hydrate concentrations in the GHZ for our focus sites

<table>
<thead>
<tr>
<th>Site</th>
<th>$q_f$ (mm yr$^{-1}$)</th>
<th>$q_r$ (mW m$^{-2}$)</th>
<th>$q_m$ (mol m$^{-2}$ yr$^{-1}$)</th>
<th>$S$ % pore volume</th>
<th>TGHZ (mbf)</th>
<th>RGHZ (mbf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1178</td>
<td>20</td>
<td>65</td>
<td>2.6</td>
<td>7</td>
<td>3</td>
<td>403</td>
</tr>
<tr>
<td>608</td>
<td>20</td>
<td>140</td>
<td>3.7</td>
<td>30</td>
<td>3</td>
<td>195</td>
</tr>
<tr>
<td>1040</td>
<td>5</td>
<td>22</td>
<td>0.34</td>
<td>20</td>
<td>4</td>
<td>405</td>
</tr>
<tr>
<td>1041</td>
<td>20</td>
<td>66</td>
<td>2.4</td>
<td>35</td>
<td>3</td>
<td>401</td>
</tr>
<tr>
<td>685</td>
<td>1</td>
<td>41</td>
<td>0.194</td>
<td>5</td>
<td>40</td>
<td>615</td>
</tr>
<tr>
<td>688</td>
<td>1</td>
<td>45</td>
<td>0.175</td>
<td>8</td>
<td>35</td>
<td>475</td>
</tr>
<tr>
<td>GB388</td>
<td>100</td>
<td>152</td>
<td>8.4</td>
<td>25</td>
<td>2</td>
<td>145</td>
</tr>
</tbody>
</table>
CHAPTER V
SEISMIC IMAGING OF A FAULTED HYDRATE RESERVOIR

5.1. Introduction

Recent studies suggest that increased fluid and methane flux along permeable pathways through a gas hydrate zone (GHZ), such as faults, may evolve into localized regions of concentrated hydrate (Wood and Ruppel, 2000; Nimblett and Ruppel, 2003). Hydrate concentrations in the porous sediments of the GHZ at the Blake Ridge have been estimated at 5-7% total porosity (Holbrook et al., 1996). A localized, nearly 100% concentration of hydrate was recovered from a drill hole at Site 997 (ODP Leg 164), however this hydrate plug is likely to be associated with a fault. Seismic lines show that the Blake Ridge is pervasively cut by faults extending through the GHZ (Rowe and Gettrust, 1993; this study), and significant concentrations of hydrate may be present within these faults. Given data of sufficient resolution, local concentrations of hydrate can be seismically detected because of the velocity contrast between pure hydrate (~3.8 km s\(^{-1}\)) and sediments (~1.7 km s\(^{-1}\)). A sufficiently large region of concentrated hydrate juxtaposed with more disseminated hydrate in porous sediments should manifest itself as lateral velocity contrasts or gradients. Knowledge of the volumes of hydrate along and near faults may alter estimates of the total hydrate present within this reservoir and aid in understanding the fluid flow processes in these systems.

The purpose of this study is to quantify the lateral variability of gas hydrate concentration across a section of the Blake Ridge reservoir where sediments are known to be cut by faults. Using high-resolution multi-channel seismic (MCS) data collected on the Blake Ridge in September and October 2000, we determine the velocity structure of
the hydrated sediments in the vicinity of Site 997 by conducting a tomographic inversion of large-aperture reflection traveltimes from the BSR. Adopting the effective medium model developed by Helgerud et al. (1999), we determine the lateral variation of hydrate concentration associated with velocity contrasts in the faulted sediments.

5.2. Background

5.2.1 Previous Seismic Velocity studies of Blake Ridge Gas Hydrate Reservoir

Seismic studies of gas hydrate reservoirs have focused primarily on determining the nature of the BSR, the location of the gas hydrate zone in the sediment column, and the seismic velocities of hydrated sediments. Results of these studies often vary, mainly due to the techniques employed to study the velocity structure and data quality and resolution. For example, analyzing wide-angle, ocean-bottom-seismometer (OBS) and single-channel-seismic (SCS) data collected on the Blake Ridge, Katzman et al. (1994) determined the average velocity of the hydrated sediments to be 1.9 km s\(^{-1}\). In their analysis, they first inverted traveltimes of wide-angle and normal-incidence reflections and obtained interval velocities and ray paths to determine velocity gradients in the gas hydrate zone. Using vertical incidence reflection coefficients they constructed vertical incidence synthetic seismograms to further constrain the velocities in the GHZ. Lastly they performed amplitude vs. offset (AVO) analysis of the data and analyzed reflection synthetic seismograms of their velocity models to determine the nature of the BSR. In a related study, Korenaga et al. (1997) using the same data set but employing a 1D waveform inversion corroborated Katzman et al.’s (1994) findings that the hydrate zone on the Blake Ridge was approximately 400 to 500 m thick with an average velocity of 1.9
to 2.0 km s\(^{-1}\) and underlain by a section of free gas. Based on the inversion of vertical seismic profile (VSP) data collected on the Blake Ridge, Holbrook et al. (1996) estimated that the seismic velocities of the sediments there lie between 1.7 and 1.9 km s\(^{-1}\). Using MCS data Wood et al. (1994) conducted a study to determine lateral changes in P-wave velocities in the GHZ on the flanks of Blake Ridge. They performed a velocity analysis by fitting exact traveltime curves to \(\tau-p\) transformed data followed by waveform inversion of every 100th CDP gather, each spaced 12.5 m apart. They concluded that lateral changes in P-wave velocity on the order of 1.8 to 2.0 km s\(^{-1}\) exist in the GHZ and that velocities here are slightly elevated where a strong BSR and underlying low velocity zone are present. These results suggest a positive correlation between high P-wave velocities and regions of high flux, since a free gas zone is predicted to coincide with the BGHZ where gas flux is higher (Xu and Ruppel, 1999).

More recently, studies have focused on understanding the distribution and concentration of gas hydrate in marine sediments. Two such studies at the Blake Ridge examined variations in seismic velocities and hydrate concentration associated with seismic indicators such as the BSR, bright spots, chimneys and amplitude blanking (Gorman et al., 2002; Hornbach et al., 2003). Gorman et al. (2002) adopted a similar approach to that of Korenaga et al. (1996) to examine localized concentrations of gas hydrate associated with regions of amplitude blanking and gas chimneys, and bright spots. They determined that there are increased seismic velocities in the GHZ associated with low-amplitude chimneys and bright spots and further conclude that these phenomena are indicative of increased hydrate concentration. Similarly, Hornbach et al. (2003) examined the seismic velocities in a seismic section characterized by low
amplitude events and bright spots. They performed a semblance analysis from which they determined rms velocities at discrete depths in the GHZ. They then used Dix's equation to determine the interval velocities in and around their region of interest. Their results indicate velocities on the order of 1.9 km/s within a hydrate lens as opposed to surrounding velocities on the order of 1.84 km/s.

5.2.2. Estimates of hydrate concentration from seismic data

Based on their estimates of seismic velocities for the Blake Ridge sediments in the study previously mentioned, Korenaga et al. (1997) applied Wyllie's time average equation (Wyllie et al., 1958) and determined an average 3% concentration of hydrate with increased concentrations at the base of the gas hydrate zone (maximum of 20%). Similarly Holbrook et al. (1996) determined that sediments are on average approximately 2-5% filled with methane gas hydrate using a weighted mean of Wood (Wood, 1941) and Wyllie's equation. Using a rock physics model that describes the effect of methane hydrate on P-wave velocities in sediments both Helgerud et al. (1999) and Holbrook (2000) determined that hydrate occupies 3 to 4% of bulk volume on the crest of the Blake Ridge.

More detailed analyses suggest that hydrate may be concentrated in amounts as high as 30 to 42% of bulk volume in localized deposits associated with bright spots (Gorman et al., 2002) and 13 to 22% of bulk volume in low amplitude features (Hornbach et al., 2003). Using high-resolution data sets these studies strongly suggest the existence of lateral variations of hydrate concentration in marine reservoirs, and they
demonstrate that local variations in hydrate concentrations can be detected using seismic methods.

5.2.3. Estimates of hydrate concentration from downhole logs

Downhole logging measurements have also been used to determine in situ hydrate concentrations. Sonic velocities and electrical resistivity increases with the presence of gas hydrates in pore space. Collett and Ladd (2000) used Archie's Law and downhole measurements of electrical resistivity and pore water salinity to determine that the sediments in the vicinity of ODP Leg 164 drill holes 994, 995 and 997 are 3% to 6% saturated with gas hydrate. Analysis of acoustic logs at sites 994, 995 and 997 by Lee (2000) revealed that hydrate saturation varies between 4% and 12% on the Blake Ridge. Lee's (2000) concentrations were estimated using a combination of the weighted mean of the Timur (Timur, 1968) and Wood (Wood, 1941) equations.

5.2.4. Estimating the elastic properties of gas hydrate-bearing sediments

The elastic properties of gas hydrate-bearing sediments have been estimated based on measurements of seismic velocities and effective medium modeling relating elastic moduli to hydrate saturations (Guerin et al., 1999; Helgerud et al., 1999). Guerin et al. (1999) used consolidation models in conjunction with acoustic velocity and resistivity logs to determine the elastic properties of gas hydrate sediments and showed that the sediments above the BSR may be overconsolidated because of the presence of hydrates. Their consolidation models were based on two end-members models (Wood, 1941; Gassmann, 1951) that relate the elastic properties of the medium to their degree of
lithification. Using their estimates of elastic moduli they calculated the amount of gas hydrate concentrated in the sediments using rock physics models and conclude that 0% to 10% of pore space on the Blake Ridge is filled with hydrate. Helgerud et al. (1999), using an effective medium formulation based on a combination of the rock physics model of Dvorkin et al. (1999) and Gassmann's (1951) equation to account for the presence of a fluid phase, estimated that the concentration of gas hydrate in the Blake Ridge sediments surrounding Site 995 varies on average between 2% and 4% by volume and peaks at around 8.9%.

5.3. Study Site

Our velocity analysis focuses on a portion of a MCS transect extending across the Blake Ridge and crossing ODP Sites 994, 995 and 997 (Figure 5.1). Our study area is a 3.7 km region over which Common Depth Point (CDP) gathers were acquired from 180 shots fired continuously; beginning approximately 3 km west of the first CDP gather and ending 3 km east of the last. A post-stacked, depth-migrated section of the study region is illustrated in Figure 5.2. The seafloor is present as a bright dipping reflector at ~2.8 km. Approximately ~0.45 km below is the BSR, another bright reflector that crosscuts strata across the length of the section. In between the seafloor and the BSR are numerous other sub-horizontal reflectors that are frequently cut by high-angle normal faults extending from tens of meters below seafloor through the gas hydrate zone to the BSR. The faults are concentrated at locations between 6.5 and 7.5 km, at 9 km and between 9.5 to 10.5 km in the section.
Figure 5.1. Location map of the Blake Ridge Depression. The solid gray line represents the Regional Line R22 along which MCS data was acquired in 2000. Our focus area is a small transect of the line indicated by small black stars. Leg 164 drill sites are depicted as dark diamonds. The schematic below illustrates the relative positions of the first and last shots and the CDP gathers analyzed in this study.
Figure 5.2. Stacked and migrated data of our study area. The seafloor and BSR reflectors are present at depths of 2.77 km and 3.22 km respectively.
5.4. Data Acquisition

The data used in this study were collected on board the R/V Maurice Ewing in Fall 2000 on the Blake Ridge. We will refer to these data as the Blake 2000 dataset. The MCS survey was conducted using two generator-injector (GI) airguns as a source and a 480-channel, 6-km-long streamer as a receiver. The guns, towed at 5 m below sea surface, provided a relatively high frequency source (30 - 200 Hz), and were fired approximately every 37.5 m. Hydrophones were spaced 12.5 m apart and towed at ~3 m below sea surface (Figure 5.3). The streamer data were binned into 80-fold CDP gathers, spaced 6.25 m apart. These gathers were moveout corrected, stacked, and depth migrated to produce Figure 5.2.

5.5. Velocity Analysis

The primary hypothesis of the present study is that concentrations of gas hydrate may be present along likely fluid migration pathways such as faults. We test this hypothesis through a detailed seismic velocity analysis of the faulted sediments in the vicinity of Site 997. This analysis is premised on the notion that hydrate deposits along faults should be seismically resolvable, and so we begin by testing this notion in two ways. First, we calculate the synthetic seismic response of velocity models that include embedded “faults” characterized by ~10% increase in velocity with respect to the surrounding material. We find resolvable traveltime anomalies associated with such features. Second, we examine the Blake Ridge seismic dataset for evidence of traveltime anomalies associated with hydrate along faults. In particular, deposits of sufficiently concentrated hydrate along faults should result in patterns of localized traveltime
Figure 5.3. Schematic representation of the geometry of the MCS data acquisition system used in the Blake2000 survey.
residuals with respect to the traveltimes predicted for a constant velocity model. We calculate residual maps that reveal patterns that are consistent with anomalies due to faults, though the magnitude of the residuals is quite small. The results of these two initial feasibility studies were sufficiently positive to warrant a thorough tomographic imaging analysis of the dataset. We describe the details of these initial studies and the tomographic analysis below.

We assess the propagation effects of velocity anomalies along faults by computing synthetic seismograms for a simple model scaled similar to the GHZ of the Blake Ridge. The model consists of a 2.8-km-thick water layer overlying a 0.4-km-thick sedimentary layer with a velocity of 1.6 km/s. A “fault” dipping at 45° is defined within the sedimentary layer by increased velocities, with 1.9 km/s velocity is the center of the fault decaying to 1.6 km/s over ~50 m distance on either side (Figure 5.4 a and b).

Synthetic seismograms were calculated for surface source and receivers using a pseudospectral approach (e.g. Kosloff and Baysal (1982)) to model the scalar wave equation on a 1024x1024, 5-m grid using a 1-ms time step and a Ricker-wavelet source function with a center frequency of 50 Hz. The source was located at model X=1 km, giving a nominal maximum source/receiver offset of 4.115 km, but an 81-point (0.40 km) absorbing boundary was used, and so the maximum modeled offset across the fault is 3.715 km. This offset range is sufficient to observe reflection events that have interacted with the fault as well as reflections at both near and far offsets that have not interacted with the fault.

The calculated reflection event from the base of the sedimentary layer is shown in Figure 5.4 c flattened by shifting each trace in time by an amount equal to the predicted
Figure 5.4. (a) Velocity model used to generate the seismogram in (c) - 2.8-km-thick water layer overlying a 0.4-km-thick sedimentary layer of average velocity 1.6 km/s with a fault dipping at 45° defined by an increased seismic velocity of 1.9 km/s; (b) 1.9 km/s velocity in the center of the fault decaying to 1.6 km/s over a 50 m distance on either side; (c) reflection synthetic seismogram flattened to the predicted traveltime.
reflection traveltimes from the base of the fault-free sedimentary layer. The traveltime effects of the fault are seen as deviations from horizontal in trace-to-trace alignment. We will refer to these deviations as traveltime residuals, or residuals. The events most strongly affected by the fault are those between 2.0 – 2.7 km offset. In this region, phases with rays passing through the fault at a low angle (i.e., rays nearly traveling along the fault) arrive ~12 ms early. The latter arriving, second positive peak of the Ricker triplet is a diffraction phenomena arising from the disruption of the primary reflection event. The details of the phase beyond 2 km depend on the wavelet shape and frequency content and on the details of the fault zone. The effects of the fault on the waveform will scale with these factors, however. At twice the frequency, and with a fault zone half as wide as this one, the waveform of the reflection event would appear very similar to that of Figure 5.4 c, though the residuals would be reduced by half. The traveltime residuals of the fault synthetic with respect to the reference model are of a magnitude that is easily resolvable by the Blake 2000 dataset. As will be seen below, traveltimes can be picked to an accuracy of ~1ms, and so systematic traveltime anomalies of several milliseconds should be identifiable.

The traveltime residuals for the fault model are a function of fault dip and location with respect to the source, as well as, of course, the strength and dimension of the velocity contrast. For a given fault-zone velocity anomaly, the pattern of residuals as a function of source-to-receiver offset will vary as the position of the shot with respect to the fault changes. A contour or image plot of traveltime residuals varying as a function of both offset and shot location (or shot number for evenly spaced shots) would reveal this pattern. Such a plot is shown in Figure 5.5 for a separate parameterization of the
Figure 5.5. Traveltime residuals for the fault model shown in Figure 5.4 as a function of shot and offset. The pattern of the residuals is indicative of the traveltime residual map expected for our data set assuming increased seismic velocities are associated with concentrated hydrate along faults.
fault model of Figure 5.4 a, where we used the ray-based code of Zelt and Smith (1992) to calculate travelt ime residuals for a fault zone defined by discrete, 50-m-thick, 100-m-wide lateral velocity variations similar to those of Figure 5.4 a and b. While significant inaccuracies exist in ray-based travelt ime predictions for such a model, the general pattern of the predicted residuals provides insight into the type of residual patterns that might be expected for the Blake Ridge if velocity anomalies along faults exist there.

The second “feasibility” study involves constructing a residual map similar to Figure 5.5 for the Blake 2000 dataset. We do this by picking accurate traveltimes for the seafloor and BSR reflections from the CDP gathers and calculating travelt ime residuals with respect to a one-dimensional, two-layer, reference velocity model. The aim of this analysis is to see if patterns exist in this residual map that may be indicative of velocity anomalies in the gas hydrate zone. The procedure involves obtaining a set of travelt ime picks for the reflections for CDP gather, using these picks to determine an initial 1D, two-layer velocity/depth model for each CDP, and calculating the associated traveltimes predicted by these initial models. The initial picked and predicted traveltimes are then used in a crosscorrelation analysis to generate the ‘best’ sets of travelt ime picks for each gather. Velocity models are then obtained based on the best picks and used to calculate ‘best’ predicted times for the region. Travelt ime residuals for the dataset are then calculated by subtracting the predicted traveltimes from the observed (best) picks. These residuals are then analyzed to determine whether any significant patterns exist that suggest the presence of localized regions of concentrated hydrate. Details of each of these steps are provided in the following sub-sections.
5.5.1. Initial Traveltime picks

The initial set of traveltime picks of the seafloor and BSR reflections were made by hand for a subset of traces within each CDP gather. Picks were made at the first break of wavelets and, on average 15 traces for the BSR and 10 for the seafloor were picked for each of the 600 CDP gathers. An example of these initial picks for CDP 28180 is illustrated in Figure 5.6. The initial picks were then used to determine an initial 1D velocity model for each gather as described below.

5.5.2. Initial 1D velocity model

Our model consists of 2 layers: the water column and the gas hydrate zone, extending from the seafloor to the BSR. Using the initial picks for a particular CDP gather we determine the best-fit velocity-depth model that satisfies the 1D traveltime equation:

\[ T = px + \tau, \]  

where \( T \) is the traveltime from the source down to the \( i \)th layer and back up to a hydrophone at source/receiver offset \( x \) along the streamer; \( p \) is the ray parameter and \( \tau \) is the “delay time”. In determining a 1D velocity model for a particular CDP gather we calculate the traveltimes using equation (5.1) for a large range of possible models and choose the model that best fits the observed traveltimes. The velocities and thicknesses we search over are constrained by a priori knowledge of seawater velocities, velocities of the hydrated sediments of the Blake Ridge and depth to seafloor and BSR.
Figure 5.6a. CDP gather 28180. The initial traveltime picks are indicated by small black crosses at certain offset traces. A section of the gather within the black box is illustrated in Figure 5.6b.
Figure 5.6b. Magnified section of CDP gather 28180 with initial traveltime picks indicated by black crosses.
For the water layer we found that the seafloor reflection, is very well fit assuming a single constant velocity layer. In this case $\tau$ and $X$ are given by:

$$\tau = 2 \sum_{i=1}^{n} q_i z_i,$$

(5.2)

and

$$X = \frac{2}{\rho} \sum_{i=1}^{n} \frac{q_i}{z_i} x_i,$$

(5.3)

where $\rho$ (ray parameter) and $q$ are the horizontal and vertical components of slowness, $u$ (reciprocal of velocity, $v$) respectively, and $z_i$ is the thickness of the $i^{th}$ layer.

A constant velocity second layer is not able to adequately fit the observed BSR traveltimes. We therefore parameterize this layer as having a linear slowness gradient.

In this case $\tau$ and $X$ are given by:

$$\tau = \frac{2 x_i}{u_2 - u_1} \left[ \frac{u_2}{2} \left( u_1^2 - p^2 \right)^{1/2} - \ln \left| u_1 + \left( u_1^2 - p^2 \right)^{1/2} \right| \right],$$

(5.4)

and

$$X = \frac{2 \rho_x}{u_2 - u_1} \ln \left| u_1 + \left( u_1^2 - p^2 \right)^{1/2} \right|,$$

(5.5)

where $u_1$ and $u_2$ are the slownesses at the top and bottom of the $i^{th}$ layer respectively.

Parameterization of the second layer as having a velocity gradient requires us to search through either 3D space or fix the velocity at the top of the layer. For simplification purposes we assume a fixed velocity at the top. It is important to note that for the best fit velocity model found, we observe systematic errors at large offsets due to transverse anisotropy (Pecher et al., 2003) in the sediments that we do not account for. By using an anisotropic raytracing code we found that traveltimes could be very well fit, but since the tomography code used to determine the velocity structure of GHZ is based on isotropic media, our subsequent analysis is based on isotropic traveltine calculations.
The 1D velocity models derived for the CDPs from the initial traveltimes picks are illustrated in Figure 5.7. Our seawater velocities are concentrated at 1.509 km s$^{-1}$. The quantized changes in velocity at 0.001 km s$^{-1}$ intervals reflect the velocity interval ($\Delta v$) used in the search for the best velocity/depth model using equations (5.1, 5.2 and 5.3). The scatter about a local mean indicate the velocity resolution of this data, which for the water layer is $\sim 0.001$ km s$^{-1}$. The seafloor dips from west to east and seafloor depth is resolvable to within $\pm 2.5$ m. The seafloor, as determined from equations (5.1, 5.2 and 5.3) has the same shape as that recorded by the R/V Maurice Ewing hydrorsweep system. The 10 m difference between the hydrorsweep bathymetry and our model values are due to the difference in the assumed water velocity used in the hydrorsweep calculation and that determined from the traveltimes data.

The velocity gradients and thicknesses determined for the GHZ show much more variability than those determined for the water column. We observe an overall decreasing trend in velocity gradient in the GHZ from west to east. The mean velocity gradient is 1.114 s$^{-1}$ and the standard deviation is from the mean is 0.024 s$^{-1}$. The GHZ is approximately 0.47 km thick with deviations from the mean on the order of 0.0025 km. The level of variability in the velocity gradients and thicknesses of the GHZ are due to the fact that is searching for the best fit model using equations (5.1, 5.4 and 5.5) very small changes in $u_2$ and $z$ result in very little rms differences in the calculated $X$ and $T$ values and those observed in the traveltimes data.
Figure 5.7: Initial 1D velocity depth models obtained from the initial traveltine data. Water velocities and water column thicknesses as function of CDP are illustrated in the upper plots (a); velocities as shaded dark circles, thickness as black crosses and hydrosweep depths as plus signs. The thicknesses and velocity gradients as a function of CDP in the GHZ are depicted in the lower plots (b) as black crosses and shaded dark circles respectively.
5.5.3. Automated Picker and Best traveltame picks

A final set of traveltame picks is determined using a crosscorrelation technique. These ‘best’ picks are calculated by determining the traveltame delays between adjacent traces in a gather by cross-correlating windowed portions of one trace with its nearest neighbor. The time window for the crosscorrelation is centered about the traveltame predicted by the initial velocity/depth models. Beginning with the first trace, the delay time or lag, which gives the point of maximum crosscorrelation between that trace and its neighbor is determined for all traces. The lags, when progressively summed with increasing offset, produce a traveltame curve starting at zero lag at the first trace. That is to say, the shape of this traveltame curve is correct, but it lacks a correct absolute traveltame. We use the initial ‘hand’ picks to determine an absolute time for this traveltame curve. Each initial pick represents a particular time delay at a particular offset. By passing the crosscorrelation traveltame curve through each of the n initial picks we generate n estimates of the absolute time for each trace. Our best picks are determined for each trace by averaging these n estimates (Table 5.1).
Table 5.1. Representation of the procedure involved in determining the best traveltime picks

<table>
<thead>
<tr>
<th>Trace number in CDP</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>25</th>
<th>50</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Picks</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Best Pick</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
</tbody>
</table>

* Initial 'hand' pick
* Cross correlation traveltime + initial traveltime
** Average traveltime ⇒ Best traveltime pick

The best picks for the gather CDP 28180 are illustrated in Figure 5.8. As the plot demonstrates, the automated picker generates picks that either fall on or lie very close to the first break of the traces. Using so determined best picks we employ the same procedure outlined in section 5.5.2 to calculate the 1D velocity models that best fit these data and the associated predicted times.

5.5.4. Best-fit velocity model

The best-fit velocity models are depicted in Figure 5.9. These velocity models were calculated using the full complement of traveltime picks generated by the automated picker, but with the nearest and farthest offset traveltimes pairs ignored because of streamer effects and the influence of wide-angle reflections.
Figure 5.8a. CDP gather 28180. The dashed black line indicates the best travelt ime
picks generated in the crosscorrelation analysis. A section of the gather within the
black box is illustrated in Figure 5.8b.
Figure 5.8b. Magnified section of CDP gather 28180 with the best travel times overlaid as a dashed line.
Figure 5.9. 1D velocity depth models obtained from the best traveltime data. Water velocities and water column thicknesses as a function of CDP are illustrated in the upper plots (a); velocities as shaded dark circles, thickness as black crosses. The thicknesses and velocity gradients in the GHZ are depicted in the lower plots (b) as black crosses and shaded dark circles respectively.
At near offsets (close to the ship) the streamer dips to 8 m below the sea surface (Figure 5.10); these receivers are substantially lower in the water column than the rest of the streamer and this difference in depth translates into a ~ 2 ms travelt ime error. At further offsets, wide-angle reflections from interfaces beneath either the seafloor or BSR often interfere with the picked reflection events, altering their travel times somewhat. In addition surface currents over parts of the survey cause the streamer to feather, or tail off- axis (Figure 5.11) leading to uncertainty in the actual offset to receivers near the end of the streamer. The latter effect is considered small since, as Figure 5.11 demonstrates, the streamer is well aligned for the majority of our study region.

In determining the best fit velocity models we used the average velocity in the water column, determined from the initial velocity models (Figure 5.7), and thicknesses determined by assuming that a change in velocity implies a change in the thickness of the water column if the travelt ime is constant for the starting and ending velocities. We therefore shifted the water column depths by the change in thickness associated with the change in velocity for a constant travelt ime. This collapsed the water column thicknesses to within 0.0025 km (Figure 5.9a). Using equations (5.1, 5.4 and 5.5) and the values of $u$ and $z$ for the water column (Figure 5.9a), we then determined the velocity gradients and thicknesses in the GHZ (Figure 5.9b). The GHZ is approximately 0.466 km thick with maximum variations under 0.005 km. The BSR is seen as a dipping feature and its depth is better constrained than in the initial model (Figure 5.7). In addition we observe background velocity gradients structure that decrease over the length of the study area from approximately 1.15 s$^{-1}$ to 1.10 s$^{-1}$ with variations on the order of 0.02 s$^{-1}$ superimposed over shorter distances.
Figure 5.10. 3D grid of the streamer depth in the water column as a function of shot and offset.
Figure 5.11. Plot of the relative positions of the hydrophones along the streamer behind the ship for a subset of the shots fired. A nearly straight line indicates very little feathering.
The best-fit velocity models are then used to make a reference model to look for patterns in residuals that may be indicative of velocity perturbations in the GHZ. We smoothed the thickness of the water column and the velocity gradients and thicknesses in the GHZ by applying a three-point boxcar filter (Figure 5.12). Our treatment of the best-fit velocity model is justified based on the fact that from CDP to CDP the variation in velocities/velocity gradients and thicknesses should be small since each gather contains data that have sampled wide portions of the model domain. Because each CDP gather corresponds to a point location on the reflectors, whereas the velocities are averaged over a large extent of the GHZ, we have a greater ability to resolve changes in depth to the reflector from CDP to CDP rather than changes in velocity from CDP to CDP. Given our ray coverage; 60 rays per reflection point ranging in offsets from 0.5 km to 5.5 km, the velocities we determine using the 1D travel time equation are not localized but are averaged over the region spanned by the rays. To image higher resolution velocity variations requires topographic inversion techniques.

5.5.5. Residuals

Traveltime residuals are obtained by subtracting the traveltimes predicted by the smoothed velocity/depth models from the observed, or best traveltimes picks. A plot of the residuals for CDP gather 28180 illustrates that the variance of the best picks with respect to a constant 1D velocity model is less than the variance for the initial picks (Figure 5.13). The plot also illustrates the misfit at near and far offsets due to streamer effects and wide-angle reflections. The misfit at further offsets, to some extent, also
Figure 5.12. 1D velocity depth models obtained from the best traveltime data. Water velocities and water column thicknesses are illustrated in the upper plots (a); velocities as shaded dark circles, thickness as black crosses. The thicknesses and velocity gradients in the GHZ are depicted in the lower plots (b) as black crosses and shaded dark circles respectively.
Figure 5.13. Traveltime residuals for CDP gather 28180 for the seafloor (upper plot) and BSR (lower plot) with respect to the smoothed velocity depth model. The traveltime residuals of the initial traveltime picks are indicated by gray dots and the residuals of the best traveltime picks are illustrated as the small black dots.
reflects the fact the best fit velocity models are calculated based on the a priori assumption that the GHZ is an isotropic medium.

Figure (5.14) is a gridded 3D representation of the residuals as a function of shot and offset. The residuals are small but we observe patterns in the residuals that are suggestive of localized velocity anomalies within the GHZ and are similar in some respects to traveltine residuals associated with an embedded 45° fault-defined increased hydrate concentration (i.e. velocity) (Figure 5.5). However patterns in the residual map are due to either the inability of a linear velocity gradient model to fit the data or to systematic errors in picking. We also note the presence of relatively large residuals (> -3 ms) at far offsets due to the effects of anisotropy.

To rule out the possibility of residual patterns due to bad picks we examined gathers within four regions, labeled A through D on Figure (5.14). The data in these figures have been flattened, or time shifted to the best traveltine picks and thus the flatness of the BSR reflection event, when time shifted is a measure of the accuracy of the picks. Figures 5.15a to 5.15d are CDP gathers in each of the anomalous regions. Traveltine residuals with respect to the 1D constant velocity model are plotted on the figures. The residuals are small (maximum of ~ 1 ms) but represent a resolvable signal related to lateral (i.e. non-1D) velocity variations in the study area.

Close inspection of Figure 5.15a confirms that the data have been accurately picked in the crosscorrelation analysis. By examining the gathers at eye level and focusing on the wavelets (either at the 2nd crossing or along the peak) we determine that the dominant energy in the phase is flat. The only gather in which we observe any deviation is CDP 28185 between the offsets of 3 km and 4 km. This is due to the
Figure 5.14. (a) Histogram of the travel time residuals of the best traveltime picks. (b) 3D grid of the residuals with respect to the smoothed velocity depth models obtained from the best traveltime data (Figure 5.12) as a function of shot and offset. Localized regions of higher residuals are indicated A through D with black arrows.
Figure 5.15a. CDP gathers in which the offset traces have been time shifted to the best travelt ime picks. The residuals are also illustrated as the solid black line. These gathers correspond to region A in Figure 5.14.
presence of a large amplitude trough just below the BSR reflector. We note however that this does not seem to affect the picks since the magnitude of the residuals is on the same order of the residuals for CDP 28181 and CDP 28188, in which the trough is also present but does not interfere with the BSR reflection event.

Examination of Figure 5.15b in the same manner also confirms the accuracy of the automated picker. The amplitudes of these reflection events are the largest of the gathers we discuss in this section. Analysis of the gathers indicates the presence of a fast arrival below the BSR that interferes with the BSR reflection event at far offsets (> 4.5 km) in gathers 28432 and 28433 and shifts the traces slightly. This does not contribute in any way to the residuals, as more significant signal is concentrated between 0.5 km and 4.5 km and is much less noticeable at offsets > 4.5 km. The incoming phase below the BSR is also apparent in CDP 28438, which is flat and has roughly the same residual features.

The largest negative residuals we observe are associated with the gathers illustrated in Figure 5.15c. Similar to the previous gathers in Figure 5.15b there is fast arrival below the BSR that interferes with the BSR reflection event at far offsets in gathers 28530, 28534 and 28536. However, the fast arriving phase does not affect the BSR reflections as is evident from their flatness.

The second largest positive residuals in the grid correspond to the gathers in Figure 5.15d. At first glance we observe the presence of an arriving phase above the BSR that interferes with the BSR event at offsets > 2.5 km. We do not believe that this interference impacts the data in any significant way since the BSR reflections are predominantly flat. The only deviation from flatness occurs in CDP 28652 where there is
Figure 5.15b. CDP gathers in which the offset traces have been time shifted to the best travelttime picks. The residuals are also illustrated as the solid black line. These gathers correspond to region B in Figure 5.14.
Figure 5.15c. CDP gathers in which the offset traces have been time shifted to the best travelt ime picks. The residuals are also illustrated as the solid black line. These gathers correspond to region, C in Figure 5.14.
Figure 5.15d. CDP gathers in which the offset traces have been time shifted to the best traveltine picks. The residuals are also illustrated as the solid black line. These gathers correspond to region, D in Figure 5.14.
a slight shift in the BSR reflection at very far offsets. Since the waveforms all exhibit the same pattern from CDP to CDP, and we do not observe a similar shift in CDPs 28654 and 28659 and observe the same residual patterns in all three gathers, we conclude that the data are reliable.

5.6. Tomographic Analysis

The goal of this study is to determine whether velocity contrasts associated with concentrated hydrate along faults exist in the Blake Ridge sediments around Site 997. Based on the previous reflection synthetic modeling study in which we determined that concentrated hydrate along faults can give rise to a signal in traveltime data that can be resolved using seismic reflection methods, and the analysis of the residual patterns of the data that indicate the presence of such a signal, we conduct a tomographic analysis to image the velocity structure of the faulted sediments at Site 997. We apply the traveltime tomography code developed by Van Avendonk et al. (1998) to invert wide-angle BSR reflection traveltimes for a best-fitting velocity model.

5.6.1. Inversion

Tomographic travel-time inversion generally involves two main procedures: ray tracing and linearized inversion. Ray tracing is accomplished using the shortest path method of Moser (1991) to find the approximate ray paths and the ray bending routine developed by Van Avendonk (1998) to optimize the calculated traveltimes. Traveltimes are summed up along a trajectory from each shot location to discrete nodal points in a grid of the slowness model. The trajectory of the rays is constrained by the average
slowness of the grid cell through which it travels and the requirement that the ray traverse the shortest path along the grid. The rays travel from one node to the next (each node acts as a point scatterer) starting at the source and ending at a reflection point, similarly rays are propagated back up from the reflection point to the receiver. That is, the rays constitute the shortest path in a particular layer from a point source to a reflection point and reflection point to receiver that satisfies the law of incidence and reflection. The predicted traveltimes in the inversion, which are a function of the raypaths, are further optimized using a ray bending technique that minimizes the traveltimes using a conjugate gradient search method (Van Avendonk, 1998).

The first step of the inversion is to determine the traveltime residuals, \( \delta T_i \), which can be related to the "model required" slowness perturbation \( \delta u \) through the equation:

\[
\delta T_i = \sum \delta u \, ds ,
\]

(5.6)

where \( ds \) is the distance over which the ray travels. The traveltime residual equation has the form:

\[
d = A \delta m ,
\]

(5.7)

where \( d \) is a vector matrix of the traveltime residuals scaled to the errors in traveltime picks (1 ms – \( \frac{1}{2} \) sample rate), \( \delta m \) (model parameters) is the slowness perturbation normalized to the slowness in the reference model, and \( A \) is the data kernel. The least squares solution to equation (5.2) is:

\[
\delta m = [ A^T A ]^{-1} A^T d ,
\]

(5.8)

and will minimize the functional:

\[
\| A \delta m - d \|^2 .
\]

(5.9)
Further constraints are imposed on the problem to ensure that we obtain a unique solution since many \( \delta m \) will fit the data. To ensure that slowness perturbations in cells not sampled by rays go to zero and that slowness anomalies are equally weighted in cells sampled by the same rays, Van Avendonk et al. (1998) apply a roughness penalty that minimizes the length of the first derivative of the seismic structure (i.e. variation in slowness as a function of \( x \) and \( z \)). The roughness penalty must be minimized in addition to fitting a weighted combination of the data misfit and smoothness constraints to determine a unique solution. The least squares solution to the problem will now minimize:

\[
[A \delta m - d] + \lambda R (m + \delta m) \],

(5.10)

where \( m + \delta m \) is the new slowness model, \( R \) is a linear roughening operator, and \( \lambda \) is a smoothing weight. The term on the right represents the data misfit and the term on the left represents the smoothness constraints. The smoothing weight, \( \lambda \), which controls the trade-off between misfit and model roughness is calculated during the inversion and depends on the \( \chi^2 \) that we specify:

\[
\chi^2 = \frac{1}{N} \sum_{i=1}^{N} \left[ \frac{t_o - t_p}{\sigma_o} \right]^2,

(5.11)

where \( \sigma \) is the standard deviation (standard error) of the traveltime pick, \( n, N \) is the number of traveltime data, and \( t_o \) and \( t_p \) are the observed (picked times) and predicted times (graphed times) respectively.

After specifying the traveltime data we will invert for, and a reference/starting velocity model, we trace rays through the reference velocity model to determine the traveltime residuals with respect to the starting velocity model. We then run the
inversion scheme. This entails an iterative process in which perturbations, regulated by the smoothness constraints and roughness penalties that must be minimized to arrive at a solution, are sequentially applied to the reference velocity model until the $\chi^2$ for the new model matches our target value.

5.6.2. Model parameterization

The reference model we adopt is based on the seismic velocities determined for the drill hole at Site 997 from the inversion of VSP data (Holbrook et al., 1996; Figure 2.6 of this dissertation). Within the GHZ seismic velocities increase from $\sim 1.55$ km s$^{-1}$ at 150 mbsf to 1.85 km s$^{-1}$ at 450 mbsf. Using a starting velocity model that reflected these velocities we obtained travel time residuals that indicated the starting model velocities were consistently lower than that predicted by the travel time data. In order to reduce the number of iterations during the inversion process we increased the seismic velocities by maintaining the observed velocity gradient. The starting velocity model we adopt is depicted in Figure 5.16.

The model is sampled by a grid 380 x 400 grid with equal horizontal and vertical grid spacings of 10m. To generate the most accurate rays we oversample the velocity grid so that the graph cells in which the travel times are calculated are 5 m wide and 10 m long, since our ray paths are sub-vertical and travel a further distance vertically than horizontally within any cell. In determining the best ray paths we employ a search criterion that extends seven grid points vertically, and three horizontally (i.e. for a ray propagated at any node we search through all neighboring grid points within a 3 x 7 nodal
Figure 5.16. Starting velocity profile used in the tomographic inversion.
point box for the best ray). The water velocities are constrained \textit{a priori} by the average velocity we determined in Section 5.5.5.

5.6.3. Travel time residuals

The travel time residuals with respect to the reference shows two peaks (Figure 5.17). The negative residuals are due to misfit in the data at near offset traces, implying that the velocities in the starting model are too low or the BSR is too deep. The positive residuals are due to misfit at far offsets, implying that the velocity gradient of the starting model is too high since the larger offset rays are more sensitive to velocity perturbations. The normalized $\chi^2$ associated with our starting model is 120.8 and the mean travel time residual is 6 ms.

After 1000 iterations of the inversion scheme the mean travel time residual is 2.6 ms and the normalized $\chi^2$ is $\sim 1.15$. This represents a significant variance reduction in the data ($\sim 99\%$). Although we obtained a solution that fit the data and satisfies our acceptable level of misfit, there is still structure in the residuals that is not randomly distributed, indicating that the inversion did not yield an unbiased model (Figure 5.18). There are systematic features that should not be present after successful inversion. This may be due to systematic errors in the traveltime data, systematic errors in the inversion, or problems with the starting model. We are confident that the data are accurate and represents the velocity structure of the Blake Ridge gas hydrate sediments based on the rigorous analysis undertaken in this study. We therefore conclude that the problem must reside in either the starting model we adopt or difficulties with the inversion itself. These
Figure 5.17. (a) Histogram of the travel time residuals with respect to the starting model used in the inversions. (b) 3D grid of the residuals with respect to velocity depth model in Figure 5.16 as a function of shot and offset.
Figure 5.18. (a) Histogram of the travel time residuals with respect to the best fit model obtained from the inversion. (b) 3D grid of the residuals with respect to the best fit velocity model as a function of shot and offset.
residuals should therefore be regarded with some skepticism. Nevertheless we proceed with our analysis and describe the best velocity model we arrive at after inversion.

5.6.4. Velocity model

The results of the tomographic inversion are presented as the difference between the velocities of the reference velocity model and the best fit velocity model (Figure 5.19). The model contains lateral and vertical velocity contrasts in the GHZ that vary between ± 0.03 km s⁻¹ with respect to the reference model. We observe multiple regions of localized positive velocity anomalies with respect to the reference model along and adjacent to faults in the GHZ.

The anomalies in many cases are aligned with the faults. This is expected given that wide-angle reflection rays, which are most sensitive to velocity, have a similar orientation as the faults, which are abundant and will yield positive velocity anomalies if the hypothesis that concentrated hydrate may be present along faults is correct. We therefore examine the velocity anomalies associated with two of the faults in which we see similar alignment between the anomaly and a fault.

The first fault we examine is immediately right of Site 997 at Model-km 7.0 (where Model-km 7.0 refers to the absolute lateral position in the model domain) and intersects the Model-km 7.0 line at 300 mbsf (Figure 5.19). Figure (5.20) is a plot of velocity as a function of depth in the GHZ across the fault. In (a) the velocity profile is 10 m down dip of the middle of the fault (Model-km 6.99) and in (b) 10 m up dip (Model-km 7.01); i.e. (a) and (b) are spaced 20 m apart. We observe lower velocities in the sediments just above the fault in (a) and higher velocities just deeper than the fault,
Figure 5.19. Depth-migrated, stacked section of our study area in conjunction with the velocity anomalies estimated from the inversion. The seafloor and BSR reflectors are present at depths of 2.77 km and 3.22 km respectively. The solid black lines mark steeply-dipping (45°) faults that extend from just below seafloor through the BSR.
Figure 5.20. Velocity profile across a fault at Model-km 7.0 in Figure 5.19. (a) Slice through the fault down dip of its point of intersection with maker Model-km 7.0. (b) Slice through the fault up dip of its point of intersection with maker Model-km 7.0.
and the opposite trend for (b). We might expect these results for the case in which hydrate is deposited on the hanging wall of the fault mainly from fluids (1) migrating along the fault and diffusing laterally into the adjacent porous sediments and (2) fluids migrating upwards in the porous sediments and at the footwall from fluids migrating upwards into the sediments from the fault.

The velocity profiles for the fault located between Model-km 5.88 and Model-km 8.79 are depicted in Figure 5.21. The velocity anomalies associated with this fault are the largest we observe in the data. The Model-km 8.88 mark does not intersect the fault but lies at the boundary between high velocities to the left and low velocities to the right of the fault. The Model-km 8.79 mark intersects the fault at 295 mbsf. We observe a relatively high positive anomaly that spans ~ 90 m laterally.

In addition to the velocity anomalies we observe well within the model domain, we also observe regions of significant residuals at the model boundaries. At the western boundary of the model domain the tomography code systematically decreases the velocities and we obtain anomalously low velocity zones at the BGHZ where the velocities are known to be higher. At the opposite boundary, we observe the opposite effect. The inversion code may therefore not be applying suitable constraints at the model boundaries.

5.6.5 Estimates of hydrate concentration

On the supposition that the velocity contrasts we observe well within the model domain are due to the presence of hydrate in faults, we estimate the concentration of hydrate that may be associated with the velocities we estimate for the hydrated sediments
Figure 5.21. Velocity profile across a fault at Model-km 8.8 in Figure 5.19. (a) Slice through the fault downdip of its point of intersection with marker Model-km 8.8. (b) Slice 8 m away from the Model-km 8.8 marker.
at the Blake Ridge using the formulation of Lee (2000). The model is based on a weighted combination of the time-average equation (Timur, 1968) and the Wood equation (Wood, 1941). The time-average equation predicts the velocities in a consolidated medium in which little fluid is present. The Wood equation accounts for the presence of the fluid phase and considers particles in suspension.

Based on the difference in seismic velocities across the 20 m interval between Model-km 6.99 and Model-km 7.01 we estimate that the concentration of hydrate across the fault varies from by as much as 1% at the sediments along the footwall of the fault and as much as 1.5% at the hanging wall of the fault (Figure 5.22). At Model-km 8.79 km we obtain a profile of the hydrate saturation as a function of depth along a fault that intersects the plane of Model-km 8.79 at 2.9 km depth in the GHZ (Figure 5.23). The result indicate hydrate concentrations that increase from 5% at ~50 mbsf to 32% at the base of the gas hydrate zone. These estimates are in good agreement with values obtained by Lee (2000) for the sediments at Site 997 using acoustic logs.

5.7. Discussion

The focus of this study is the seismic characterization of the hydrated sediments on the Blake Ridge in the vicinity of Site 997. Based on traveltine data for the seafloor and BSR reflectors we developed velocity depth models of the water column and GHZ using the 1D traveltine equations assuming a constant velocity in the water column and a linear velocity gradient in the GHZ. The velocity models show a long wavelength distribution that reflects lateral velocity structure in the GHZ. This is demonstrated by the trend of decreasing velocity gradients in the GHZ (Figures 5.7, 5.9 and 5.12) from
Figure 5.22. Percent variation of hydrate concentration across a fault in the CHZ as a function of depth. The variation is determined over a lateral span of 20 m. The zero line corresponds to the fault axis.
Figure 5.23. Hydrate saturation as a function of depth in the GHZ across a fault.
west to east or upslope to downslope on the Ridge. Similar results have been observed in previous studies; Paull et al. (1996) and Holbrook (2001) have observed increased seismic velocities in the GHZ toward the ridge crest. The results of the tomographic inversion, while not convincing, possibly indicate that there are lateral variations in seismic velocities that are associated with faults. The velocity anomalies in many cases are aligned in the same sense as the faults. In some cases this may indicate that a large number of the rays travel through the model domain at limited trajectories and sample the grid cells with the same geometry. This can sometimes produce smearing in the grid in the direction of the rays. However we note that is not likely to be the case in our data set since each CDP gather constitutes rays that are reflected to and from the BSR at offset ranging from ~ 0.5 km to 5.5 km. Based on our level of confidence in the traveltime data for the BSR reflection we conclude that the sources of error are either systematic (i.e. the continual overprediction of traveltimes at the western boundary of the model domain and under prediction of traveltimes at the eastern edge) or due to inappropriate starting velocity model. We believe that by addressing both these issues we can determine an accurate velocity model that is characterized by randomly distributed residuals.

While the inversion did not yield any concrete results relating velocity anomalies to hydrate concentration variations in the GHZ, we have demonstrated the utility of this analysis in characterizing some of the features that may be present in these natural reservoirs. If we assume some level of confidence in the inversion, we are able to estimate that the velocity anomalies we observe across a fault (on the order of 0.02 km/s to 0.03 km/s) in the GHZ may be as a result of variations in hydrate concentration of
~1.0% to 1.5%. In addition we estimate that the hydrate concentration along a fault in
varies from 5% at the TGHZ to 32% at the BGHZ.

5.8. Conclusions

The main objective of this study was to determine whether seismic velocity
anomalies associated with the presence of concentrated hydrate along faults exist in the
GHZ on the Blake Ridge. Ancillary goals were to determine whether (1) hydrate
deposited along faults could be seismically resolved and (2) our Blake Ridge data set
showed any evidence of traveltime anomalies associated with hydrate along faults in the
GHZ. The major conclusions emerging from our study include:

1. Based on the results of reflection synthetics we determine that increased seismic
velocities correlated with the presence of concentrated hydrate deposited along
faults can be detected using seismic reflection methods.

2. Traveltime anomalies in the Blake Ridge data set are indicative of velocity
anomalies consistent with the presence of hydrate along faults in the GHZ.

3. The GHZ on the Blake Ridge in the vicinity of Site 997 is approximately 0.47 km
thick. This is in good agreement with previous estimates based on seismic data,
wireline logging and geochemical analysis (Paull et al., 1990). In addition, our
best fit velocity models indicate that the velocities at the base of the gas hydrate
zone are ~ 2 km s⁻¹. This is also in good agreement with previous seismic
velocity studies (Katzman et al., 1994; Korenaga et al., 1997; Hornbach et al.,
2003). The velocities in the GHZ show a general decrease in traversing from

172
upslope to downslope along the Ridge; a result also consistent with previous studies.

4. The results of the tomographic inversion suggest that lateral variations in seismic velocity may be attributable to the presence of concentrated hydrate along faults in the GHZ.
CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The main purpose of this dissertation is to characterize the accumulation and distribution of methane gas hydrate in marine sediments through the application and integration of numerical modeling and seismic data analysis. In this chapter we provide a summary of the key conclusions of the independent numerical and seismic studies and discuss some of the important links between the two. We conclude with an outline of recommendations for future work in applying the techniques used in this study.

6.1. Summary of conclusions

Reservoir characterization of marine gas hydrate deposits is of particular importance in assessing the economic potential of these deposits as an alternative energy source. Few studies however have so far been able to quantify the size of these worldwide reservoirs. This dissertation attempted to address this shortcoming through the joint application of numerical and geophysical techniques. Specifically we predicted the concentration of methane gas hydrate in a one-dimensional system using numerical modeling and quantified gas hydrate concentrations in a real marine system using seismic data. In addition to integrating numerical and seismic methods, the innovations of this work include: evaluating the time scales over which permeability clogging occurs in marine gas hydrate reservoirs and linking permeability evolution to changes in the hydraulic and thermal regime of the gas hydrate zone (Chapter 3); quantifying the concentration of methane gas hydrate in worldwide marine gas hydrate reservoirs.
(Chapter 4); constraining local seismic velocity variations in a gas hydrate reservoir associated with regions of concentrated hydrate.

6.1.1. Dynamics of a gas hydrate reservoir

Chapters 3 through 5 contribute to our understanding of the dynamics of a marine gas hydrate reservoir and its dependence on the hydrologic and physical properties of the sediments in which they form.

1. Permeability clogging in a fracture or porous medium occurs fastest at the base of the gas hydrate zone and the reduction rates for permeability, fluid flux, and fracture or pore apertures continue to decrease until the base of the GHZ is sealed. Permeability seals may therefore develop at the base of the gas hydrate zone, preventing the migration of gas and pore fluids.

2. Hydrate accumulation and permeability clogging generally occur faster in a porous medium characterized by pore dimensions typical of fine-grained sediments (<1 μm pore diameter) than in fractures of similar dimensions. In addition, our results indicate that flow in hydrate reservoirs is likely to be sustained much longer in fractures than in the surrounding porous aggregate.

3. The rate of hydrate accumulation is primarily a function of fluid flux; however, the physical (e.g. pore and grain sizes) and hydrodynamic and thermal properties (e.g. energy flux, seafloor temperature and pressure) of the gas hydrate reservoir also play an important role in the development of these deposits.
6.1.2. Gas hydrate concentration in natural marine reservoirs

1. As shown by earlier work, our research confirms that concentrated hydrate deposits are associated with high flux environments; however, even in low flux systems concentrated deposits may develop if other conditions, such as high seafloor pressures exist[4].

2. The timescales over which methane gas hydrate deposits accumulate to between 10 and 30% of porosity for the sediment characteristics we tested and under conditions characteristic of many worldwide marine reservoirs are \( \sim 10^4 \) to \( 10^5 \) years. These accumulation times may be reduced for gas hydrate systems dominated by more rapid fluid flux and methane supply or with significant in situ production of methane (i.e., within the GHZ).

3. Owing to the large generation times predicted for existing gas hydrate reservoirs, it is unlikely that these deposits can be considered a renewable resource.

4. Seismic velocity anomalies on the order of 0.03 km s\(^{-1}\) may be attributable to increased local concentrations of hydrate along faults on the order of 5 \% when compared to hydrate concentration in adjacent porous media.

6.2. Recommendations for future work

6.2.1. Numerical modeling

As modeled in this study, the gas hydrate system provides a simplified representation of the complex processes that occur in the porous sediments of gas hydrate reservoirs. Several unknowns make the accurate description of these systems difficult. Among these are:
1. What is the exact mechanism of nucleation of gas hydrate in porous assemblages?

2. What are the reaction kinetics involved in the gas hydrate—free gas—dissolved gas+seawater system and how is the system partitioned?

3. How do sediment matrix surface properties affect hydrate phase equilibria and hydrate nucleation?

4. What are realistic fluid and methane flux rates for natural systems and how can the heterogeneity of these systems be accounted for?

5. What are the geochemical and geophysical properties of in situ gas hydrate?

While the questions above remain unanswered, there are areas in which the numerical model presented in this dissertation may be further developed to more adequately simulate and predict the accumulation and distribution of gas hydrate in porous marine sediments.

The model described here (Chapter 3) is one-dimensional with methane-laden fluid supplied from below the base of the gas hydrate zone at an ascribed rate. In Chapters 3 and 4 we demonstrated that through the model we are able to obtain results that show good agreement with estimates of hydrate concentration based on geophysical and geochemical methods. In the future, a more adequate representation of the hydrodynamic regime in a natural gas hydrate reservoir will require a two- or three-dimensional formulation in which both vertical and lateral flow components are incorporated. Such an approach should account for various fluid flow pathways, including those related to variations in sediment lithology and to heterogeneous distribution of faults.

177
To some extent the evolution of the gas hydrate reservoir as described in this numerical model is static. That is, the relative positions of the top and base of the gas hydrate zone are assumed to be constant as permeability clogs the sediments altering the thermal and hydrodynamic regime. As we demonstrated in Chapters 3 and 4, the location of the gas hydrate zone, as well as the rate of formation of gas hydrate, is highly dependent on the fluid and energy fluxes in the system. As fluid and energy fluxes are modified due to permeability clogging, the position of the GHZ should also vary. The model may therefore be improved by incorporating time dependence to recalculate the position of the GHZ as the reservoir properties change. Accounting for such variations may provide explanations for observations such as paleo-BSR’s (Hornbach, 2003).

6.2.2. Seismic tomography

The results of the seismic analysis (Chapter 5) demonstrate the utility of this method in characterizing the distribution of gas hydrate in faulted marine sediments related to high flux pathways. In spite of the high quality of the seismic data and accuracy of the traveltime picks, the results of the tomographic inversion do not allow us to unequivocally correlate regions of increased seismic velocities in the gas hydrate sediments of the Blake Ridge to high flux or high permeability. However, we note that there is sufficient correlation to warrant further application of inversion techniques with more stringent roughness penalties and smoothness constraints.
REFERENCES


occurrence, distribution, and detection, C. K. Paull and W. P. Dillon (Eds.), AGU, Geophysical monograph 124, 235-256.


