Numerical models for the formation of marine gas hydrate: Constraints on methane supply from a comparison of observations and numerical models

by

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Abstract

Methane hydrate is a chemical compound composed of a rigid network of water molecules that enclose methane gas. Although this abundant form of hydrate is stable under pressure and temperature conditions present in seafloor sediments of most of the world’s oceans, hydrate occurrences are confined to regions where the concentration of methane is sufficient to exceed the local solubility. Consequently, marine hydrates are generally restricted to continental margins where conversion of high inputs of organic carbon or focusing of methane bearing fluids supply the methane required for hydrate formation. Empirical extrapolation of hydrate volumes from known locations to all continental margins yields a methane abundance which exceeds all other fossil fuel resources combined. Consequently, methane hydrates have generated interest in their potential use as an energy resource and as a mechanism for climate change. However, fundamental questions about marine hydrate remain unresolved. Specifically, the source of the methane and the mechanism of methane supply required for hydrate formation is not well known. A better understanding of the source and mechanism of methane supply would help to refine global estimates and identify regions of high hydrate potential. In this thesis, I address these issues by developing numerical models for the formation of marine gas hydrate and comparing the predictions with observations from known hydrate locations.

I first develop a time-dependent model to account for the important processes during hydrate formation in marine sediments. The model predicts the methane and chlorine concentration in the pore water, organic carbon available for methanogenesis, hydrate and free gas volumes, and interstitial fluid velocity. Application of the hydrate model to both the
Blake Ridge and Cascadia margin allows for a quantitative appraisal of the mechanisms of the methane supply. I find that observations of chlorinity, hydrate and free gas from both the Blake Ridge and Cascadia margin can be explained equally well by either migration of methane bearing fluids from deep sources or in situ biogenic production of methane in the shallow sediments. In particular, observations at the Blake Ridge are reproduced by either a saturated deep source of methane migrating upward at 0.26 mm/yr or in situ production of methane requiring 50% conversion of organic carbon along with an upward fluid velocity of 0.08 mm/yr. In a similar manner, the chlorinity data at the Cascadia margin can be explained by either a saturated deep source of methane with an upward fluid velocity of 0.42 mm/yr or in situ production of methane together with an upward fluid velocity of 0.35 mm/yr. As a result, additional model constraints are needed to differentiate between the two mechanisms of methane supply.

Measurements of sulfate concentration provide an additional constraint on the source of methane because sulfate measurements can be related to the methane concentration in the pore water. To exploit the sulfate measurements I develop a steady state model to describe the formation of marine hydrate, which includes a thin sulfate reducing zone. Constraints imposed by sulfate and chlorine measurements at the Blake Ridge favour in situ methane production (located in the lower part of the HSZ) together with an incoming methane bearing fluid at 0.23 mm/yr. Comparison of model predictions with observations at the Cascadia margin requires a shallow in situ methane source together with a deep methane bearing fluid migrating upward at a velocity of 0.36 mm/yr. The volume of hydrate predicted at the Cascadia margin is substantially smaller than previous estimates from seismic velocity and resistivity modelling, but agrees well with hydrate estimates from drill core temperature measurements. In addition, the predicted sulfate profiles at both the Blake Ridge and Cascadia margin indicate that the process of anaerobic methane oxidation is the primary pathway of sulfate depletion at these locations of hydrate occurrence.
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This thesis is dedicated to my wife Chanelle.
CHAPTER 1

Introduction

Large volumes of methane are sequestered in marine sediments along deep continental margins by an icy solid known as gas hydrate. Gas hydrates belong to a unique class of chemical compounds known as clathrates, which are characterized by an open network of host molecules that enclose (without direct bonding) appropriately sized guest molecules of another substance [NETL, 2002]. Gas hydrate refers to a particular clathrate where hydrogen bonded water molecules form a rigid lattice network around guest gas molecules. In nature this gas is dominantly methane, although heavier hydrocarbons, CO₂, and hydrogen sulfide may also fill the cavities. A complete discussion of gas hydrate thermodynamics and kinetics can be found in Sloan [1998], while more geologically focused reviews can be found in Buffett [2000] or Kvenvolden [1993]. The large volumes of methane stored in natural gas hydrate has generated interest for its potential use as an energy resource, mechanism of climate change, and geohazard. This significant interest prompted US congress to introduce the Methane Hydrate Research and Development Act, which was signed by President Clinton on May 4, 2000.
1.1 History of Gas Hydrates

Clathrates were first discovered by Humphrey Davy when he observed a solid forming at temperatures above the freezing point of water during cooling experiments of chlorine-water mixtures [Davy, 1811]. During the remainder of the 19th century, scientists began to catalogue various clathrate types (i.e. host/guest molecules) and their associated thermodynamic properties under laboratory conditions. However, until the discovery of natural occurring hydrates, these compounds remained primarily a laboratory curiosity.

Interest in gas hydrates was renewed during the 1930’s when they were found to plug natural gas pipelines [Hammerschmidt, 1934]. Research was initiated to investigate the formation and stability of hydrates, with the primary focus of developing chemical additives to prevent the formation of hydrates in pipelines. This area of research is still of great interest because conditions in deep sea pipelines and Arctic permafrost fall within the stability field of gas hydrates.

The first natural occurrence of gas hydrate was reported in the late 1960’s when hydrates were discovered in the Western Siberian gas fields of Russia. Further discovery of hydrates under permafrost regions on the North Slope of Alaska led scientists to speculate that conditions for hydrate stability should exist globally, both on continents and below the seafloor. Marine hydrates were first inferred by the presence of a bottom-simulating reflection (BSR) on marine seismic profiles [Stoll et al., 1971]. Leg 11 of the Deep Sea Drilling Program on the Blake-Bahama Outer Ridge was the first to test the origin of this anomalous reflection by drilling through a BSR. Although no hydrate samples were recovered, drilling results and the cross-cutting nature of the BSR suggested that the BSR marked the base of hydrate stability [Stoll et al., 1971]. The first recovery of marine hydrate was reported in 1974 by Soviet scientists who recovered large hydrate nodules from the Black Sea. Since then, numerous studies have recovered hydrate samples or inferred their presence (through seismic surveys) around the world in both marine and continental settings (see Figure 1.1).
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Figure 1.1: Map showing the locations of known and inferred gas hydrate. The circles represent marine hydrate locations while the triangles denote continental (permafrost) occurrences. Locations referenced in this thesis include the (1) Blake Ridge, (2) Cascadia margin, (3) Peruvian margin, and (4) Chile Triple Junction. Adapted from Buffett [2000].

1.2 Energy, Climate Change and Geohazards

One cubic metre of solid methane hydrate at conditions characteristic of the continental margin seafloor yields 164 m$^3$ of methane gas upon dissociation at atmospheric pressure and temperature. This capacity to store large volumes of methane has attracted interest for the use of gas hydrates as an energy resource. Extrapolation of known hydrate locations (see Figure 1.1) over global oceans has produced estimates of the methane carbon stored in hydrate that range between $2 - 4000 \times 10^{15}$ kg. Conservative estimates, $10 \times 10^{15}$ kg [Kvenvolden, 1988] and $11.4 \times 10^{15}$ kg [MacDonald, 1990], are over a factor of 2 greater than the carbon present in all known coal, oil, and natural gas deposits (Figure 1.2) [Kvenvolden, 1993]. A major obstacle that prevents the exploitation of this energy resource is the absence of a viable economic method for the recovery of deep sea gas hydrates. Recent success of hydrate recovery in permafrost regions of the Canadian Arctic [Dallimore et al., 2002] may provide a foundation for the beginning of economic hydrate recovery.
The large volumes of hydrate in the shallow geosphere have led to speculation that gas hydrates may play an important role in global climate change since methane is a strong greenhouse gas [Shine et al., 1990]. Methane released from hydrate into the atmosphere would increase the atmospheric temperature; leading to further dissociation of hydrate and thus providing a positive feedback mechanism for global warming. Marine hydrates have been implicated in limiting the extent of glaciation due to de-stabilization of oceanic hydrates in response to the sea level drop associated with ice sheet growth [Paull et al., 1991]. Additional studies have examined the effects of seafloor warming as a release mechanism for methane from hydrate during the late Paleocene thermal maximum [Dickens et al., 1997] and Quaternary ice ages [Kennett et al., 2000]. Some concerns with these studies are the timescales and transfer mechanism necessary for the methane trapped within the seafloor sediments to be transferred to the overlying ocean and subsequently to the atmosphere. A mechanism involving slope instability and submarine landslides [Paull et al., 2002; Dickens, 2001a] provides a plausible pathway for the transfer of methane from deep sea hydrates to
CHAPTER 1. INTRODUCTION

the atmosphere. An alternative explanation of the role of hydrates in climate change involves the dissociation of hydrate trapped beneath ice sheets. Nisbet [1990] presents a conceptual model whereby the release of methane from hydrates beneath the ice sheets contributes to the increase in atmospheric methane, associated atmospheric warming, and rapid retreat of the ice sheets. Recent work by Weitemeyer and Buffett [2002] provides quantitative support for this theory by modelling the mass balance of continental carbon for hydrate formation during glacial cycles.

Dissociation of gas hydrate has also been associated with submarine landslides. Seafloor warming or decreased sealevel could result in the dissociation of solid hydrate to a gas-water mixture at the base of the hydrate stability zone, causing the sediments to be underconsolidated. This underconsolidation could create a zone of weak sediments (low shear strength) that may fail due to gravitational loading or seismic disturbances [Kvenvolden, 1993]. Such failure would result in submarine debris flows, slumps or slides that could release large volumes of methane to the overlying oceans. Reports of submarine landslides that coincide with gas hydrate occurrences have been reported world-wide [Bugge et al., 1987; Carpenter, 1981; Kayen and Lee, 1991], and are summarized in Henriet and Mienert [1998]. As a local geohazard, hydrate stability during drilling is a major concern in petroleum exploration. The heat generated by drilling through a hydrate reservoir can potentially lead to the dissociation of large volumes of hydrate and result in uncontrolled gas releases (including blowouts), collapse of drill casing, or gas leakage to the surface outside the drill casing [Collett and Dal-limore, 2002]. Therefore knowledge of the location and stability of gas hydrate occurrences is necessary to take the appropriate precautions (i.e. additives to drilling muds) in order to avoid these potentially fatal consequences.

Gas hydrates in the shallow geosphere are subject to a number of unanswered questions. An important unresolved issue is the source and mechanism of methane supply for marine gas hydrates. Although methane found in marine hydrate is dominantly biogenic in origin [Kvenvolden, 1995], the depth at which this methane is being produced (shallow vs. deep) and the mechanism of methane supply still remains unresolved. The supply of methane from
deep sources by upward fluid migration is favoured at accretionary margins [Hyndman and Davis, 1992], while the in situ production of methane in shallow sediments is suggested at passive margins [Claypool and Kaplan, 1974]. However, there remains a lack of quantitative evidence to support either of these hypotheses. In addition the large global hydrate estimates, which generate interest in hydrates as an energy resource and mechanism of climate change, are subject to large uncertainties because they represent empirical extrapolations from known locations. These estimates rely on the understanding of hydrates at a limited number of locations to generate these global volumes. However, the hydrate volumes at the limited known locations are also subject to uncertainty because the relationship between the elastic/physical properties of gas hydrate sediments and the interpretation of remote sensing techniques (e.g. recovered seismic velocities, resistivity models) are not well understood.

A method of addressing these issues is to use quantitative models to study the formation of marine hydrate. Quantitative models for hydrate formation can be linked to observable features of marine hydrate deposits (e.g. chlorine, sulfate profiles) and estimated volumes of hydrate and free gas. Consequently, model results can be compared with observable features at known hydrate locations to make inferences about the source and mechanism of methane supply. In addition, models provide a means of estimating the geographic distribution of hydrate if the required parameters are known. Parameters required by the model may include the fluid flow, organic matter accumulation, sedimentation rates, porosity, water depth, temperature at the seafloor, and geothermal gradient. Since many of these parameters are available in global databases, it is feasible to use numerical models to refine estimates of the global hydrate inventory.

1.3 Previous Modelling

Previous quantitative studies of hydrate formation in marine sediments can be grouped into two categories. One group deals primarily with hydrate accumulation when the supply of methane is prescribed. Rempel and Buffett [1997] obtained a convenient analytical expression
for the rate of hydrate formation when methane is transported into the hydrate stability zone by upward fluid migration. Subsequent work by Rempel and Buffett [1998] and Xu and Ruppel [1999] extended these calculations by allowing for the influences of methane diffusion through the pore fluid, as well as the presence of methane sources inside the stability zone. These calculations predict spatial distributions of hydrate accumulation which are similar in many respects to the profiles inferred at several ODP sites [Yuan et al., 1999]. In all of these models, however, the supply of methane is prescribed without regard for the source of carbon. As long as the methane supply is maintained in these calculations, hydrate can accumulate until most of the pore volume is filled. In contrast, indirect estimates of the average hydrate volume in most marine locations rarely exceed 10% to 20% of pore volume, so it is important to understand how the methane supply is regulated.

An alternative line of inquiry has dealt with the pore fluid chemistry. Egeberg and Barth [1999] used observations of Br\(^-\) and I\(^-\) ions together with a simple physical model based on species conservation to estimate the rate of fluid flow at the Blake Ridge. Subsequent work by Egeberg and Dickens [1999] used these flow estimates in a coupled model for pore fluid chlorinity and hydrate accumulation. Because this model did not account for the methane concentration in the pore fluid, it was not possible for the authors to evaluate the rate of hydrate production on thermodynamic grounds. Instead, the rate of hydrate production was imposed in their calculations. The rate of hydrate production was adjusted so that the predicted profile of Cl\(^-\) matched the observations at the Blake Ridge. In effect, Egeberg and Dickens [1999] were able to use the observed chlorinity profile to infer the rate of hydrate formation as a function of depth. However, this approach does not explain why hydrate production has the assumed spatial form or rate.

The model presented in this thesis differs from the previous work in several important respects. First, the concentration of dissolved methane in the pore fluid is explicitly modelled so that the rate of hydrate formation can be predicted in a thermodynamically consistent fashion. Second, a simple model for biological production of methane which depends on the available supply of organic carbon in the sediments is included. Conversion of organic
CHAPTER 1. INTRODUCTION

material to methane by bacteria gradually depletes the carbon supply with time and limits the production of methane. This component of the model links the methane supply to the rate at which organic material is added through sedimentation. In this way a testable connection is established between the geological conditions near the seafloor and the predicted characteristics of a hydrate occurrence. The model is tested using observations from the Blake Ridge and Cascadia margin (see Figure 1.1), where many of the model parameters are known, to investigate the influence of methane sources on the observable properties of hydrate deposits.

1.4 Description of Chapters

The thesis develops quantitative models describing the formation of hydrate below the seafloor. Model predictions are compared with observations from known hydrate locations to resolve the source of methane and mechanism of methane supply that prevails at these sites. The following is a short summary of the contents of each chapter in this thesis.

Chapter 1 presents a brief background discussion of gas hydrates. Quantitative models of hydrate formation are needed to resolve outstanding issues such as the source of methane, important processes that contribute to hydrate formation at different tectonic settings and their use in global hydrate inventory.

Chapter 2 presents a method of predicting the methane solubility in a marine setting for a given water depth, seafloor temperature, and geothermal gradient. An expression for the methane solubility at the base of the hydrate stability zone is presented based on the results of Zatsepina and Buffett [1997] and Zatsepina and Buffett [1998], while simple parametric models extend the solubility into and below the HSZ.

Chapter 3 develops a time-dependent model that describes the formation of hydrate in the marine environment. A conceptual model characterizing the physical conditions of the hydrate environment is transcribed to a set of governing equations describing the evolution and distribution of marine hydrate. Comparison of model results with drill core chlorinity
data from the Blake Ridge shows that the model can be applied successfully in a marine setting.

Chapter 4 uses the time-dependent model to assess the influence of methane supply on observable features of hydrate occurrences. Model predictions for the pore fluid chlorinity and the volumes of hydrate and free gas are compared with observations from the Blake Ridge and Cascadia margin to evaluate the importance of methane sources.

Chapter 5 develops a steady-state model to describe the formation of hydrate below the seafloor. The model incorporates the sulfate reducing zone, which allows sulfate measurements to be used in conjunction with chlorinity data to better constrain the mechanism of methane supply at hydrate locations. The steady state model is applied at the Blake Ridge and Cascadia margin to resolve the source of methane at these locations.

Chapter 6 summarizes the main conclusions of the thesis and outlines future modelling prospects.
Modelling of gas hydrate formation below the seafloor requires accurate estimates of the methane solubility in marine sediments. Although the methane solubility is relatively well-established, a practical method for calculating solubilities under marine conditions is currently unavailable in the literature. In this chapter, I present a method of predicting the solubility in a marine setting for a given water depth, seafloor temperature, and geothermal gradient. In this method, pressure and temperature conditions at the base of the hydrate stability zone (HSZ) are determined by finding the intersection of the local $P,T$ conditions with the experimentally determined conditions for three-phase equilibrium between water, hydrate, and free gas. Phase equilibrium calculations of Zatsepina and Buffett [1997] are used to predict the methane solubility at the base of the HSZ, while simple parametric models are used to extend the solubility into and below the HSZ. Depth profiles of methane solubility are computed at four known hydrate locations to provide constraints on the primary source of methane at these locales.
2.1 Background

Marine hydrates are restricted to locations where the necessary pressure and temperature conditions are met and where the abundance of methane is sufficient to exceed the local solubility [Kvenvolden, 1988]. Although pressure and temperature conditions are satisfied throughout most of the world's oceans, hydrate occurrences are generally restricted to continental margins where conversion of high inputs of organic carbon or focusing of methane bearing fluids supply the methane required for hydrate formation. The equilibrium methane concentration (or solubility) is important as it determines the minimum methane concentration needed for hydrate stability. In addition, the shape of the solubility profile through the top few hundred meters of marine sediments influences the distribution and volume of hydrate.

The hydrate stability zone (HSZ) extends from the seafloor to a depth where the local pressure and temperature conditions match the conditions for three-phase equilibrium between water, hydrate and free gas (Fig. 2.1). Only two phases are expected to coexist above and below the base of the HSZ. The abundance of water in marine settings ensures that water coexists with hydrate inside the HSZ, while water and free gas are the stable phases at depths below the HSZ. Several previous studies have obtained estimates of the methane solubility at conditions appropriate for natural hydrate settings. The experimental study of Culberson and McKetta [1951] measured the solubility of methane at conditions appropriate for the region below the HSZ, while Handa [1990] theoretically examined the influence of pressure on methane solubility inside the HSZ. Applying these results to marine hydrate occurrences indicates that the solubility within the HSZ decreases towards the seafloor [Rempel and Buffett, 1997]. A subsequent study by Zatsepina and Buffett [1997] used thermodynamic calculations to predict the methane solubility within and below the HSZ. This work was later extended to include the influence of salts [Zatsepina and Buffett, 1998]. More recent experimental work of Yang et al. [2001] and Servio and Englezos [2002] confirm the decrease in methane solubility towards the seafloor inside the HSZ.
Although the solubility of methane is now relatively well-established, a practical method of predicting the solubility under marine conditions is not presently available in the literature. In this chapter, a method of predicting the solubility in a marine setting is presented. The base of the hydrate stability zone (HSZ) is defined by the temperature $T_S(P)$ for three-phase equilibrium between water, hydrate and free gas. Locating the base of the HSZ is done by finding the intersection of the local geotherm with the phase boundary at $T_S(P)$. The methane solubility is evaluated at the conditions of three-phase equilibrium using the phase equilibrium predictions of Zatsepina and Buffett [1997]. The solubility is then extended into the region within and below the HSZ using simple parametric models that have been fit to the calculated solubilities.

2.2 Hydrate Stability Zone

The phase boundary for methane hydrate has been determined experimentally for both pure water [Sloan, 1990] and seawater [Dickens and Quinby-Hunt, 1994]. Intersection of the local geotherm with $T_S(P)$ defines the base of the HSZ (Fig. 2.1). At greater depths hydrate decomposes and releases large volumes of methane. This methane is incorporated into free gas, causing a large P-wave velocity contrast which is commonly observed as a bottom simulating reflector on marine seismic profiles [Stoll et al., 1971; Shipley and et al., 1979]. Good agreement is often found between experimental estimates of $T_S(P)$ and the observed $P,T$ conditions at the base of the HSZ from hydrate locations (Fig. 2.2). Pressure in marine settings is defined by the water depth while temperature is defined by both the seafloor temperature and the local geothermal gradient. By providing these parameters at a specific site, an estimate of the depth of the base of the HSZ can be made.

The depth below the seafloor, $z$, is converted to a corresponding pressure by assuming a hydrostatic relationship

$$P(z) = \rho_f g (H + z),$$

(2.1)

where $\rho_f$ is the density of seawater (1000 kg/m$^3$), $g$ is the gravitational acceleration (9.8
CHAPTER 2. METHANE SOLUBILITY

m/s²), and \( H \) is the water depth. Temperature in the sediments is expressed as a linear function of depth,

\[
T(z) = T(0) + Gz,
\]

where \( T(0) \) is the seafloor temperature and \( G \) is the local geothermal gradient. The theoretical base of the HSZ can be established by incrementally increasing \( z \) from the seafloor until \( T(z) \) intersects \( T_3(P) \). At each \( z \), \( T(z) \) is calculated using (2.2) and \( P(z) \) is evaluated using (2.1). The value of \( T_3(P) \) is determined using either an empirical formula [Brown and Bangs, 1995] or by interpolating experimental measurements [Sloan, 1990; Dickens and Quinby-Hunt, 1994]. When \( T(z) < T_3(P) \), the depth is incremented and the calculation is repeated until \( T(z) = T_3(P) \). The final \( T(z) \) and \( P \) defines the base of the HSZ.

2.3 Methane Solubility Profile

A practical method for determining methane solubility below the seafloor should rely on simple parametric equations to accurately reproduce the solubilities obtained from thermodynamic calculations or experiments. The thermodynamic predictions of Zatsepina and Buffett [1997] are used to determine the methane solubility in two steps. First the solubility is approximated at the conditions of three-phase equilibrium. Next, this solubility is extended into the HSZ using simple parametric equations. The region below the HSZ is handled separately.

Figure 2.3 shows the thermodynamic predictions of methane solubility in pure water as a function of temperature for three values of pressure. The peak in the solubilities occurs at \( T_3(P) \), which coincides with the base of the HSZ. The solubility at \( T_3(P) \) can be represented as a linear function of temperature and pressure according to

\[
C_3(T, P) = C_3(T_o, P_o) + \frac{\partial C_3}{\partial T}(T - T_o) + \frac{\partial C_3}{\partial P}(P - P_o),
\]

where \( C_3(T_o, P_o) \) is the solubility in mM at a suitable reference temperature \( T_o \) and pres-
sure $P_0$. The partial derivatives $\partial C_3/\partial T$ and $\partial C_3/\partial P$ are estimated by fitting (2.3) to the solubilities listed in Table 2.1. The resulting values are

$$\frac{\partial C_3}{\partial T} = 6.34\text{ mM/K}, \quad \frac{\partial C_3}{\partial P} = 1.11\text{ mM/MPa}, \quad (2.4)$$

when the reference solubility is $C_3(T_0, P_0) = 156.36\text{ mM}$ at $T_0 = 292\text{ K}$ and $P_0 = 20\text{ MPa}$. Using (2.3) with the reference solubility and constants in (2.4) gives an accurate estimate of solubility at the base of the HSZ.

At temperatures lower than $T_3(P)$ (within the HSZ), water and hydrate are the stable phases. Because the compressibility of both water and hydrate is small, the solubility profile is relatively insensitive to pressure. In fact, the solubility can be accurately represented within the HSZ as an exponential function of temperature

$$c_{eq}(T) = C_3(T_3, P) \exp\left(\frac{T - T_3}{\alpha}\right), \quad (2.5)$$

where $C_3(T_3, P)$ is evaluated using (2.3) at conditions coinciding with the base of the HSZ and $\alpha = 14.4^\circ\text{C}$ is determined by fitting (2.5) to the theoretical values listed in Table 2.1. The solubility $c_{eq}(T)$ is written solely as a function of $T$ because the pressure dependence of $C_3$ refers to the base of the HSZ and not the pressure inside the HSZ where $c_{eq}(T)$ is being evaluated. A graphical comparison of the theoretical solubilities and the predictions of (2.5) is shown in Fig. 2.3. The good agreement confirms the accuracy of the simple representation in (2.5).

At temperatures above $T_3(P)$, water and free gas are the stable phases. In this case, the solubility profile is a function of both the temperature and pressure because free gas is highly compressible. An increase in depth $z$ causes an increase in both pressure and temperature according to (2.1) and (2.2). From Fig. 2.3, we see that increases in pressure and temperature affect the solubility below the HSZ in opposite ways. Increased pressure causes an increase in solubility, while an increase in temperature causes a decrease in solubility. At conditions representative of natural hydrate settings, equilibrium calculations show that the solubility
is relatively constant for depths below the HSZ due to counteracting effects of pressure and temperature (see Fig. 3 of Zatsepina and Buffett [1997]). Consequently, we approximate the solubility profile below the HSZ as

$$c_{eq}(z) = c_{eq}(T_3).$$

(2.6)

More accurate approximations can be obtained by interpolating between the values listed in Table 2.1.

The variations in methane solubility with depth can now be calculated at a marine setting using the water depth, seafloor temperature, and geothermal gradient. The thermodynamic conditions \((P, T)\) and depth at the base of the HSZ are determined iteratively using estimates for \(T_3(P)\). The solubility at three-phase equilibrium is then calculated using (2.3) with the constants in (2.4). Finally, the solubilities in the two-phase regions are calculated using (2.5) within the HSZ and (2.6) below. The profile of solubility within the HSZ can be expressed as a function of depth by converting the temperature to depth according to (2.2).

### 2.4 Influence of Salt

The presence of salts in seawater shifts the base of the HSZ zone to shallower depths and causes a small reduction in the solubility of methane. Estimates for the change in \(T_3(P)\) have been given by Dickens and Quinby-Hunt [1994], and these results are incorporated into the empirical formula of Brown and Bangs [1995]. Fig. 2.1 shows the predicted stability curve for a typical concentration of salts in seawater. Changes in methane solubility have been calculated by Zatsepina and Buffett [1998] using a 0.6 molality solution of NaCl in water as an approximation for seawater. Their calculation for \(C_3\) indicates a linear dependence on the concentration of salt \(S\), so we account for the influence of salt using

$$C_3(T, P, S) = (1 - \beta S) C_3(T, P, 0),$$

(2.7)
where \( C_3(T, P, 0) \) is calculated from (2.3) and \( \beta = 0.1 \) is determined from the results of Zatsepina and Buffett [1998].

Changes in methane solubility within the HSZ have a more complicated dependence on \( S \). Calculations for a 0.6 molality solution of NaCl predicts a reduction in the solubility, but most of this reduction relative to pure water occurs as \( S \) is increased from \( S = 0 \) to \( S = 0.1 \) molality (see Fig. 5 of Zatsepina and Buffett [1998]). Further increases in \( S \) cause a very small increase in \( c_{eq} \), although the rate of increase is so small that the overall reduction in \( c_{eq} \) (above \( S = 0.1 \) molality) is nearly independent of \( S \). The temperature dependence of \( c_{eq} \) in seawater is accurately described by (2.5) within the HSZ, so the procedure described in the previous section for pure water is readily extended to account for the influence of salt. First the base of the HSZ is determined using the stability curve for seawater. The solubility at three-phase equilibrium is then calculated using (2.7). This value is extended into the HSZ using (2.5). (A fit of (2.5) to the solubilities calculated in saltwater yields \( \alpha = 14.5 \), which is nearly identical to the value in pure water). Finally, equation (2.6) is used to determine the solubilities immediately below the stability zone.

2.5 Discussion

The solubility defines the minimum methane concentration that is necessary to form hydrate. This concentration of methane must be established and maintained by conversion of organic matter in hydrate bearing sediments, so higher solubilities imply higher requirements for conversion of organic matter. Additional insight into the methane production is obtained from the slope of the solubility profile within the HSZ. The slope of the solubility profile fixes the rate of methane loss by diffusion towards the seafloor and provides a lower bound on the rate of methane supply. An examination of solubility profiles at specific hydrate locations allows us to speculate about the mechanism of methane supply which prevails at these sites. As an example, I consider four known hydrate locations (see Figure 1.1), namely the Blake Ridge, Peru Margin, Cascadia Margin and Chile Triple Junction using solubility profiles that
have been calculated according to the procedure outlined in Section 2.3 (see Fig. 2.4).

Qualitative interpretation of the mechanism of methane supply can be made by examining the solubility profiles at each location. The pressure and temperature conditions at the Blake Ridge and Peruvian Margin result in thick zones of hydrate stability (450 and 400 m respectively). As a result, the slopes of the solubility profiles (within the HSZ) at the Blake Ridge and Peruvian margin are smaller than those of the other two sites (Fig. 2.4). This smaller slope results in slower loss of methane due to chemical diffusion within the HSZ, reducing the rate of methane supply necessary to maintain the distribution of hydrate. In addition, the solubility concentration for the Blake Ridge and Peruvian margin is lower than that at the other two sites over the same depth interval (0–200 m). This lower solubility concentration lowers the concentration of dissolved methane needed to form hydrate at these locations. The lower solubility concentrations required for hydrate formation, combined with smaller slopes of the solubility profiles within thick HSZ’s, require less in situ biogenic conversion of total organic carbon (TOC) to sustain the hydrate distribution. Higher than average TOC at both the Blake Ridge and Peruvian Margin (1.5% and 3% respectively) make both sites more likely to accumulate hydrate through in situ conversion of organic material.

On the other hand, pressure and temperature conditions at both the Cascadia Margin and Chile Triple Junction yield thin zones of hydrate stability (~ 230 and 160 m respectively). Consequently, the slope of solubility profiles (within the HSZ) are steeper at both the Cascadia Margin and Chile Triple Junction (Fig. 2.4). As a result, more rapid losses of methane occur within the HSZ, increasing the demand on the methane supply. Increased solubility concentrations over the HSZ intervals (relative to the Blake Ridge and Peruvian margin) also contribute to the demand for greater methane supply. However, low average TOC within the sediments at both the Cascadia Margin and Chile Triple Junction (<1% and <0.5% respectively) indicates that in situ biogenic conversion of organic carbon may not provide the necessary supply of methane to maintain the hydrate occurrence at these sites. These low TOC values argue for alternative mechanisms of methane supply. Focusing
of deep methane sources is thought to be the primary mechanism of methane supply at the Cascadia Margin [Hyndman and Davis, 1992] and the Chile Triple Junction [Brown et al., 1996].

Locations of hydrate occurrence are controlled by the combination of the pressure and temperature conditions (which define the solubility profile) and an adequate supply of methane. In order to make better predictions of hydrate occurrence and global hydrate inventories, numerical models must account for the solubility and mechanism of methane supply. Recent numerical models of Davie and Buffett [2001] show that the conditions for hydrate formation cannot be defined simply by the TOC in the sediments or by a critical flux of methane due to fluid migration. The shape of the solubility profile and even the rate of sedimentation can also be important factors for determining whether hydrates form. Previous attempts to estimate the global abundance of hydrate based on estimates of TOC [Kvenvolden, 1988] or on satellite data of phytoplanton concentration as a proxy for TOC [Gornitz and Fung, 1997] do not account for site-dependent pressures and temperatures, which greatly influence the profile of methane solubility and thus the demands on the methane supply. Some improvements in the global estimate of hydrate volume might be obtained by adjusting the required TOC (or methane flux) to account for variations in the rate of methane loss due to diffusion, although more reliable results will require the use of site-dependent solubility profiles in numerical models.

### 2.6 Summary

I present a practical method of calculating the solubility profile within and below the hydrate stability zone in a marine setting. The water depth, seafloor temperature, and geothermal gradient at a specific location, determine the pressure and temperature conditions at the base of the HSZ. The methane solubility is then calculated at the conditions of three-phase equilibrium using the phase equilibrium results of Zatsepina and Buffett [1997]. Simple parametric models are used to extend the results into the regions above and below the HSZ.
CHAPTER 2. METHANE SOLUBILITY

The solubility profiles at four hydrate locations were examined to qualitatively interpret possible mechanisms of methane supply. It was found that sites with steep solubility profiles and low TOC (i.e. Cascadia Margin and Chile Triple Junction) favour the focusing of deep methane sources as the main mechanism of methane supply, while sites with a smaller slope of the solubility profile within the HSZ and higher TOC (Blake Ridge and Peruvian Margin) suggest that biogenic production of methane may be important at these locations.
### CHAPTER 2. METHANE SOLUBILITY

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Table 2.1: Solubility of methane in pure water as a function of temperature predicted by the thermodynamic calculations of *Zatsepina and Buffett* [1997] at fixed pressures of 10 MPa, 20 MPa, and 30 MPa.
Figure 2.1: Schematic profile of the hydrate stability zone (HSZ) in marine sediments. The intersection of the local geotherm with the temperature $T_3$ for three-phase equilibrium of the water-hydrate-free gas system defines the base of the HSZ. Experimental data for three-phase equilibrium of pure [Sloan, 1990] and salt water [Dickens and Quinby-Hunt, 1994] are shown as dots, while the empirical fit of Brown and Bangs [1995] are shown as solid lines. Salt water reduces the three-phase equilibrium temperature $T_3(P)$ by $\sim 1.5$ °C.
Figure 2.2: Comparison of $P, T$ conditions at the base of the HSZ in natural hydrate settings (solid squares) with the three-phase equilibrium pressure and temperature (i.e. $T_3, P_3$) of the water-hydrate-free gas system. $T_3(P)$ is shown for the pure and salt water systems. Relatively good agreement is observed between the pressure-temperature conditions in natural settings and experimental three-phase pressure-temperature.
CHAPTER 2. METHANE SOLUBILITY

Figure 2.3: Solubility of methane in pure water as a function of temperature at fixed pressures of 10 MPa (squares), 20 MPa (circles), and 30 MPa (crosses) calculated by Zatsepina and Buffett [1997] (from Table 2.1). The peak in the solubilities occurs at $T_3(P)$, which coincides with the base of the HSZ. Good agreement between the results of Zatsepina and Buffett [1997] and solubilities predicted according to (2.5) (solid lines) is observed at temperatures below $T_3(P)$. (Dashed lines connect solubility data above $T_3(P)$.) The influence of salt tends to shift the solubility profiles to lower methane concentrations and temperatures.
Figure 2.4: Calculated solubility profiles of four known hydrate locations. Pressure and temperature conditions at the Blake Ridge and Peruvian Margin result in thicker zones of hydrate stability and smaller slopes in the solubility profile within the HSZ (thick lines). On the other hand, the Cascadia Margin and Chile Triple Junction have thin HSZ's and a steeper slope of the solubility profile within the HSZ.
CHAPTER 3

A Time-Dependent Model for Marine Hydrate Formation

In this chapter a time-dependent model is developed to describe the formation of hydrate in the marine environment. I begin by describing the physical conditions prevalent below the seafloor that need to be included in the quantitative description of the hydrate environment. These conditions are subsequently transcribed to a set of governing equations describing the evolution and distribution of marine hydrate. Initial, boundary and interface conditions are applied and a numerical method for solving the equations is discussed. An illustrative evolution sequence of the model is shown and key parameters are identified. Finally, a simple comparison with chlorine data from the Blake Ridge shows that the model can be applied successfully in a marine setting.

3.1 Marine Environment

Marine occurrences of gas hydrate are normally confined to deep continental margins where high pressure, low temperature, and adequate supplies of methane permit hydrate stability. The maximum zone of hydrate stability (HSZ) extends from the seafloor to the depth where the geotherm exceeds the temperature $T_3(P)$ for three-phase equilibrium (Figure 3.1A). This depth marks the limit of hydrate stability in the sediments; hydrate vanishes below the base of the HSZ and is replaced by methane bubbles (free gas). The phase boundary
 CHAPTER 3. TIME-DEPENDENT MODEL

between hydrate and free gas causes a discontinuity in the P-wave velocity across the base of the HSZ, which is commonly observed as a bottom simulating reflection (BSR) on marine seismic profiles (Figure 3.1B).

Hydrate forms when the methane concentration inside the HSZ exceeds the local solubility. Phase equilibrium calculations from Chapter 2 show that the solubility of methane in seawater increases from the seafloor to the base of the HSZ. In this zone of the sediments we expect hydrate to nucleate from dissolved methane above the solubility (Figure 3.2). This view is supported by the phase equilibrium calculations \cite{Zatsepina1997} and by laboratory experiments \cite{Buffett2000}. Below the HSZ, methane bubbles nucleate when the solubility is exceeded. Here the solubility is nearly constant with depth because of the counteracting effects of pressure and temperature (see Figure 3.2). The methane needed to maintain hydrate stability is supplied mainly by microbial conversion of organic material in the sediments \cite{Claypool1983}, though thermogenic processes may also contribute \cite{Sassen1999}. Methane may be produced locally within the stability zone or transported from a remote source by fluids. Persistent in situ production of methane relies on sedimentation to add new organic material. Accumulation of methane in the pore fluid eventually exceeds the local solubility and hydrate begins to form (Figure 3.2). Alternatively, the migration of methane-bearing fluid from a remote source can also produce hydrate within the HSZ. Changes in the solubility with depth allow a fluid which is saturated (and even undersaturated) in methane at depth to become oversaturated as it migrates into the HSZ \cite{Zatsepina1997} (Figure 3.2).

In situ production of methane is expected on all continental margins. It may be the principal source of methane for hydrate on passive margins \cite{Kvenvolden1993}, whereas migration of methane-bearing fluid is thought to be more important on active margins \cite{Hyndman1992, Ginsburg1994}. In situ methane sources are incorporated in the model by linking the biogenic methane production to the available organic carbon within the sediments. The organic carbon is constrained by drill core records and limits the supply of methane produced through biogenic conversion. Alternatively, the methane may be supplied
by the migration of methane bearing fluids from remote sources. In this case, a methane flux is imposed at the base of the computational domain to reflect the methane concentration and velocity of the incoming fluid. The methane carried by this fluid may have a biogenic, thermogenic, or a mixed origin.

In this study fluid flow within the sediment column is a function of both sediment compaction and external sources of fluid. Fluid flow due to compaction is assumed to arise solely from the effects of sedimentation. As new sediments are added, older sediments are buried and compacted. The decrease in sediment porosity induces fluid flow by squeezing out the pore fluid [Bonham, 1980; Hutchinson, 1985]. Allowances are also made for external sources of fluid flow, which are driven by mechanisms outside the sediment column of interest. These mechanisms may include fluid expulsion during accretionary thickening, pressure, or thermally driven fluid flow. These effects are superimposed on the fluid flow generated by sediment compaction, giving rise to a net fluid flow within the sediment column.

Sedimentation also buries hydrate below the base of the HSZ. Consequently, the hydrate is exposed to pressure/temperature conditions where it is unstable, causing the hydrate to dissociate. Dissociation of hydrate below the HSZ releases large amounts of methane and causes freshening of the pore fluid (Figure 3.3). Some of the methane is recycled back into the HSZ by diffusion through the pore fluid, and some is transferred into methane bubbles below the HSZ. The appearance of bubbles below the HSZ contributes to the seismic reflection that parallels the seafloor in many regions where gas hydrates are found [Singh et al., 1993; Mackay et al., 1994; Holbrook et al., 1996]. The bubbles are trapped in the sediments by the effects of surface tension and buried to greater depths when the fraction of the pore volume filled with bubbles is <15-20% [Henry et al., 1999]. Indeed, the deep layer of gas bubbles detected below the HSZ at several sites on ODP Leg 164 [Holbrook et al., 1996] can probably be explained by this process.
Figure 3.1: (A) Schematic of the hydrate stability zone in marine sediments. The intersection of the geotherm with the three phase temperature $T_3(P)$ defines the base of the hydrate stability zone. (B) Marine seismic profile from the Blake Ridge showing a BSR which marks the base of the hydrate stability zone. Adapted from Paull et al. [1996].
Figure 3.2: Solubility of methane in seawater as a function of depth below the seafloor. Hydrate is stable inside the HSZ when the concentration of dissolved methane exceeds the solubility. Similarly, methane bubbles nucleate from excess methane below the HSZ. Methane may be supplied by either microbial production or the upward migration of methane bearing fluids from depth.
Figure 3.3: Schematic illustration of methane recycling due to sedimentation. The base of the HSZ remains fixed relative to the seafloor when the geotherm is constant. Hydrate dissociates as it is buried below the stability zone. Some of the methane released by hydrate dissociation migrates back into the stability zone. The remainder is trapped in gas bubbles below the stability zone.
3.2 Governing Equations

The goal of the quantitative model is to translate the conceptual model described in the previous section to an appropriate mathematical representation of the hydrate environment. Mass balance equations are derived using the continuum theory of mixtures [Bedford and Ingram, 1971] to quantitatively model the formation of hydrate in the marine environment.

3.2.1 Physical Properties

The marine environment is modelled as a continuum mixture of sediment, fluid, and a separate methane component (either hydrate or methane bubbles) in a reference frame which is fixed to the seafloor (Figure 3.4).

The bulk volume within the HSZ can be defined as the sum of the individual components, namely

\[ V_B = V_s + V_f + V_h, \]  

(3.1)

where the subscripts \( s, f, \) and \( h \) denote the sediment, fluid and hydrate. A similar expression is obtained below the HSZ, with the subscript for methane bubbles \( (b) \) replacing hydrate.

The porosity is defined as the void space between the sediment grains, which includes both fluid and hydrate. In terms of the component volumes, the porosity may be expressed as

\[ \phi = \frac{V_f + V_h}{V_B}. \]  

(3.2)

The hydrate component occupies a fraction of the porespace \( \phi \). The hydrate fraction \( h \) can be defined as

\[ h = \frac{V_h}{V_f + V_h}, \]  

(3.3)

Manipulating equations (3.1-3.3), we can obtain expressions for the volumes of the sediment, fluid and hydrate in terms of the bulk volume \( V_B \)

\[ V_s = (1 - \phi)V_B, \quad V_f = \phi(1 - h)V_B, \quad V_h = \phi h V_B. \]  

(3.4)

The bulk density is defined as the mass per volume, and can be defined in terms of the
individual components as

$$\rho_B = \frac{\rho_s V_s + \rho_f V_f + \rho_h V_h}{V_B}. \quad (3.5)$$

Substituting for the component volumes defined in equation (3.4), we can express the bulk density as

$$\rho_B = \rho_s (1 - \phi) + \rho_f \phi (1 - h) + \rho_h \phi h, \quad (3.6)$$

where each component is assumed to have a constant density. In the case of methane bubbles below the HSZ, the density $\rho_b$ at the base of the HSZ is calculated from the ideal gas law using the prevailing thermodynamic conditions at a particular hydrate setting. Therefore the methane bubbles are assumed to have a constant density, with its value being dependent on the specific setting.

![Components of a volume of sediment below the seafloor. This includes (A) Sediment, fluid and hydrate within the HSZ and (B) Sediment, fluid and methane bubbles below the HSZ.](image)

Figure 3.4: Components of a volume of sediment below the seafloor. This includes (A) Sediment, fluid and hydrate within the HSZ and (B) Sediment, fluid and methane bubbles below the HSZ.

### 3.2.2 Conservation of Mass

Conservation principles are applied to a control volume that moves along with identified particles as described in Appendix A. The conservation of mass is applied to each component of the continuum mixture (sediment, hydrate, fluid) within the HSZ. We begin with the conservation of sediment. The total mass of sediment

$$m_s = \int_V \rho_s (1 - \phi) \, dV, \quad (3.7)$$
satisfies global balance equation

\[
\frac{dm_s}{dt} = \rho_s \int_V \frac{\partial}{\partial t} (1 - \phi) + \nabla \cdot [\mathbf{v}_s (1 - \phi)] \, dV = 0,
\] (3.8)

where the sediments are assumed to have a constant density \( \rho_s \) and move at a velocity \( \mathbf{v}_s \). By referring the coordinate system to the seafloor, the base of the HSZ is fixed for a constant geotherm. The porosity profile \( \phi(z) \) is also fixed relative to the seafloor. Sediments are assumed to compact at a uniform rate and the decrease in porosity may be described as

\[
\phi(z) = \phi(0) \exp(-z/L),
\] (3.9)

where \( \phi(0) \) is the seafloor porosity and \( L \) is the characteristic length scale for compaction. By assuming that the porosity \( \phi \) is independent of time, we can simplify (3.8) to its local form

\[
\nabla \cdot [\mathbf{v}_s (1 - \phi)] = 0.
\] (3.10)

Hydrate represents the stable methane component within the HSZ and forms in the sediment pore space from excess dissolved methane above the solubility. The mass of hydrate can be written

\[
m_h = \int_V \rho_h \phi h \, dV.
\] (3.11)

whose conservation equation satisfies

\[
\frac{dm_h}{dt} = \rho_h \int_V \frac{\partial}{\partial t} \phi h + \nabla \cdot [\mathbf{v}_h \phi h] \, dV
\]

\[
= \rho_h \int_V \phi \Phi_h \, dV,
\] (3.12)

where \( \Phi_h \) is the volume rate of hydrate growth in the pore space. Hydrate is transported at the same velocity as the sediments, so I set \( \mathbf{v}_h = \mathbf{v}_s \). Simplification of (3.12) allows the local form of the hydrate equation to be expressed as

\[
\frac{\partial h}{\partial t} + \frac{1}{\phi} \nabla \cdot [\mathbf{v}_s \phi h] = \Phi_h.
\] (3.13)
The remaining pore volume is filled with pore fluid (water), which contains dissolved methane and chlorine ions. The mass of fluid within the pore volume can be written as

\[ m_f = \int_V \rho_f \phi (1 - h) \, dV. \]  \hspace{1cm} (3.14)

The total mass of water in the fluid and hydrate components is conserved in the absence of chemical reactions with the sediments. While hydrous minerals may release water at high temperature, these effects occur well below the HSZ and are not included here. Transfers of water between the fluid and hydrate components cause a small change in volume, but the effect on the fluid velocity is small compared to the effects of compaction. Consequently, the volume rate of fluid production is balanced by the volume rate of hydrate dissociation \((\dot{\Phi}_f = \dot{\Phi}_h)\). The conservation equation for the fluid component obeys

\[ \frac{dm_f}{dt} = \rho_f \int_V \frac{\partial}{\partial t} [\phi (1 - h) + \nabla \cdot (v_f \phi (1 - h))] \, dV \]

\[ = -\rho_h \int_V \phi \dot{\Phi}_h \, dV. \]  \hspace{1cm} (3.15)

Simplification of this equation yields

\[ -\frac{\rho_f}{\rho_h} \frac{\partial h}{\partial t} + \frac{\rho_f}{\rho_h \phi} \nabla \cdot (v_f \phi (1 - h)) = -\dot{\Phi}_h. \]  \hspace{1cm} (3.16)

Adding (3.13) and (3.16) for the total mass of the hydrate and fluid components results in

\[ \frac{\rho_h - \rho_f}{\rho_h} \frac{\partial h}{\partial t} + \frac{\rho_f}{\rho_h} \nabla \cdot (v_f \phi (1 - h)) + \nabla \cdot (v_s \phi h) = 0 \]  \hspace{1cm} (3.17)

Equations (3.10) and (3.17) are solved for the sediment \(v_s\) and fluid \(v_f\) velocities, while (3.13) is integrated numerically to determine the hydrate volume fraction \(h\). The rate of hydrate growth is controlled by local thermodynamic conditions, which include temperature, pressure and methane concentration in the pore fluid.
3.2.3 Sediment and Fluid Velocities

We restrict our attention to one-dimensional models where the rate of sedimentation is spatially uniform and the porosity varies solely with depth \( z \). The sediment velocity is vertical in this case and is found through the integration of (3.10)

\[
v_s(z)(1 - \phi(z)) = C_1,
\]

where the integration constant \( C_1 \) may be dependent on time. Setting the sediment velocity at the seafloor \( (z = 0) \) equal to the sedimentation rate \( \dot{S} \) yields the expression for the sediment velocity

\[
v_s(z) = \left( \frac{1 - \phi(0)}{1 - \phi(z)} \right) \dot{S} \mathbf{h}.
\]

As sediments are buried, the sediment particles become more closely packed due to the weight of the overlying sediment column. This decreased porosity causes the sediment velocity to decrease with depth.

There are two components to the fluid velocity. One component of the fluid velocity is caused by the expulsion of pore fluids as the sediment column compacts. The resulting fluid velocity is less than the sediment velocity in a downward direction, away from the sediment-water interface (see Figure 3.5A). An expression for the fluid velocity due to sediment compaction is found through the integration of a simplified form of equation (3.17), where the small change in volume associated with hydrate production is assumed to be negligible compared to the effects of fluid flow induced by compaction. Consequently I set \( \rho_f = \rho_h \) and equation (3.17) may be written as

\[
\nabla \cdot [v_f \phi(1 - h)] + \nabla \cdot [v_s \phi h] = 0.
\]

Assuming that the fluid flow varies only with depth \( z \), integration of (3.20) yields

\[
\phi(z)(1 - h(z))v_f(z) + \phi h(z)v_s(z) = C_2,
\]

where the integration constant \( C_2 \) is eliminated by applying the condition that the fluid moves
with the sediments \((v_f = v_s)\) once the porosity is very low [Hutchinson, 1985]. Imposing this condition at \(z = L\), which is much greater than the depth of the HSZ, yields \(C_2 = \phi(L)v_s(L)\). Introducing the transport velocity \(u_f = v_f\phi(1 - h)\) and substituting for \(v_s\), the fluid velocity due to compaction may be written

\[
u_f(z) = (1 - \phi(0)) \left( \frac{\phi(L)}{1 - \phi(L)} - \frac{\phi(z)h(z)}{1 - \phi(z)} \right) \hat{S} \hat{z}
\]  

(3.22)

Imposed on the fluid velocity due to sediment compaction, is fluid flow driven by external sources, which may include fluid expulsion during accretionary thickening or thermally driven fluid flow. It should be emphasized that these external fluid flows are assumed to be diffuse and thus occur within the porespace of the sediments. No allowances are made for fluid flow along distinct pathways such as faults or fractures. The effects of deeper fluid sources are included in the model by assuming that the fluid at depth \((z = L)\) is moving up relative to the sediments at a prescribed velocity \(v_{ext}\) (Figure 3.5B). Equation (3.22) is modified to include the external fluid velocity

\[
u_f(z) = (1 - \phi(0)) \left( \frac{\phi(L)}{1 - \phi(L)} - \frac{\phi(z)h(z)}{1 - \phi(z)} \right) \hat{S} \hat{z} - \phi(L)v_{ext} \hat{z}.
\]  

(3.23)

In summary, the sediment velocity decreases with depth according to (3.19) due to sediment compaction. Hydrate is frozen to the sediments and is also transported at this sediment velocity \(v_s\). The fluid velocity \(u_f\) is influenced by both sediment compaction and external sources of fluid flow. These effects are described by (3.23), where sediment compaction is represented by the first term on the right-hand side, and the external fluid velocity is given by the second term. In marine settings where external fluid flow is not expected, we set \(v_{ext} = 0\).

### 3.2.4 Rate of Hydrate Growth

Hydrate growth is controlled by local thermodynamic conditions in the sediments. When the concentration of dissolved methane gas \(c_m\) exceeds the equilibrium concentration \(c_{eq}\), we
Figure 3.5: (A) Fluid velocity relative to the sediment-water interface due to compaction only (B) Fluid velocity relative to the sediment-water interface with an external upwards fluid velocity

expect hydrate to accumulate. Conversely, if $c_m$ is less than $c_{eq}$ when hydrate is present, then some of the hydrate dissociates to re-establish the equilibrium concentration. We represent this adjustment to thermodynamic equilibrium using a first-order model

$$
\Phi_h = R_h (c_m - c_{eq}),
$$

(3.24)

where $R_h$ is the reaction rate constant. Adopting a sufficiently large value for $R_h$ effectively enforces (local) thermodynamic equilibrium, but this creates numerical difficulties because of the large disparity between the timescale for thermodynamic adjustment and slower timescales associated with mass transport. Instead, the value of $R_h$ is progressively increased from an intermediate value of $R_h$ until the numerical solution is insensitive to further increases in this parameter. This approach ensures that the rate of hydrate growth is not limited by (3.24). Limitations on hydrate growth are more likely to result from the transport of dissolved gas. This view is supported by recent experimental studies of hydrate growth in natural porous media [Buffett and Zatsepina, 2000].

A method for predicting the methane solubility at marine hydrate locations was presented in Chapter 2. The methane solubility is calculated using the expressions from Chapter 2 for the site specific parameters of water depth, seafloor temperature and local geothermal gradient. The solubility at the base of the HSZ is described by (2.3) in pure water and (2.7) in seawater. The solubilities in the two-phase regions are calculated using (2.5) within the
HSZ and (2.6) below. The profile of solubility within the HSZ can be expressed as a function of depth by converting the temperature to depth according to (2.2).

3.2.5 Bubble Fraction and Growth

Below the hydrate stability zone, the stable methane reservoir is methane bubbles (free gas). The mass balance equations for the methane bubbles are completely analogous to (3.13), with the hydrate fraction \( h \) being replaced with the methane bubble fraction \( b \). Consequently, the equation governing the methane bubble growth can be expressed

\[
\frac{\partial b}{\partial t} + \frac{1}{\phi} \nabla \cdot [\mathbf{v} \phi b] = \Phi_b,
\]

where the bubbles are assumed to be trapped within the porespace and move with the sediments at a velocity \( \mathbf{v} \). The rate of methane bubble production is also analogous to the rate of hydrate production

\[
\Phi_b = \mathcal{R}_b (c_m - c_{eq}),
\]

where the reaction rate \( \mathcal{R}_b \) is assigned the same value as \( \mathcal{R}_h \). The density of methane bubbles is assumed to be constant but its value is dependent on the thermodynamic conditions at the specific geologic setting. The density is calculated using the ideal gas law, which states

\[
P V = nRT.
\]

The volume \( V \) occupied by 1 mole of methane gas (i.e. \( n = 1 \)) can be calculated using the temperature \( T \) and pressure \( P \) at the base of the HSZ, as well as the ideal gas constant \( (R = 8.314 \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \text{ mol}^{-1}) \). The density can then be calculated using the molar mass of methane (16 g/mol) according to

\[
\rho_b = \frac{0.016}{V}.
\]

For conditions relevant for the Blake Ridge, the bubble density is approximately 200 kg/m³.
3.2.6 Conservation of Solute

The concentration of methane dissolved in the pore fluid is a key variable to track as it controls the volume and distribution of hydrate and bubbles in the sediments. The concentration of methane is expressed as a mass fraction

\[ c_m = \frac{m_m}{m_f + m_m}, \] (3.29)

where \( m_m \) and \( m_f \) are the masses of methane and fluid respectively. The mass of methane dissolved in the fluid is always small compared to the total mass of fluid (i.e. \( m_f \approx m_f + m_m \)). Consequently, the mass of methane can be written

\[ m_m = c_m m_f = \int_V c_m \rho_f \phi(1-h) dV, \] (3.30)

where we have substituted for the mass of fluid according to (3.14). In the absence of sources, changes in \( m_m \) arise solely from chemical diffusion of methane across the surface of the control volume \( V \). However, there are two potential sources of dissolved methane. One source is due to the biogenic production of methane, which we denote as \( \Phi_m \). The other source of methane is due to the dissociation of hydrate, which adds methane to the fluid at a rate that depends on the mass fraction of methane stored in the hydrate \( c_h \) and the rate of dissociation \(-\Phi_h\). The global mass balance equation for the methane concentration satisfies

\[
\frac{dm_m}{dt} = \rho_f \int_V \frac{\partial}{\partial t} c_m \phi(1-h) + \nabla \cdot [c_m \mathbf{v}_f \phi(1-h)] dV \\
= \int_S \rho_f \phi(1-h) D_m \nabla c_m dS + \int_V \rho_f \phi(1-h) \Phi_m - c_h \rho_h \phi \Phi_h dV. \tag{3.31}
\]

As hydrate forms, the dissolved methane concentration above the solubility is depleted until the excess methane is transferred into hydrate. Conversely, the dissociation of hydrate will release methane until the solubility is re-established or hydrate vanishes. Converting the surface integral to a volume integral using Gauss’ theorem, and equating the integrands we
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write

\[ \phi(1-h) \frac{\partial c_m}{\partial t} - \phi c_m \frac{\partial h}{\partial t} + \mathbf{u}_f \cdot \nabla c_m + c_m (\nabla \cdot \mathbf{u}_f) = \nabla [\phi(1-h)D_m \nabla c_m] - \frac{\rho_h}{\rho_f} \phi c_h \Phi_h + \phi(1-h) \Phi_m. \]  

(3.32)

We substitute for \( \partial h/\partial t \) and \( \nabla \cdot \mathbf{u}_f \) from equations (3.13) and (3.17) respectively. Further simplification yields the local form of the methane equation

\[ \frac{\partial c_m}{\partial t} + \frac{1}{\phi(1-h)} \mathbf{u}_f \cdot \nabla c_m = \frac{1}{\phi(1-h)} \nabla \cdot [\phi(1-h)D_m \nabla c_m] + \frac{\rho_h (c_m - c_h)}{\rho_f (1-h)} \Phi_h + \Phi_m. \]  

(3.33)

Methane dissolved in the pore fluid is transported by the effects of chemical diffusion and advection within the pore fluid, while being produced by the dissociation of hydrate \( (-\Phi_h) \) and the biogenic production of methane \( (\Phi_m) \).

Anomalous chlorinity measurements are commonly associated with occurrences of gas hydrate [Hesse and Harrison, 1981; Kastner et al., 1995; Paull et al., 1996]. The production of hydrate excludes chlorine ions from its structure, causing an increase of the chlorine concentration in the pore fluid. In a similar manner, the dissociation of hydrate releases fresh water and results in a freshening of the pore fluid. Freshening of the pore fluid is usually observed below the HSZ due to the dissociation of hydrate associated with sedimentation and methane recycling. We determine the evolution of the chlorine concentration to relate the model predictions to observed chlorinity measurements from drill cores. The mass of chlorine ions can be expressed

\[ m_c = \int_V c_c \rho_f \phi(1-h) dV, \]  

(3.34)

where \( c_c \) is the mass fraction of chlorine ions. Chlorine is generally assumed to be a conserved quantity with no sources or sinks. Dehydration of clay minerals can reduce the chlorinity at depth, but these reactions are unlikely to occur in the top few hundred metres of sediments. In the absence of sources/sinks, changes in \( m_c \) arise solely due to the diffusion of chlorine.
ions across the surface of the volume \( V \). The mass balance equation therefore satisfies

\[
\frac{dm_c}{dt} = \rho_f \int_V \frac{\partial}{\partial t} c_c \phi (1 - h) + \nabla \cdot [c_c \mathbf{v}_f \phi (1 - h)] \, dV \\
= \int_S \rho_f \phi (1 - h) D_c \nabla c_c \, dS. \tag{3.35}
\]

The surface integral may be converted to a volume integral using Gauss' theorem, resulting in the integrands being equal for an arbitrary volume \( V \)

\[
\phi (1 - h) \frac{\partial c_c}{\partial t} - \phi c_c \frac{\partial h}{\partial t} + c_c (\nabla \cdot \mathbf{u}_f) + \mathbf{u}_f \cdot \nabla c_c = \nabla \cdot [\phi (1 - h) D_c \nabla c_c]. \tag{3.36}
\]

Substituting for \( \partial h/\partial t \) and \( \nabla \cdot \mathbf{u}_f \) from equations (3.13) and (3.17) allows further simplification, resulting in the local form of the chlorinity equation

\[
\frac{\partial c_c}{\partial t} + \frac{\mathbf{u}_f \cdot \nabla c_c}{\phi (1 - h)} = \nabla \cdot [\phi (1 - h) D_c \nabla c_c] + \frac{\rho_h}{\rho_f (1 - h)} \frac{c_c}{\phi (1 - h)} \Phi_h. \tag{3.37}
\]

Chlorine ions are transported through the pore fluid by the combined effects of chemical diffusion and fluid advection. In addition, the growth of hydrate \( \Phi_h \) causes an increase in chlorinity, while the dissociation of hydrate \( -\Phi_h \) acts as a source of freshening.

Equations (3.33) and (3.37) govern the evolution of \( c_m \) and \( c_c \) within the HSZ; nearly identical equations apply below the HSZ. To obtain these equations, we replace the hydrate volume \( h \) with the bubble volume \( b \) in both (3.33) and (3.37). In addition, we replace \( \Phi_h \) with \( \Phi_b \) and \( \rho_h \) with \( \rho_b \). The biogenic production of methane \( \Phi_m \) is the only remaining component of the model to prescribe.

### 3.2.7 Biogenic Production of Methane

A simple model for biogenic methane is proposed in which the rate \( \Phi_m \) is limited by the availability of organic carbon in the sediments. Conversion of organic carbon into methane may involve a diverse collection of bacterial populations \([\text{Cragg et al.}, 1996]\) and a complex sequence of chemical reactions \([\text{Reeburgh}, 1983]\). These complex reactions are commonly summarized by considering hypothetical compounds such as \( \text{CH}_2\text{O} \) \([\text{Berner}, 1980]\). As a
representative example, Paull et al. [1994] considered the reactions

\[
\begin{align*}
2\text{CH}_2\text{O} & \longrightarrow \text{CH}_4 + \text{CO}_2 \\
\text{CO}_2 + 4\text{H}_2 & \longrightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\end{align*}
\] (3.38)

in which 2 mol of organic carbon are converted to 2 mol of carbon in methane. Organic carbon in the sediments is usually described by the weight percent of organic carbon in dry sediments. A typical estimate of the total organic carbon (TOC) along continental margins is 1%. Only a fraction of the TOC is converted to methane by bacteria. We refer to this fraction as the available organic carbon \(\alpha\). As the available organic carbon is depleted by bacteria, the rate of methane production should decrease. Since the depleted carbon source is buried with the velocity of the sediments \(v_s\), we expect \(\Phi_m\) to decrease with depth. The total mass of metabolizable carbon within the sediments can be expressed as

\[m_\alpha = \int_V \alpha \rho_s (1 - \phi) \, dV. \] (3.39)

If the rate of methane production is proportional to the mass fraction \(\alpha\) of available organic carbon, the mass balance equation for the evolution of \(\alpha\) can be described by

\[
\frac{dm_\alpha}{dt} = \rho_s \int_V \frac{\partial \alpha (1 - \phi)}{\partial t} + \nabla \cdot [v_s \alpha (1 - \phi)] \, dV
\]

\[= - \int_V \lambda_m \alpha \rho_s (1 - \phi) \, dV, \] (3.40)

where the rate constant \(\lambda_m\) describes the vigor of biological activity. The timescale \(\lambda_m^{-1}\) gives an estimate of the time required to consume the available organic carbon. Application of the conservation of sediment (3.10) allows (3.40) to be simplified to its local form

\[
\frac{\partial \alpha}{\partial t} = -v_s \cdot \nabla \alpha - \lambda_m \alpha. \] (3.41)

Sedimentation continually adds new organic material to the stability zone. The available organic carbon \(\alpha(0)\) at the seafloor defines the carbon supply for the gas hydrates. Subsequent decreases in \(\alpha(z)\) with depth are readily predicted under the conditions of steady
sedimentation rate and constant organic content. This steady profile is obtained by setting \( \partial \alpha / \partial t = 0 \) in (3.41) and integrating for \( \alpha(z) \) to give

\[
\alpha(z) = \alpha(0) \exp \left( -\lambda_m \int_0^z \frac{dz}{v_s} \right) .
\]  

(3.42)

This steady profile serves as a useful starting condition for our numerical computations. It does not change in the numerical computations unless \( v_s \) and \( \alpha(0) \) vary with time.

The production of methane is directly related to the loss of the available organic carbon. The mass of methane produced by this reaction is calculated by considering the molar masses of \( \text{CH}_2\text{O} \) organic carbon (30 g/mol) and \( \text{CH}_4 \) methane (16 g/mol). Since the mass loss of \( \text{CH}_2\text{O} \) per unit volume occurs at a rate \( \lambda_m \alpha \rho_s (1 - \phi) \), the corresponding rate of methane production is

\[
\Phi_m = \left( \frac{16 \rho_s (1 - \phi)}{30 \rho_f \phi (1 - h)} \right) \lambda_m \alpha .
\]  

(3.43)

Equation (3.43) together with (3.41) determines the rate and distribution of methane production in the marine sediments. Methane production is limited to depths below the sulfate reducing zone (SRZ), which is typically on the order of 5-20 m in hydrate settings. We expect most of the methane production in the shallow sediments when \( \lambda_m \) is large, whereas small values of \( \lambda_m \) spread the methane production to greater depths. A range of values for \( \lambda_m \) are considered in our numerical solutions.

### 3.2.8 Summary of Governing Equations

Equations that govern the formation of hydrate in marine sediments are summarized. The hydrate \( h \) and bubble \( b \) volumes are described by the mass balance equations (3.13) and (3.25), in which the source terms \( \Phi_h \) and \( \Phi_b \) depend on local thermodynamic conditions. The concentration of dissolved methane \( c_m \) and chlorine \( c_c \) are determined by (3.33) and (3.37). The sediment and fluid velocities are given by (3.19) and (3.23), respectively. The most speculative component of the model deals with the biogenic production of methane. The rate \( \Phi_m \) of methane production in (3.33) depends on the mass fraction of available organic carbon, \( \alpha \), which varies in depth and time according to (3.41).
Considerable simplifications to the governing equations are possible if the dependent variables \( h, b, c_m, c_c, \) and \( \alpha \) do not vary laterally. Although this is not strictly true, lateral variations tend to be small compared with the vertical variations. Consequently, we adopt a one-dimensional approximation of the governing equations in which the spatial derivatives (\( \nabla \cdot \)) are replaced by vertical derivatives (\( \partial / \partial z \)), and vector quantities (ie. \( \mathbf{v} \)) are replaced with the vertical component (ie. \( v_z \)).

### 3.3 Initial and Boundary Conditions

The system of equations is integrated numerically using the method of lines [Schiesser, 1991]. Spatial derivatives are approximated using fourth-order finite differences to obtain a set of ordinary differential equations in time for \( h, b, c_m, c_c, \) and \( \alpha \) at each node on the grid. The resulting differential equations are integrated using the Matlab ODE solver for stiff equations (ODE15s).

Initial conditions are required for \( h(z,t), b(z,t), c_m(z,t), c_c(z,t), \) and \( \alpha(z,t) \). I let \( h(z,0) = b(z,0) = c_m(z,0) = 0 \) and assign \( c_c(z,0) \) the nominal value for seawater (which is denoted by \( c^o \)). The initial distribution of available organic carbon \( \alpha(z,0) \) is defined by the steady solution to (3.42).

The computational domain is divided into two regions. The HSZ extends from the seafloor \( z = 0 \) to the base of the HSZ at \( z = z_h \), which typically coincides with the BSR. The region below the HSZ extends to \( z = z_n \), which we take to be twice the depth of the HSZ \( (z_n = 2z_h) \).

Two boundary conditions are required for the methane and chlorine concentrations. I set \( c_m = 0 \) at \( z = 0 \) and impose the second condition at the base of the computational domain. In the absence of an upward fluid velocity, a no-flux condition \( dc_m / dz = 0 \) is imposed at \( z = z_n \), which allows the composition of the pore fluid to adjust to the in situ generation of methane. When an upward fluid velocity is imposed, \( c_m \) at \( z = z_n \) is prescribed to reflect the composition of the incoming fluid. A similar approach is used to impose the boundary conditions of \( c_c \). The chlorine concentration at the seafloor \( (z = 0) \) is set to the present
day value of seawater and the second condition is imposed at \( z = z_n \). A no-flux condition \( dc_c/dz = 0 \) is imposed at \( z = z_n \) in the absence of an upward fluid velocity, which allows the extent of the pore fluid freshening to be governed by hydrate recycling at the base of the HSZ. On the other hand, when the upward fluid velocity is imposed, the composition of \( c_c \) at \( z = z_n \) is set to the value of the chlorine concentration measured at depth.

Additional boundary conditions are required for the organic carbon \( \alpha \), hydrate \( h \), and bubble fraction \( b \). However, each of these variables requires only one boundary condition because their governing equations contain only a first-order spatial derivative. The amount of available organic carbon is prescribed at the seafloor \( z = 0 \) as a fraction of the average organic carbon at the particular site. The hydrate fraction is set to zero at the seafloor, while the boundary condition on the bubble fraction is imposed at the base of the HSZ to enforce conservation of methane when \( h \) vanishes below the HSZ.

### 3.4 Interface Conditions

The base of the HSZ represents a thermodynamic boundary where the stable methane-bearing phase changes from hydrate in the overlying sediments to methane bubbles below. Consequently, gradients in hydrate and methane bubbles are not continuous at the interface and so the governing equations for \( c_m \) and \( c_c \) (which contain gradients in \( h \) and \( b \)) cannot be applied across this interface. Instead, conservation of methane and chlorinity is imposed by equating the fluxes across the HSZ interface as schematically shown in Figure 3.6. Two cases need to be distinguished for the methane concentration. When the methane concentration exceeds the solubility at the interface both hydrate and bubbles will be present. The hydrate fraction \( h \) at the interface is found by assuming that hydrate is advected from above in the absence of hydrate production (\( \Phi_h = 0 \)). In this case, the equilibrium methane concentration is imposed and the conservation of methane is solved for the bubble fraction according to

\[
\frac{\rho_h}{\rho_f} hv_s (c_h - c_{eq}) - \frac{\rho_h}{\rho_f} bv_s (c_b - c_{eq}) = (1 - h) D_m \frac{dc_{eq}}{dz} - (1 - b) D_m \frac{dc_{eq}}{dz},
\]

(3.44)
where \( c_{eq}^- \) is taken to be the value of the solubility above the interface and \( c_{eq}^+ \) is the solubility below. The values \( c_h \) and \( c_b \) are the mass fractions of methane stored in the hydrate and bubbles respectively. (We take \( c_b = 1 \) when the gas is pure methane). When the dissolved methane is undersaturated at the interface, both \( b \) and \( h \) must vanish at the interface, so equation (3.44) reduces to

\[
\frac{dc_m^-}{dz} = \frac{dc_m^+}{dz},
\]

where \( c_m^- \) and \( c_m^+ \) are no longer fixed by the solubility. A similar expression for the chlorinity interface condition is obtained by balancing the fluxes of chlorine across the HSZ interface. The chlorinity at the interface can be expressed as

\[
\left( \frac{\rho_b}{\rho_f} b - \frac{\rho_h}{\rho_f} h \right) v_s c_c = (1 - h) D_c \frac{dc_c^-}{dz} - (1 - b) D_c \frac{dc_c^+}{dz},
\]

when both hydrate and methane bubbles are present at the interface. This expression simplifies to

\[
\frac{dc_c^-}{dz} = \frac{dc_c^+}{dz},
\]

when hydrate and methane bubbles are absent at the interface.
CHAPTER 3. TIME-DEPENDENT MODEL

(A) Conservation of Mass
\[ \rho_h \phi h v_s + \rho_f \phi (1-h) v_f \]

hydrate
no hydrate

\[ \rho_b \phi b v_s + \rho_f \phi (1-b) v_f \]

(B) Conservation of Chlorine
\[ \rho_f \phi (1-h) v_f c_c - \rho_f \phi (1-h) D_c \nabla c_c \]

hydrate
no hydrate

\[ \rho_f \phi (1-b) v_f c_c - \rho_f \phi (1-b) D_c \nabla c_c \]

(C) Conservation of Methane
\[ \rho_h \phi h v_s c_h + \rho_f \phi (1-h) v_f c_m \]
\[ -\rho_f \phi (1-h) D_m \nabla c_m \]

hydrate
no hydrate

\[ \rho_b \phi b v_s c_b + \rho_f \phi (1-b) v_f c_m \]
\[ -\rho_f \phi (1-b) D_m \nabla c_m \]

Figure 3.6: Interface conditions for (A) total mass (B) chlorine (C) methane
3.5 Model Results

In order to apply the hydrate model, several parameters specific to the marine environment must be assigned. The Blake Ridge is selected as a suitable model setting because it is a well-studied area with known hydrate occurrences. The Ocean Drilling Program (Leg 164) drilled several sites on the Blake Ridge in a comprehensive study that was dedicated to gas hydrate [Paull et al., 1996]. In particular, geologic parameters consistent with the Site 997 are assigned and drill core chlorinity data is used to compare the model predictions and observations.

Table 3.1 lists the physical properties of the hydrate, fluid and sediment components. Only the density of gas is specific to the Blake Ridge because a nominal depth of 3.2 km (sealevel + BSR depth) is assumed in the calculation of $\rho_b$ using the ideal gas law. Other parameters that are specific to Blake Ridge are listed separately in Table 3.2. Notably, the depth of the HSZ is set by the overlying water depth, the seafloor temperature, and the geothermal gradient. However at Site 997, the observed base of the HSZ does not coincide with the 3-phase depth (see Figure 2.2). In this case, the temperature gradient $G$ is adjusted so the calculated base of the HSZ (as per Chapter 2) coincides with the observed base of the HSZ at 451 m. Sedimentation rates vary with time, but 22 cm/kyr is a representative estimate [Borowski et al., 1996]. Using the porosity of the sediments at the seafloor, $\phi(0) = 0.69$, the porosity profile can be approximated by equation (3.9) where $L=2000$ m is the characteristic length scale for compaction for the Blake Ridge. Figure 3.7A shows the observed porosity at Site 997 (ODP Leg 164) from Paull et al. [1996] and the fit obtained from equation (3.9). The corresponding sediment velocity as a function of depth is shown in Figure 3.7B. The total organic content TOC on Blake Ridge varies from 0.8 to 2.3% [Paull et al., 1996]. An average value of 1.5% is adopted for the model calculations.
Figure 3.7: (A) Comparison between the model porosity (solid line) and porosity measurements from Site 997 (dots). (B) Sediment velocity at Site 997.
CHAPTER 3. TIME-DEPENDENT MODEL

<table>
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<th>Symbol</th>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
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<tbody>
<tr>
<td>$\rho_s$</td>
<td>sediment density</td>
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</tr>
<tr>
<td>$\rho_f$</td>
<td>water density</td>
<td>1000</td>
<td>kg/m$^3$</td>
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<td>$\rho_h$</td>
<td>hydrate density</td>
<td>930</td>
<td>kg/m$^3$</td>
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<td>$\rho_g$</td>
<td>gas density</td>
<td>200</td>
<td>kg/m$^3$</td>
</tr>
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<td>$D_c$</td>
<td>chemical diffusivity of chlorine</td>
<td>$1.01 \times 10^{-9}$</td>
<td>m/s$^2$</td>
</tr>
<tr>
<td>$D_m$</td>
<td>chemical diffusivity of methane</td>
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<tr>
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<td>methane concentration in hydrate</td>
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<td></td>
</tr>
<tr>
<td>$R_h$</td>
<td>rate constant for hydrate formation</td>
<td>$10^{-6}$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$R_b$</td>
<td>rate constant for free gas formation</td>
<td>$10^{-6}$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>ideal gas constant</td>
<td>8.314</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
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Table 3.1: Physical parameters

<table>
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<th>Symbol</th>
<th>Parameter</th>
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<tr>
<td>$H$</td>
<td>water depth</td>
<td>2781</td>
<td>m</td>
</tr>
<tr>
<td>$z_h$</td>
<td>depth of HSZ</td>
<td>451</td>
<td>m</td>
</tr>
<tr>
<td>$T(0)$</td>
<td>seafloor temperature</td>
<td>3</td>
<td>°C</td>
</tr>
<tr>
<td>$G$</td>
<td>geothermal gradient</td>
<td>0.043</td>
<td>°C/m</td>
</tr>
<tr>
<td>$\phi(0)$</td>
<td>seafloor porosity</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>$L$</td>
<td>depth scale for porosity</td>
<td>2000</td>
<td>m</td>
</tr>
<tr>
<td>$\dot{S}$</td>
<td>sedimentation rate</td>
<td>22</td>
<td>cm/kyr</td>
</tr>
<tr>
<td>TOC</td>
<td>weight % of average TOC</td>
<td>1.5%</td>
<td></td>
</tr>
<tr>
<td>$\alpha(0)$</td>
<td>available organic carbon at seafloor</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>rate constant for methanogenesis</td>
<td>$3 \times 10^{-13}$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$t$</td>
<td>integration time</td>
<td>10</td>
<td>Myr</td>
</tr>
</tbody>
</table>

Table 3.2: Model parameters for Site 997 at the Blake Ridge. Sources are Paull et al. [1996] and Borowski et al. [1996]
Predictions of the hydrate model are based on integrations over a simulated time interval of 10 Myr using the parameter values listed in Tables 3.1 and 3.2. Such long integrations are necessary to allow the model to evolve into a quasi-steady state. In interpreting the results we need to bear in mind that the sediments may be disrupted by a variety of geological processes [Rowe and Gettrust, 1993]. Fortunately, the last major tectonic activity in the region ceased in the Cretaceous period. In this section, model results are shown at four specific times. Each marks a distinctive stage of hydrate development.

Figure 3.8 shows the evolution of the dissolved methane $c_m$, hydrate volume $h$, chlorinity $c_c$, and bubble volume $b$ for the case of in situ biogenic production of methane with fluid flow arising solely due to compaction. An early stage of the evolution is depicted at $t = 0.05$ Myr. Methane begins to accumulate in the pore fluid, although the concentration is everywhere less than the solubility $c_{eq}$ (shown by the dashed line). Accordingly, the volumes of hydrate and gas bubbles remain zero and the chlorinity is undisturbed from the initial value for seawater.

At $t = 0.81$ Myr the methane concentration exceeds the solubility over the upper portion of the HSZ. Dissolved methane in excess of the solubility is transferred into hydrate, which occupies upwards of 5% of the pore volume at its peak value. Exclusion of chlorine ions from the hydrate structure causes an increase in chlorinity at the depth where the hydrate is forming. The combined effects of diffusion and fluid transport spread the chlorinity anomaly to greater depths. The volume of gas bubbles remains zero because the methane concentration is still less than the solubility below the HSZ. This situation changes once hydrate is buried by sedimentation below the base of the HSZ.

Hydrate is present at the base of the HSZ at $t = 4.18$ Myr. The concentration of dissolved methane matches the solubility over most of the HSZ. Only the uppermost sediments are undersaturated with methane because $c_m$ must deviate from the equilibrium concentration to match the vanishingly low concentration at the seafloor. Over this shallow interval in depth, hydrate is absent. The hydrate volume increases with depth, reaching a peak value of nearly 8% of the pore volume at the base of the HSZ. Below the stability zone the hydrate
volume vanishes.

The chlorinity anomaly at $t = 4.18$ Myr is positive over most of the HSZ because of the exclusion of salts during hydrate formation. However, freshening of the pore fluid is evident immediately below the HSZ because of the dissociation of hydrate. Some of the methane released by hydrate dissociation is transferred into gas bubbles, which forms a thin layer (~100m) occupying up to 4% of the pore volume. The rest of the methane is dissolved into the pore fluid and diffuses back up into the HSZ. Diffusion of methane toward the seafloor is eventually lost to the ocean. This persistent flux of methane is consistent with profiles of sulfate concentrations in sediments above hydrate occurrences [Borowski et al., 1996].

Figure 3.8 shows the final state after 10 Myr. The dissolved methane concentration, hydrate volume, chlorinity and bubble volume all achieve steady profiles. The peak hydrate volume is 8% and the bubble volume reaches 6%. The chlorinity below the HSZ is nearly constant and 7% fresher than typical seawater. All of these features remain unchanged after longer integration times. This steady behavior was unexpected, but it can be attributed to losses of methane due to diffusion through the pore fluid and transport of gas bubbles trapped in the sediments. The existence of a steady state is important because it means that hydrate volume is not a good indication of accumulation time when methane is produced solely by in situ conversion of organic material.

The solution sequence depicted in Figure 3.8 is representative of most of the numerical calculations. This sequence of events is largely unaltered by other choices of parameter values or by including upward fluid flow, though specific estimates for the hydrate volume or freshening below the HSZ are changed. Discussion of alternative mechanisms of methane supply is deferred until Chapter 4, when we will compare the supply of methane by in situ conversion of organic carbon and the upward migration of methane bearing fluids at both the Blake Ridge and Cascadia margin.
Figure 3.8: Evolution sequence of hydrate formation for 4 characteristic stages of hydrate growth
3.6 Sensitivity to Parameters

Different values for the parameters yield different numerical predictions for the hydrate volume. It is important to identify the key physical parameters and to quantify their influence on the numerical predictions. The parameters that are most uncertain or most site-specific include the available organic carbon at the seafloor \( \alpha(0) \), the rate of sedimentation \( \dot{S} \), and the rate constant \( \lambda_m \) for biogenic production of methane. The effects of each of these parameters are examined separately in this section.

3.6.1 Available Organic Carbon

The supply of carbon to the hydrate zone is defined by the available organic carbon at the seafloor \( \alpha(0) \). This parameter depends on both the quantity and quality of the total organic carbon (TOC). The preceding calculations assumed that >3/4 of the TOC is available to bacteria to produce methane. Increasing the TOC implies an increase in the available carbon when this fraction is held fixed. Holding all other parameters in Tables 3.1 and 3.2 fixed, we estimate the average hydrate volume

\[
\bar{h} = \frac{1}{D} \int_0^D h(z) \, dz
\]

at steady state and the chlorinity immediately below the HSZ when the TOC is varied. The results are shown in Figure 3.9A and B.

The numerical calculations shown in section 3.5 used TOC = 1.5%, which yields an average fractional hydrate volume of \( \sim 8\% \). The chlorinity relative to the initial value for seawater was 0.93. Increasing the organic carbon supply increases the volume fraction of hydrate and decreases the chlorinity due to enhanced freshening by hydrate dissociation. Values of TOC below 0.5% produce very low concentrations of hydrate and vanishingly small quantities of gas bubbles. Such hydrate occurrences would be difficult to detect seismically because of the probable absence of a bottom-simulating reflector (e.g., [Holbrook et al., 1996]).
3.6.2 Sedimentation Rate

The relationship between sedimentation rate and hydrate volume is not straightforward. On the one hand, the sedimentation rate controls the rate of carbon supply for a fixed TOC. However, a faster sedimentation rate means that bacteria spend less time converting organic material to methane inside the hydrate stability zone. The first column of plots in Figure 3.10 shows how $\bar{h}$ varies with sedimentation rate when different values of $\lambda_m$ are used in the calculations. For the nominal value, $\lambda_m = 10^{-14} \text{ s}^{-1}$, $\bar{h}$ decreases as the sedimentation rate increases. This is because unused carbon is transported through the HSZ. Adopting larger values for $\lambda_m$ causes faster conversion of organic material and less unused carbon passes through the HSZ. For $\lambda_m = 5 \times 10^{-14} \text{ s}^{-1}$ the hydrate volume increases with sedimentation rate over an intermediate range of sedimentation rates (e.g., 10–20 cm kyr$^{-1}$). However, as the sedimentation rate increases above 20 cm kyr$^{-1}$, unused carbon once again begins to pass through the HSZ and the volume of hydrate decreases. Further increase in $\lambda_m$ ensures that the organic carbon is depleted within the HSZ. A value of $\lambda_m = 3 \times 10^{-13} \text{ s}^{-1}$ is selected for future calculations to ensure that the organic carbon is consumed within the HSZ.

The chlorinity below the HSZ also exhibits a complicated dependence on sedimentation rate, as shown in Figure 3.10 (right column). Increasing the rate of sedimentation causes an increase in the rate of freshening below the HSZ. However, the volume of hydrate at the base of the hydrate zone also contributes to the amount of freshening, and we have previously seen that higher sedimentation rates can lower the hydrate volume. The interplay between hydrate volume and its rate of transport account for the predicted variability in chlorinity with sedimentation rate. These results illustrate the sensitivity of the calculations to the value of $\lambda_m$ and emphasize the importance of biological processes in determining the physical and chemical character of hydrate occurrences.

3.6.3 Rate Constant for Methane Production

Relatively little is known about the biological communities that coexist with gas hydrates in deep marine sediments [Cragg et al., 1996]. The discussion in section 3.6.2 suggests
that the rate constant for biogenic methane production is a key parameter in the hydrate model, yet the value of this constant is unconstrained by observations. Even the form of the model in which this constant appears is speculative. Nevertheless, we hope to constrain $\lambda_m$ by comparing our predictions with measurements from ODP Leg 164. Encouragement is taken from the fact that most of the other model parameters at this site are relatively well constrained. With this goal in mind, the effects of $\lambda_m$ on the average hydrate volume and chlorinity below the HSZ are investigated when all other parameters are held fixed.

The results are shown in Figure 3.9C and D. Estimates of $\bar{h}$ increase sharply as $\lambda_m$ increases from the nominal value of $10^{-14}$ s$^{-1}$. However, progressively larger values in $\lambda_m$ produce less rapid increases in $\bar{h}$. In the limit of large $\lambda_m$, $\bar{h}$ reaches a constant value of $\sim 6.5\%$. In effect, the available organic carbon is totally converted to methane inside the HSZ, and the predictions become increasingly insensitive to further changes in $\lambda_m$ after approximately $\lambda_m = 1 \times 10^{-13}$ s$^{-1}$. Predictions for the chlorinity below the HSZ show a similar dependence. As the hydrate volume increases, the amount of freshening increases. Since measurements from ODP Leg 164 constrain both the hydrate volume and the freshening below the stability zone, these measurements are used to constrain $\lambda_m$. 
Figure 3.9: Sensitivity of hydrate volume and chlorinity to the total organic carbon (TOC) and reaction rate ($\lambda_m$). (A) Average hydrate volume for varying TOC (B) Freshening below HSZ for varying TOC (C) Average hydrate volume for varying $\lambda_m$ (D) Freshening below HSZ for varying $\lambda_m$. 
CHAPTER 3. TIME-DEPENDENT MODEL

Figure 3.10: Sensitivity of hyrate volume and chlorinity to the sedimentation rate. First column shows the dependence of the average hydrate volume on sedimentation rates for 5 different reaction rates. Second column shows the dependence of the freshening below the HSZ on sedimentation rates for 5 different reaction rates.
3.7 Application to the Blake Ridge

Leg 164 of the Ocean Drilling Program was dedicated to the study of gas hydrate on the Blake Ridge (see Figure 1.1). Physical and chemical properties were measured at several drilling sites. Here we restrict our attention to Site 997, where the drilling depth exceeded the predicted base of the HSZ. One of the most useful measurements is the pore fluid chlorinity, which is obtained from recovered core samples. During recovery, hydrate in the pore volume dissociates and freshens the pore fluid. The amount of freshening is usually taken as a measure of the volume of hydrate that was present in the sediments before recovery. Quantitative estimates of the hydrate volume are routinely based on the assumption that the chlorinity of the pore fluid prior to the dissociation of hydrate is equal to that of seawater.

Our numerical predictions of chlorinity indicate that this assumption is not strictly correct, but few options exist if the in situ chlorinity is unknown. In the numerical model, however, the in situ chlorinity is known, so the pore fluid chlorinity of a recovered core sample can be predicted. Model predictions are compared with the actual measurements from ODP Leg 164.

The observed chlorinity $c_{c}^{\text{obs}}$ of the pore fluid in the core sample is related to the in situ chlorinity $c_{c}(z)$ by Hesse and Harrison [1981]

$$c_{c}^{\text{obs}} = [1 - h(z)] c_{c}(z). \quad (3.49)$$

Observations of anomalous freshening below the HSZ are sometimes questioned on the grounds that hydrate is absent from this region [Paull et al., 1996], but the modelling results indicate that this freshening is an inevitable consequence of hydrate recycling at the base of the HSZ. In fact, the observed chlorinity below the HSZ at Site 997 is $\sim 93\%$ of the seawater value. In order to reproduce this observed freshening with the hydrate model, a large value for $\lambda_m$ is required (see Figure 3.9D). For subsequent comparisons, the value $\lambda_m = 3 \times 10^{-13}$ s$^{-1}$ is used in the numerical calculations. Roughly 60\% of the available carbon is consumed in the top 60 m of sediments. The resulting profiles of the in situ chlorinity and hydrate
volume are shown in Figure 3.11A and B. The peak hydrate volume is 8%, and the average across the HSZ is slightly <6%, in remarkably good agreement with estimates from vertical seismic profiling [Holbrook et al., 1996]. Methane bubble volumes of up to 7% below the HSZ (Figure 3.11D) are also in good agreement with direct in situ measurements of methane volume [Dickens et al., 1997]. The in situ chlorinity is slightly in excess of the seawater value in a small region near the seafloor, where hydrate formation is most vigorous. Elsewhere, the chlorinity is anomalously low (Figure 3.11A).

Using the predicted values of $h$ and $c_c$ in equation (3.49), estimates for the chlorinity of the recovered pore fluid are obtained. These estimates are compared with the actual measurements in Figure 3.11C. Agreement is very good through the top 200 m of sediments and below 450 m. Between 200 m and 450 m the observations exhibit more scatter, but the trend is consistent with the prediction. The increased scatter in the observations does not necessarily mean that the measurements are less reliable. The model predicts a smoothly varying distribution of hydrate through the sediments, but other processes may operate at the pore scale to redistribute hydrate into more massive forms [Clennell et al., 1999]. Such processes are not included in the model, but they could contribute to the scatter in the observations. Sediment cores with small nodules of solid hydrate would produce more freshening than sediments where the hydrate has been depleted. The model predicts a dispersed distribution of hydrate, but it does not rule out a subsequent redistribution of hydrate about the predicted average. It is also possible that the observations are biased toward low hydrate volumes because samples with large volumes of hydrate may be disrupted during recovery by rapid decomposition. In extreme cases the sediments may be disrupted to such an extent that fluid samples cannot be collected. Loss of samples with high hydrate volume would bias the inferences of hydrate volume toward lower values. This problem is expected to be most serious near the base of the HSZ, where $h$ is predicted to be largest. Estimates of bubble volume below the HSZ provide a further constraint on the hydrate model. A deep layer of gas bubbles is predicted below the HSZ (see Figure 3.11D). Predicted bubble volumes of 7% agree well with the 10% inferred from direct measurements of methane.
quantities on the Blake Ridge [Dickens et al., 1997].
Figure 3.11: Results from Site 997. (A) In situ chlorinity. (B) Hydrate occupies up to 8% of the pore space in remarkably good agreement with previous studies. (C) Predicted drill core chlorinity (solid) agrees well with the observations (circles). (D) A deep layer of free gas occupying up to 6% of the pore space forms below the HSZ.
3.8 Summary

In this chapter a time-dependent model was developed to describe the formation of hydrate in the marine environment. Conditions characteristic of the deep marine environment were translated to a set of time-dependent partial differential equations governing the formation of hydrate. Initial, boundary, and interface conditions were applied, allowing the equations to be solved numerically, and yielding time evolution sequences for hydrate formation. The solution became insensitive to longer integration times after approximately 10 Myrs. This time independence has important implications as it suggests the volume of hydrate at a particular location is not dependent on the accumulation time after approximately several million years. A typical evolution sequence was examined for methane production by biogenic conversion of organic carbon, and the key physical parameters that influence the model results were identified. In particular, the organic carbon deposited at the seafloor ($a(0)$), sedimentation rate ($\dot{S}$), and reaction rate ($\lambda_m$) had the greatest influence on the numerical predictions. The model results were applied successfully at the Blake Ridge and showed that a shallow in situ biogenic source could reproduce the chlorinity observations at Site 997 in the absence of upward fluid migration. However, a large amount of conversion of organic carbon (>80% TOC) was required to reproduce the chlorinity observations. In Chapter 4, we will explore alternative mechanisms of methane supply at the Blake Ridge and Cascadia Margin to draw inferences about the specific source of methane at these two locales.
CHAPTER 4

Sources of Methane for Marine Gas Hydrate: Inferences from a comparison of observations and numerical models

The supply of methane for marine gas hydrate is commonly attributed to local conversion of organic material within the zone of stability or to migration of methane-bearing fluids from a deeper source area. However, the relative importance of these methane sources is not well known. In this chapter, numerical models for the formation of gas hydrate are used to assess the influence of methane supply on observable features of hydrate occurrences. Model predictions for the pore fluid chlorinity and the volumes of hydrate and free gas are compared with observations from the Blake Ridge and Cascadia margin. Observations from the Blake Ridge can be explained with a deep methane source if a saturated fluid rises with a velocity of 0.26 mm yr\(^{-1}\). An equally good fit to the observations is obtained by combining in situ production of methane with an upward fluid velocity of 0.08 mm yr\(^{-1}\), which is compatible with estimates of fluid velocity at Site 997. Observations from the Cascadia margin can be explained with a deep methane source if the upward fluid velocity is 0.42 mm yr\(^{-1}\). The predicted volume of hydrate (~2% of the pore space) is much smaller than some previous estimates and a layer of free gas (~1% of the pore space) develops below the stability zone. Allowing for in situ production at the Cascadia margin lowers the upward fluid velocity (0.35 mm yr\(^{-1}\)) needed to explain the pore water chlorinity.
CHAPTER 4. SOURCES OF METHANE FOR MARINE GAS HYDRATE

4.1 Background

Although thermodynamic conditions for hydrate stability are satisfied throughout most of the world’s oceans, locations of gas hydrate are controlled by the availability of methane within the sediments. Most marine deposits of hydrate have been discovered along continental margins where methane is supplied by conversion of organic carbon in sediments or by migration of methane bearing fluids from deeper sources. The origin of the methane in recovered gas hydrate is predominantly biogenic [Kvenvolden, 1995] although specific locations (Gulf of Mexico, Black Sea, Guatemala) have a thermogenic or mixed origin for the methane [Kvenvolden, 1995, and references within]. An important question about the formation of marine gas hydrate is not the origin of the methane, but the mechanisms of methane supply. Two main mechanisms have been proposed. Production of methane by in situ conversion of carbon within the hydrate stability zone (HSZ) has been suggested for passive margins where high input of organic material occurs by sedimentation [Claypool and Kaplan, 1974; Paull et al., 1994]. Alternatively, methane may be produced remotely and subsequently focused into the HSZ by fluid flow. This mechanism is favoured at accretionary margins with large upward fluid flow [Hyndman and Davis, 1992].

During the last decade, several Ocean Drilling Program (ODP) Legs have been dedicated to the study of gas hydrates. Detailed seismic, core logging and downhole techniques have yielded estimates of the concentration and distribution of gas hydrates. This study focuses on two locations which represent archetypal hydrate settings. The Blake Ridge (ODP Leg 164) is a passive margin characterized by high organic content [Paull et al., 1996] and low fluid flow (0.2 mm yr\(^{-1}\)) [Egeberg and Dickens, 1999], where in situ biogenic production of methane is the favoured mechanism of methane supply. Recovered seismic velocity models, resistivity, and chlorinity measurements indicate small volumes of hydrate (4-8% of pore space) at the Blake Ridge (see Fig. 4.1). On the other hand, the Cascadia margin (ODP Leg 146) is an accretionary margin with low organic content [Westbrook et al., 1994] and high fluid flows in the range of 1-2 mm yr\(^{-1}\) [Wang et al., 1993; Hyndman et al., 1993].
Focusing of remotely produced methane by high fluid flows has been proposed [Hyndman and Davis, 1992] to explain the large hydrate volumes (20-30% of pore space) estimated from seismic velocity models, resistivity, and chlorinity measurements at this site (Fig. 4.1). A fundamental question raised by the observations from these two locations can be posed as follows: To what extent is the volume of hydrate related to the mechanism of methane supply?

The answer to this question is important for our understanding of hydrate formation. It also influences our expectations about the locations of large hydrate occurrences. To resolve this question numerical models are developed to predict the volumes of hydrate and free gas when the sources of methane are prescribed. Observations from ODP legs can then be used to test the predictions of the model and make inferences about the methane supply. A particularly useful observation is the porewater chlorinity, which is used in this study to establish plausible estimates for the methane sources. In addition, the predicted hydrate and free gas volumes are compared to those of previous studies, which use seismic velocity models and resistivity measurements to estimate volumes of hydrate and free gas. A range of models that are compatible with the observations is explored to make inferences about the mechanism of methane supply and associated volumes of hydrate and free gas. Constraints are imposed on a number of model parameters, including the fluid flow, methane concentration at depth and percentage of total organic carbon (TOC) available for methanogenesis.
Figure 4.1: Hydrate volumes (shown as a % of pore space) inferred from various measurements at the Cascadia Margin and Blake Ridge. Hydrate volumes at the Cascadia Margin are interpreted from seismic observations [Yuan et al., 1996], resistivity measurements [Hyndman et al., 1999], and chlorinity profiles [Yuan et al., 1996] to occupy 20-35% of the pore space. In contrast hydrate volumes at the Blake Ridge range between 4-8%, based on seismic observations [Holbrook et al., 1996; Paull et al., 1996], resistivity measurements [Collett and Ladd, 2000], and chlorinity profiles [Paull et al., 1996; Egeberg and Dickens, 1999].
4.2 Numerical Model

The model of Chapter 3 is applied to both the Blake Ridge and the Cascadia margin. Differences in these two settings are described by a set of model parameters that define the thermodynamic and geologic conditions near the seafloor for the specific site (see Table 4.1). Several sources of methane are considered at these two sites. A description of how the methane sources are modelled is given below.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Blake Ridge</th>
<th>Cascadia Margin</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>water depth</td>
<td>2781</td>
<td>1315</td>
<td>m</td>
</tr>
<tr>
<td>$T(0)$</td>
<td>seafloor temperature</td>
<td>3</td>
<td>3</td>
<td>°C</td>
</tr>
<tr>
<td>$G$</td>
<td>geothermal gradient</td>
<td>0.043*</td>
<td>0.060</td>
<td>°C/m</td>
</tr>
<tr>
<td>$\phi_o$</td>
<td>seafloor porosity</td>
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<td>0.60</td>
<td></td>
</tr>
<tr>
<td>$L$</td>
<td>depth scale for porosity</td>
<td>2000</td>
<td>1500</td>
<td>m</td>
</tr>
<tr>
<td>$S$</td>
<td>sedimentation rate</td>
<td>22</td>
<td>25</td>
<td>cm/kyr</td>
</tr>
<tr>
<td>TOC</td>
<td>weight % of average TOC</td>
<td>1.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>rate of methanogenesis</td>
<td>$3 \times 10^{-13}$</td>
<td>$3 \times 10^{-13}$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$D_m$</td>
<td>Diffusivity of methane</td>
<td>$0.87 \times 10^{-9}$</td>
<td>$0.87 \times 10^{-9}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_c$</td>
<td>Diffusivity of chlorine</td>
<td>$1.01 \times 10^{-9}$</td>
<td>$1.01 \times 10^{-9}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>free gas density</td>
<td>200</td>
<td>100</td>
<td>kg/m$^3$</td>
</tr>
</tbody>
</table>

Table 4.1: Site specific parameters for the Blake Ridge and Cascadia Margin. *Value was increased to compensate for the discrepancy between the theoretical BSR depth (500 m salt water; 533 m pure water) and the observed depth (451 m). Diffusivities of methane and chlorine are taken from Iversen and Jorgensen [1993] and Li and Gregory [1974] respectively, while the free gas density is computed at the base of the HSZ using the ideal gas law.

Deep sources of methane are modelled by imposing the methane concentration and upward fluid velocity as boundary conditions below the HSZ (see Fig. 4.2). These boundary conditions describe the composition and rate of pore water entering the system but the origin of the methane is not specified; it may be thermogenic, biogenic, or some mixture. Another boundary condition is imposed on the methane concentration at the seafloor, the concentration is required to match the vanishingly small value in the overlying ocean.

Our model for a deep methane source is conceptually similar to the model of Xu and
Ruppel [1999] but differs in several respects. The model of Xu and Ruppel [1999] describes the distribution of methane using an analytical solution to mass transport and energy equations. Their equations assume no sedimentation or compaction, so methane is transported solely by fluid advection and dispersion in a constant porosity medium. Their analysis yields a critical methane flux for hydrate to be present at the base of the hydrate stability zone.

Our model accounts for the effects of sedimentation and compaction. Transport of hydrate due to sedimentation represents an important flux of methane in our calculations. Sedimentation eventually buries hydrate below the HSZ, releasing methane upon dissociation. This process permits hydrate and free gas to co-exist at the base of the HSZ, even in the absence of a methane flux from depth. Because the time required to equilibrate the fluid with free gas and hydrate is quite short [Buffett and Zatsepina, 2000], supersaturated source fluids are not permitted. Consequently, we restrict our attention to fluids which are either saturated or undersaturated with respect to methane. Undersaturated fluids can form hydrate and free gas at the base of the HSZ because of the transport of methane (in hydrate) due to sedimentation. Other details of the model are given in Chapter 3. In this study we make predictions for volumes of hydrate and free gas, and profiles of the in situ chlorinity, methane concentration, and interstitial fluid velocity. The predicted hydrate volume and in situ chlorinity are used to estimate the pore water chlorinity recovered from the drill core. Direct comparison of the model predictions with observations from two well-studied hydrate locations constrain the supply of methane.

In situ production of methane is due to microbial conversion of carbon to methane within the sediments [Claypool and Kaplan, 1974]. This process is modelled by relating the production of methane to the loss of organic carbon [Berner, 1980; Davie and Buffett, 2001] (Fig. 4.2). Production of methane is restricted to depths below the sulfate reducing zone. Methane is produced locally in the sediments and transported by the effects of hydrate burial, fluid flow and chemical diffusion. The recycling of methane due to the burial and decomposition of hydrate are also included in the model. The model of Egeberg and Dickens [1999] also assumes in situ production of methane by prescribing a hydrate source function at shallow
depths. Our model extends this work by determining the hydrate source function from the concentration of dissolved methane in the pore water. In this way, hydrate production can be predicted in a thermodynamically consistent fashion.

The effects of sedimentation and compaction cause the fluid velocity to vary with depth in our calculations. This effect must be included in our description of a deep methane source, which relies on an imposed upward fluid velocity. To incorporate upward fluid flow in the model, an externally induced fluid velocity is superimposed on the flow generated by the effects of sediment compaction. Throughout this paper, values of fluid flow are reported as interstitial velocities at the seafloor.

Chlorinity measurements provide an important link between the model predictions and direct observations from the ODP sites. Model predictions of the in situ chlorinity profile and hydrate fraction are used to estimate the chlorinity of pore waters recovered from the drill core using the formulation of Hesse and Harrison [1981]. Profiles of the predicted pore water chlorinity may then be compared with drill core data from the two ODP sites. In our model, a constant chlorinity at the seafloor is assigned to reflect present-day seawater. The boundary condition on chlorinity at depth depends on the specific ODP site and mechanism of methane supply. In the case of a deep methane source at either site, the chlorine concentration at the lower boundary is set to the value measured at depth below the HSZ. In this approach the fluid entering the HSZ is assumed to have a deeper source of freshening. Based on ODP measurements, the chlorinity concentration is set to 511 mM at the Blake Ridge and to 375 mM at the Cascadia margin. A different boundary condition is adopted for in situ production, although this condition is only applied at the Blake Ridge. In this case, the chlorinity gradient is set to zero at the base of the model domain to reflect the approximately constant chlorinity data below the HSZ. By doing so, the extent of observed freshening is free to evolve and is governed by the recycling of hydrate at the base of the HSZ.
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Figure 4.2: Schematic representation of the two mechanisms of methane supply and their relationship to the methane phase diagram. The solid line indicates the equilibrium solubility of methane in seawater as a function of depth calculated by Zatsepina and Buffett [1997]. Hydrate is stable within the HSZ when the concentration of dissolved methane exceeds the solubility. Free gas forms below the HSZ when the solubility is exceeded. (A) Changes in the solubility with depth allow a saturated (and even an undersaturated) methane-bearing fluid to form hydrate as it migrates upwards into the HSZ. (B) Microbial production of methane locally within the sediments increases the concentration in the pore water until the solubility is exceeded and hydrate forms.
4.3 The Blake Ridge

The Blake Ridge is a sediment drift deposit characterized by relatively homogeneous sediments in both lateral and vertical directions. Previous studies have found little evidence of large scale fluid flow along localized faults in the basement or sedimentary column [Wood and Ruppel, 2000], so estimates of fluid flow are thought to represent the interstitial flow through the sediment matrix. The studies of Egeberg and Dickens [1999] use the ratio of bromide and iodide measurements to estimate an external upward fluid flow of 0.2 mm yr\(^{-1}\) at a depth of fully compacted sediment. This estimate is superimposed on the effects of downwards fluid flow induced by sedimentation, yielding a net upward interstitial fluid velocity of 0.08 mm yr\(^{-1}\) at the seafloor. (This velocity was calculated using the equation for the fluid velocity [Egeberg and Dickens, 1999, Appendix A] and a fully compacted sediment porosity of \(P^{\infty}=0.43\) [Egeberg and Dickens, 1999, personal communication]). This value is adopted as a starting estimate of the fluid velocity, although the interpretation of conserved elements (like Br\(^{-}\), I\(^{-}\), Cl\(^{-}\)) is significantly influenced by hydrate formation. By taking the ratio of Br\(^{-}\) to I\(^{-}\), Egeberg and Dickens [1999] attempt to minimize the influences of hydrate formation. However this ratio is also less sensitive to the effects of fluid flow, so the velocity inferred from Br\(^{-}\)/I\(^{-}\) is subject to large uncertainties.

We begin our examination of the Blake Ridge by considering the end-member case of a deep methane source. A deep methane source at Site 997 has been postulated on the basis of elevated bromide and iodide concentrations in the pore water [Egeberg and Barth, 1999] and their significantly older ages than the surrounding sediments [Fehn et al., 2000]. While the concentration of methane in the source fluid is unknown, we can safely assume that it does not exceed the local solubility. When the fluid is locally saturated, the methane flux is set by imposing the upward fluid velocity. In situ production is not permitted in this end-member case. The hydrate model is first evaluated using a saturated source fluid with a velocity of 0.08 mm yr\(^{-1}\). The resulting methane profile does not exceed the methane solubility within the HSZ (Fig. 4.3A), so hydrate does not form. The fluid is also undersaturated
below the HSZ so free gas is absent. Thus the predicted freshening is due solely to the 
chlorinity of the deep fluid source which we require to match the measured chlorinity at 
depth. Elsewhere, the agreement between the predicted and measured chlorinity is poor 
(see Fig. 4.3B). Similarly, the predicted profiles for bromide and iodide both underestimate 
the observations (Fig. 4.3C), even though the Br⁻/I⁻ ratios are reproduced (Fig. 4.3D). In 
summary, the model fails to produce hydrate in the HSZ, free gas below the HSZ, and is 
unable to explain the measured geochemical profiles.

Progressively increasing the upward fluid flow eventually causes hydrate and free gas to 
form. A similar result was obtained in the study of Xu and Ruppel [1999], which required a 
critical methane flux to form hydrate and free gas at the base of the HSZ. Our study yields 
a critical velocity of 0.26 mm yr⁻¹, which is over 3 times greater than the fluid velocity 
estimated by Egeberg and Dickens [1999]. Despite this discrepancy in fluid velocity, the 
model predictions are in good agreement with several observations (see Fig. 4.4). The 
predicted distribution of hydrate occupies up to 3.25% in the lowermost 300 m of the HSZ 
(Fig. 4.4C), which is in good agreement with previous estimates [Paull et al., 1996; Holbrook 
et al., 1996]. A layer of free gas is predicted to occupy approximately 2% of the pore space 
(Fig. 4.4D), also in agreement with previous estimates of free gas [Holbrook et al., 1996; 
Dickens et al., 1997]. In addition, the predicted chlorinity profile reproduces the observed 
chlorinity measurements (Fig. 4.4B), except for the near surface chlorinity maxima. The 
presence of a chlorinity maxima in the near surface chlorinity measurements is a pervasive 
feature of the three drill sites at the crest of the Blake Ridge [Paull et al., 1996]. This maxima 
may reflect the effects of vigorous hydrate production at shallow depths [Davie and Buffett, 
2001] and/or the variation of sea bottom chlorinity during sea level changes [Egeberg and 
Dickens, 1999]. Recall that for this study a constant chlorinity is applied at the seafloor, so 
that the model does not include the effects of variations in seawater chlorinity. The lowest 
value in the predicted chlorinity occurs at the base of the HSZ, indicating that decomposition 
of hydrate is producing localized freshening at the interface, similar to the observation of 
Egeberg and Dickens [1999].
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The previous cases assumed a source fluid which is saturated with methane. This represents the maximum allowable methane concentration in the fluid. However, the source fluids can be undersaturated, so the critical methane flux requires higher fluid velocities. For example, the critical fluid velocity exceeds 0.70 mm yr\(^{-1}\) when the methane concentration is 140 mM (75\% saturated). Below this velocity, hydrate forms within the HSZ but does not extend to the base of the HSZ because it is continually ablated by the upward migration of undersaturated fluids. These high fluid velocities result in poor matches of the observed chlorinity profiles.

An alternative source for methane at the Blake Ridge is due to microbial conversion of organic matter in the sediments [Paull et al., 1994]. We incorporate an in situ source and initially allow deep saturated fluids that move upward with a velocity of 0.08 mm yr\(^{-1}\). A key parameter in the model for the in situ source is the fraction of total organic carbon (TOC) which is available for conversion to methane. In the calculations below, we assume that 50\% of the average TOC at Site 997 is converted to methane. With this level of conversion, the methane saturation is exceeded at the base of the HSZ (Fig. 4.5A) for an upward fluid velocity of 0.08 mm yr\(^{-1}\). As a result, free gas is present below the HSZ (Fig. 4.5D). The observed chlorinity is in good agreement with the model results, including the maxima near the surface (Fig. 4.5B). Hydrate occupies up to 4.5\% of the pore space and is maximum at the base (Fig. 4.5C). These estimates of hydrate volume agree with estimates from previous field studies [Paull et al., 1994; Holbrook et al., 1996], although the model predicts a small volume of hydrate (< 2\%) above 200 m, which is not evident in these field studies. A deep layer of free gas is predicted below the HSZ, which occupies up to 3\% of the pore space, in good agreement with volumes suggested in previous studies [Holbrook et al., 1996; Dickens et al., 1997].

The influence of undersaturated fluids at depth are investigated by progressively lowering the methane concentration at the base of the model. When the methane concentration is above 95 mM (50\% saturated) the predicted chlorinity profile still reproduces the observations and the predicted hydrate volume is unaltered. The only significant difference is a
CHAPTER 4. SOURCES OF METHANE FOR MARINE GAS HYDRATE

distinct base to the free gas layer at 820 m due to the imposed undersaturation at depth. This suggests that the methane concentration of the deep fluid is not as important in this case.
Figure 4.3: Results from the Blake Ridge calculated using a saturated deep methane source with an upward fluid velocity of 0.08 mm yr\(^{-1}\) [Egeberg and Barth, 1999; Egeberg and Dickens, 1999]. (A) The pore water methane concentration (solid) does not exceed the equilibrium solubility (dashed) anywhere in the HSZ. Consequently, hydrate and free gas are absent. (B) The measured drill core chlorinity (squares) is poorly matched by the predicted chlorinity (solid) except where the value of chlorinity is imposed at depth. (C) The predicted profiles (solid) underestimate the bromide (squares) and iodide (triangles) measurements. (D) The predicted \(\text{Br}^-/\text{I}^-\) profile is in good agreement with the \(\text{Br}^-/\text{I}^-\) observations (triangles).
Figure 4.4: The best match to the chlorinity observations at the Blake Ridge, assuming a deep methane source, is obtained with a fluid velocity of 0.26 mm yr\(^{-1}\). (A) The methane concentration matches the solubility throughout the HSZ except for the upper 100 m since the concentration is set to zero at the seafloor. (B) The predicted chlorinity profile (solid) agrees well with the measured chlorinity (squares) except near the surface, where a peak occurs in the observations. (C) Hydrate occupies upwards of 3% of the pore space from a depth of 180 m to the base of the HSZ. (D) A deep layer of free gas is present below the HSZ occupying up to 2% of the pore space.
Figure 4.5: Good agreement with the chlorinity observations at the Blake Ridge is also obtained with in situ methane production and an upward fluid velocity estimated from bromide/iodide profiles (0.08 mm yr\(^{-1}\)) [Egeberg and Barth, 1999; Egeberg and Dickens, 1999]. (A) The methane concentration matches the solubility throughout the HSZ due to biogenic methane production locally within the sediments. (B) The predicted chlorinity profile (solid) agrees well with the measured chlorinity (squares) and reproduces the near surface maxima. (C) Hydrate occupies upwards of 5% of the pore space from a depth of 50 m to the base of the HSZ. (D) A deep layer of free gas is present below the HSZ, occupying up to 3% of the pore space.
4.4 The Cascadia Margin

The Cascadia margin represents an accretionary margin setting where the effects of fluid flow are expected to be important. In particular, we use data from ODP Leg 146, Site 889 which was drilled into the accretionary prism off the west coast of Vancouver Island. Site 889 was located approximately 18 km landward from the deformation front, on the crest of the prism. In contrast to the Blake Ridge, the Cascadia margin has a lower organic carbon content (averages < 1.0% TOC) and is characterized by pervasive upward fluid migration. Previous studies suggest that methane rich fluids are expelled from incoming sediments of the subducting oceanic plate [Hyndman and Davis, 1992]. As the upwelling methane-rich fluids migrate into the HSZ, a reduction in solubility causes hydrate to form. Fluid velocities of 1–2 mm yr\(^{-1}\) at Site 889 have been inferred from regional fluid expulsion models [Wang et al., 1993; Hyndman et al., 1993]. The effects of a deep methane source are investigated with and without in situ production to draw inferences about the relative importance of methane sources in accretionary settings.

A deep source of methane is first considered in the absence of in situ production. Model results are shown in Fig. 4.6 for the case of an upwelling methane saturated fluid with a velocity of 1 mm yr\(^{-1}\). The predicted distribution of hydrate extends from a depth of 50 m below the seafloor to the base of the HSZ. The hydrate volume increases with depth and reaches 5% of the pore space at the base of the HSZ. A layer of free gas is predicted below the HSZ, occupying 6% of the pore space. However, the large fluid flow causes a poor match between the predicted and observed chlorinity profiles as shown in Fig. 4.6B. The large fluid flow causes a steep curvature in the chlorinity profile that poorly reproduces the observations.

The fluid velocity is progressively lowered until a good match with the chlorinity observations is obtained. An upward fluid velocity of 0.42 mm yr\(^{-1}\) is used to obtain the chlorinity results shown in Fig. 4.7B. This velocity is only marginally larger than the critical velocity of 0.40 mm yr\(^{-1}\) which is the minimum value required to form hydrate at the base of the
HSZ. However, the velocity of 0.42 mm yr$^{-1}$ is over a factor of 2 smaller than the velocity estimated for the Cascadia margin based on accretionary thickening. Fig. 4.7C shows that hydrate is present between 100 m and the base of the HSZ, occupying a small fraction of the pore space (2% at the base). This estimate of hydrate is substantially lower than the 20–30% hydrate volume inferred from previous studies [Yuan et al., 1996; Hyndman et al., 1999]. We return to this point in the discussion. In addition, a thick layer of free gas is formed, occupying 2% of the pore space (Fig. 4.7D). On the other hand, a thin layer of free gas has been inferred at Site 889 based on MCS and VSP data [Singh and Minshull, 1994; Yuan et al., 1996]. The thin gas layer can be explained as a transient feature of the model, which occurs as the gas layer begins to grow from the BSR downwards. It is also possible to reproduce the thin layer of free gas if the upwelling fluid is undersaturated. However, undersaturated source fluids require higher velocities to maintain hydrate at the base of the HSZ, and this causes a poor match to the chlorinity observations. An alternative explanation may involve migration of gas bubbles through the sediments. If gas bubbles migrate upward faster than the rate of burial by sedimentation, then we would expect a narrow layer of gas bubbles. Conversely, a deep layer of gas bubbles, like that observed at the Blake Ridge, suggests that gas bubbles are held in place by the effects of surface tension and buried by sedimentation [Henry et al., 1999].

Allowing for in situ production at the Cascadia margin reduces the demand on the deep fluid source. As an example, we investigate a scenario where 50% of the TOC (1% dry wt seds) at Site 889 is converted to methane. In this case, a fluid velocity of 0.35 mm yr$^{-1}$ is sufficient to reproduce the chlorinity observations (Figure 4.8B). In addition, hydrate occupies a greater fraction of the pore space (~ 5%) over a larger depth interval (Figure 4.8C). The volume of free gas is also greater than it is for the case of a deep source and occupies upwards of 6% of the pore space (Figure 4.8D). The boundary condition on the dissolved methane at depth is progressively lowered to determine the minimum methane concentration that could explain the observations. An undersaturated fluid of 95 mM reproduces the chlorinity observations, while the hydrate distribution and volume are very similar to that
of the saturated case. The free gas still occupies 6% of the pore space but a distinct base develops at a depth of 440 m.
Figure 4.6: Results from the Cascadia Margin using a saturated deep methane source with an upward fluid velocity estimated from accretionary thickening models (1.0 mm yr\(^{-1}\)) \([\text{Wang et al., 1993; Hyndman et al., 1993}]\). (A) The pore water methane concentration (solid) matches the equilibrium solubility throughout the HSZ except near the seafloor. (B) The measured chlorinity (squares) is poorly matched by the predicted chlorinity (solid) throughout the HSZ due to the high fluid velocity. (C) Hydrate occupies up to 5\% of the pore space from a depth of 50 m to the base of the HSZ. (D) A thick layer of free gas occupies up to 3\% of the pore space below the HSZ.
Figure 4.7: The best match to the chlorinity observations at the Cascadia margin, assuming a deep methane source, is obtained with a fluid velocity of $0.42 \text{ mm yr}^{-1}$. This fluid velocity is only marginally greater than the critical velocity needed to form both hydrate and free gas at the base of the HSZ. (A) The pore water methane concentration (solid) matches the equilibrium solubility throughout the HSZ except near the seafloor. (B) The measured chlorinity (squares) agrees well with the predicted chlorinity (solid) throughout the HSZ. (C) Hydrate occupies up to 2% of the pore space from 100 m depth to the base of the HSZ. (D) A thick layer of free gas occupies less than 1% of the pore space below the HSZ.
Figure 4.8: Good agreement with the chlorinity observations at the Cascadia Margin is also obtained with in situ methane production and an upward fluid velocity of 0.35 mm yr$^{-1}$. (A) The pore water methane concentration (solid) matches the equilibrium solubility throughout the HSZ except near the seafloor. (B) The measured chlorinity (squares) agrees well with the predicted chlorinity (solid) throughout the HSZ. (C) Hydrate occupies a greater fraction of the pore space (up to 5%) over a larger depth interval from 40 m to the base of the HSZ. (D) A thick layer of free gas occupies 3% of the pore space below the HSZ.
4.5 Discussion

We have used a numerical model to study the influence of the methane supply on observable properties of hydrate deposits. The results show that observations at both active and passive margins can be reproduced equally well with either in situ production or the migration of methane from deep sources. In order to distinguish between the sources of methane at specific locations, we must either appeal to measurements of physical parameters to constrain the model or we must introduce additional data (e.g. sulfate observations) to complement the chlorinity observations.

Observations of chlorinity, hydrate and free gas from Site 997 at the Blake Ridge can be explained by a deep source with an upward fluid velocity of 0.26 mm yr\(^{-1}\) or by an in situ source with 50% conversion of organic carbon and an upward fluid velocity of 0.08 mm yr\(^{-1}\). Although the model parameters required for the in situ source are in better agreement with previous parameter estimates, we cannot discount the deep source due to the uncertainties in these model parameters. Ratios of Br\(^-\)/I\(^-\) were used to estimate the fluid velocity at Site 997 in an attempt to minimize the influence of hydrate production on the profiles. Unfortunately, a wide range of fluid velocities can reproduce the observations because the Br\(^-\)/I\(^-\) ratio is less sensitive to fluid flow. Distinguishing between methane sources using numerical models requires additional information. A potential resolution of the methane source is suggested by a comparison of the methane fluxes for the two competing sources. Shown in Table 4.2 are the methane fluxes at the seafloor and base of the HSZ for the two best fit cases. Of particular interest is the difference between the methane fluxes at the seafloor for the two sources because this flux can be related to the sulfate flux at the base of the sulfate reducing zone. Use of sulfate measurements in conjunction with chlorinity observations may be sufficient to distinguish between methane sources, although this will require the incorporation of a thin sulfate reducing zone into the model.

Fluid velocities of 1–2 mm yr\(^{-1}\) have previously been reported at the Cascadia margin [Wang et al., 1993; Hyndman et al., 1993]. However, these values result in poor agreement
between the predicted and observed pore water chlorinity at Site 889. Much better agreement is obtained using lower fluid velocities. For the end-member case of methane supply from a saturated deep source, the best fit to the chlorinity is obtained with a fluid velocity of 0.42 mm yr\(^{-1}\), which is only slightly larger than the critical velocity of 0.40 mm yr\(^{-1}\) (Fig. 4.7B). We speculate that regional variations in upward fluid flow could result in fluid velocities less than the critical value and thus a patchy distribution of the BSR. We emphasize that fluid velocities less than the critical value still produces hydrate within the HSZ but hydrate and free gas cannot be sustained at the base of the HSZ. An alternative explanation of the chlorinity observations at Site 889 requires a combination of in situ methane production and an upward fluid velocity of 0.35 mm yr\(^{-1}\) as was shown in Fig. 4.8B. Both of these explanations entail fluid velocities that are over a factor of 2 smaller than previous estimates. This discrepancy may be related to the possibility that a large fraction of the fluid expelled from an accretionary prism is channelled along fractures, yielding lower estimates for the pervasive fluid flow in shallow sediments.

Regardless of the methane supply, the predicted volume of hydrate is significantly lower than the volume estimated by previous studies at Site 889. Hydrate volumes upwards of 30% of the pore space have been proposed on the basis of seismic velocity analysis and interpretation of resistivity measurements [Yuan et al., 1996; Hyndman et al., 1999]. These large hydrate volumes can be reproduced with a deep methane source (Fig. 4.9A), but

<table>
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<th>Location</th>
<th>Flux</th>
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<th>In situ source (mol/m(^2) kyr)</th>
</tr>
</thead>
<tbody>
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<td>Diffusive</td>
<td>17.98</td>
<td>32.28</td>
</tr>
<tr>
<td>Base of HSZ</td>
<td>Hydrate</td>
<td>23.62</td>
<td>30.13</td>
</tr>
<tr>
<td>Base of HSZ</td>
<td>Recycling</td>
<td>8.09</td>
<td>8.00</td>
</tr>
<tr>
<td>Base of HSZ</td>
<td>Bubble</td>
<td>15.53</td>
<td>22.13</td>
</tr>
<tr>
<td>Base of HSZ</td>
<td>Advective</td>
<td>33.67</td>
<td>9.74</td>
</tr>
</tbody>
</table>

Table 4.2: Methane fluxes at the Blake Ridge. The flux at the base of the HSZ is decomposed into four components. The downward flux of hydrate is balanced by the recycled and bubble components. The advective component is due to fluid flow below the HSZ.
only if sedimentation rates are small. The results shown in Fig. 4.9 assume a methane-saturated fluid with an upward velocity of 1.3 mm yr$^{-1}$ and a sedimentation rate of 5 cm kyr$^{-1}$. A decrease in sedimentation rate means that hydrate spends longer within the HSZ and therefore allows for greater accumulations. The model predicts a large jump in chlorinity at the base of the HSZ due to dissociation of large volumes of hydrate upon recovery of the core (Fig. 4.9B). However, this large jump is not evident in the chlorinity observations. In addition, the large fluid velocity required to produce the large hydrate volumes yields a very poor match to the measured chlorinity in the shallow sediments as shown in Fig. 4.9B. The absence of the chlorinity jump at the base of the HSZ and the poor match within the HSZ, implies lower volumes of hydrate at this locale. The hydrate volumes predicted by the model that best reproduces the chlorinity observations are only 2-5% of the pore space. Interestingly, hydrate volumes of 3% have been reported at Site 889 from temperature measurements of drill core upon recovery [Kastner et al., 1995]. The offset in chlorinity caused by dissociating a hydrate volume of 3% is small enough to be contained within the scatter of the chlorinity measurements, similar to the model results of Figs. 4.7B, 4.8B.

Predictions of lower hydrate volumes at accretionary margins have an important consequences for global hydrate estimates. Previous studies often assume that hydrate in high fluid flow settings (e.g. accretionary margins) occupies 50% porosity at the base of the HSZ. Our modelling suggests that this estimate may be over a factor of 10 too large, and consequently the amount of hydrate estimated in high fluid flow settings may have been substantially overestimated. Reducing the pore fluid migration model estimates of Gornitz and Fung [1997] would result in global hydrate estimates closer to the volumes predicted by MacDonald [1990] and Kvenvolden [1988].

Models provide a means of estimating the geographic distribution of hydrate if the required parameters are known. Parameters required by the model include the fluid flow, organic matter accumulation, sedimentation rates, porosity, water depth, temperature at the seafloor, and geothermal gradient. Since many of these parameters are available in global
databases, it is feasible to use numerical models to refine estimates of the global hydrate inventory. Perhaps the most serious uncertainty at the present time involves the upward fluid velocity. Predictions with no upward fluid velocity would yield a lower bound on the hydrate abundance. However, these results may still be useful in identifying undiscovered locations of large hydrate accumulations.

Figure 4.9: Large hydrate volumes are obtained at the Cascadia margin using a saturated deep methane source with a large upwards fluid velocity (1.3 mm yr\(^{-1}\)) and a small sedimentation rate (5 cm kyr\(^{-1}\)). (A) Hydrate occupies up to 30% of the pore space from 50 m depth to the base of the HSZ. (B) The chlorinity observations (squares) are poorly reproduced by the predicted chlorinity profile (solid). There is a large jump in the predicted chlorinity profile at the base of the HSZ, due to the presence of large hydrate volumes, which is not observed in the measurements. In addition, chlorinity measurements in the HSZ are poorly matched by the steep curvature of the predicted profile.
4.6 Summary

Two distinct geological settings were studied to determine whether a comparison of observations and models can be used to distinguish between alternative mechanisms of methane supply. Model results showed that either in situ production of methane or migration of methane from deep sources can reproduce the pore water chlorinity measurements and estimated volumes of hydrate and free gas. Therefore to distinguish between sources of methane, we require either tighter constraints of physical model parameters or additional data to complement the chlorinity observations.

Good agreement with observations at the Blake Ridge (passive margin) is found for a saturated deep methane source with an upward fluid velocity of 0.26 mm yr\(^{-1}\). If the fluid velocity is restricted to 0.08 mm yr\(^{-1}\), based on estimates of Egeberg and Dickens [1999], then the in situ source must convert 50% of the organic carbon. A potential method of differentiating between the methane sources is suggested by differences in the methane flux at the seafloor (see Table 4.2). Sulfate measurements can provide an additional data constraint by relating the methane and sulfate fluxes at the base of the sulfate reducing zone. However, use of sulfate measurements would require the incorporation of a thin sulfate reducing zone into the model.

The model also reproduces observations at the Cascadia Margin (active margin). The best match to the chlorinity observations for the deep methane source was obtained with a fluid velocity of 0.42 mm yr\(^{-1}\), which is only slightly larger than the critical velocity of 0.40 mm yr\(^{-1}\). In this case, hydrate occupied a maximum of 2% of the pore space at the base of the HSZ. This hydrate volume is much lower than the previous estimates of 20–30% [Yuan et al., 1996; Hyndman et al., 1999] but agrees well with hydrate volumes of 3% inferred from drill core temperature measurements [Kastner et al., 1995]. Free gas occupies 2% of the pore space below the HSZ. Addition of biogenic methane production allowed further reduction of the upward fluid velocity while still reproducing the chlorinity observations. In this case hydrate was distributed through a larger vertical region of the HSZ and occupied up to 5%
of the pore space, over double that of the upwelling case. In addition, free gas occupied 6% of the pore space below the HSZ. Undersaturated fluids of 95 mM were able to reproduce chlorinity observations, while yielding similar hydrate and free gas distributions.
CHAPTER 5

A steady state model for marine hydrate formation: Constraints on methane supply from pore water sulfate profiles

In this chapter a steady state model is developed to describe the formation of hydrate below the seafloor. The model includes the sulfate reducing zone (SRZ), which allows sulfate measurements to be used in conjunction with chlorinity data to better constrain the mechanism of methane supply at hydrate locations. The steady state model is applied at ODP Site 997 to resolve the source of methane at the Blake Ridge. Sulfate measurements rule out a shallow source of methane directly below the SRZ because the predicted sulfate profile overestimates the measurements by a factor of 2 or more. Although a deep source of methane reproduces the main features of the sulfate and chlorinity data when the upward fluid velocity is 0.25 mm/yr, the deep source fails to reproduce the increased freshening observed between 200–450 m. An in situ methane source (located in the lower part of the HSZ) together with an incoming methane bearing fluid at 0.23 mm/yr gives the best fit to both the sulfate and chlorinity data. In addition, the predicted sulfate profile indicates that the process of anaerobic methane oxidation is the primary pathway of sulfate depletion at the Blake Ridge.


5.1 Background

Hydrates of methane gas form in marine sediments under suitable pressure and temperature when the dissolved methane concentration exceeds the local solubility [Sloan, 1990; Claypool and Kaplan, 1974]. Persistence of the hydrates over time requires the dissolved methane concentration to remain at the local solubility despite persistent losses of methane due to diffusion and advection. Such losses demand a continual supply of methane, which is thought to be maintained by bacterial conversion of organic carbon [Kvenvolden, 1995], although the depth of this conversion is not well established. Methane is also consumed by bacteria in shallower sediments through a process known as anaerobic methane oxidation [Valentine and Reeburgh, 2000; Boetius et al., 2000]. At these shallow depths, the methane concentration cannot be sustained at the level required for hydrate stability, so hydrates are normally absent from this region. A schematic illustration of the methane concentration through a typical hydrate occurrence is shown in Figure 5.1. Methane sources maintain the concentration at the local solubility in deeper sediments, allowing hydrates to form, whereas methane oxidation causes the concentration profile to deviate from the local solubility in shallower sediments.

The occurrence of hydrate is therefore directly related to the methane concentration in the sediment pore-fluid. However, measurements of the interstitial dissolved methane concentration are usually unreliable because of sampling difficulties. In fact, Dickens et al. [1997] estimate that as much as 99% of the original interstitial methane concentration may be lost to out-gassing during core recovery. An alternative approach is to use other, more reliable, observations (such as chlorine and sulfate concentrations) as a proxy for the methane concentration. These observations can be related to the interstitial methane concentration using numerical models.

This approach was used by Borowski et al. [1996] and Dickens [2001b] to predict the methane flux entering the base of the sulfate reducing zone (SRZ). Borowski et al. [1996] fit linear profiles to the sulfate data and equated the molar fluxes at the sulfate-methane
interface, as required by the process of anaerobic methane oxidation. A subsequent study of Borowski et al. [1999] showed that occurrences of hydrate correlate with steep sulfate gradients (and hence large methane fluxes). However, no quantitative links between the hydrate volume and associated methane flux were established in these studies. Chlorinity measurements are another widely used proxy for detecting hydrate occurrences [Hesse and Harrison, 1981; Kastner et al., 1995; Paull et al., 1996]. Measurements are commonly interpreted by assuming that the initial in situ chlorinity is equal to the value of seawater. In contrast, Davie and Buffett [2002] used numerical models to interpret chlorinity measurements in terms of the source of methane supply. They showed that the chlorinity measurements and hydrate/free gas volumes at the Blake Ridge can be reproduced with either in situ biogenic methane production or upward migration of methane bearing fluids from deeper sources. In order to distinguish between the two mechanisms of methane supply, additional constraints on the velocity and composition of the fluids at depth are required.

Use of sulfate measurements in modelling studies provides an alternative means of distinguishing between the sources of methane because the depth of methane production influences the interstitial methane concentration and thus the sulfate flux at the base of the SRZ. The relationship between the methane and sulfate profiles is shown schematically in Figure 5.2. In this chapter, the sulfate reducing zone is incorporated into a steady state model for the formation of hydrate below the seafloor. The model for the sulfate concentration is coupled to the available organic carbon and the interstitial methane concentration through the processes of sulfate reduction and anaerobic methane oxidation. The predicted sulfate profile is compared with sulfate measurements from the Blake Ridge and Cascadia Margin to draw inferences about the specific mechanisms of methane supply that operate at these sites. Measured sulfate profiles, used in conjunction with the chlorinity data, provide two separate constraints on the quantity and distribution of hydrate and free gas in the sediments.
CHAPTER 5. STEADY-STATE MODEL

Figure 5.1: Schematic illustration of the pore-water methane profile at Site 997 and the seismic section across the crest of the Blake Ridge (adapted from Dickens [2001a]; Paull et al. [1996]). Hydrate forms in the deeper sediments as the continual supply of methane sustains the methane concentration at the solubility. The methane concentration deviates from the solubility in the shallow sediments as anaerobic methane oxidation (operating at the base of the SRZ) depletes the methane concentration.
Figure 5.2: Schematic representation of the relationship between the methane and sulfate concentration above a zone of gas hydrates. The sulfate reducing zone (SRZ) extends from the seafloor to a depth where the sulfate concentration vanishes (22 m at Site 997). Below this depth, methane production increases the methane concentration in the pore water (solid line) until the solubility (dashed line) is reached, allowing the formation of hydrate. The sulfate and methane concentration are related by the process of anaerobic methane oxidation (equation (5.20)) that takes place at the sulfate-methane interface (SMI).
5.2 Governing Equations

We adopt the numerical model of Chapter 3 to incorporate the influences of a sulfate reducing zone. The governing equations for this model were derived through the application of conservation of mass to a continuum mixture of sediment, seawater, and a separate methane-bearing component (either hydrate or methane bubbles) in a reference frame fixed to the seafloor. Time-dependent differential equations were obtained for the evolution of the hydrate and methane bubble fractions, metabolizable carbon, methane and chlorine concentrations within marine sediments.

The equations describing the hydrate volume $h$ (within the HSZ) and methane bubble volume $b$ (below the HSZ) are given by

$$\frac{\partial h}{\partial t} + \frac{1}{\phi} \nabla \cdot [v_s \phi h] = \Phi_h, \quad (5.1)$$

and

$$\frac{\partial b}{\partial t} + \frac{1}{\phi} \nabla \cdot [v_s \phi b] = \Phi_b, \quad (5.2)$$

where $\Phi_h$ and $\Phi_b$ are the volumetric rates of hydrate and methane bubble growth, and $v_s$ is the sediment velocity relative to the seafloor. The hydrate and methane bubbles are assumed to be trapped within the sediments and transported with velocity $v_s$. The porosity $\phi(z)$ as a function of depth below the seafloor can be approximated by

$$\phi(z) = \phi(0) \exp(-z/L), \quad (5.3)$$

where $\phi(0)$ is the porosity at the seafloor and $L$ is a characteristic length scale for compaction.

As new sediments are added to the seafloor, older sediments are buried and compacted. Consequently the sediment velocity decreases with depth. Under steady sedimentation, the solid velocity is obtained from the equation for conservation of sediment. When the equations are restricted to one spatial dimension (varying only with depth $z$), the steady solution for
\(v_s\), can be written as

\[
v_s(z) = \left(1 - \phi(0) \right) \frac{1 - \phi(z)}{1 - \phi(0)} \hat{S} \hat{z},
\]

(5.4)

where \(\hat{S}\) is the sedimentation rate at the seafloor and \(\hat{z}\) is the unit vector in the vertical direction (positive into the sediments). Fluid flow within the sediment column depends on effects of compaction and external sources of fluid. The fluid flow due to compaction is determined from the decrease in sediment porosity, according to (5.3), which induces fluid flow by squeezing out the pore fluid [Bonham, 1980; Hutchinson, 1985]. Imposed on this fluid velocity are flows driven by other mechanisms, which may include fluid expulsion during accretionary thickening or thermally driven fluid flow. The fluid transport velocity can be written as the sum of compaction and external sources of fluid as

\[
u_f(z) = (1 - \phi(0)) \left[ \frac{\phi(L)}{1 - \phi(L)} - \frac{\phi(z) h(z)}{1 - \phi(z)} \right] \hat{S} + \phi(L) v_{ext} \hat{z}.
\]

(5.5)

The first term describes the fluid flow induced through sediment compaction, while the second term refers to an external source of fluid with a velocity imposed at the depth \(z = L\).

The growth of hydrate and methane bubbles is controlled by the local thermodynamic conditions in the sediments. The rate of hydrate growth can be described as a first-order model

\[
\Phi_h = R_h (c_m - c_{eq}),
\]

(5.6)

where \(c_m\) is the dissolved concentration of methane and \(c_{eq}\) is the local solubility (or equilibrium concentration), both expressed as mass fractions of the pore fluid. Hydrate forms when the concentration of the dissolved methane in the pore fluid exceeds the solubility of methane in seawater. Conversely, a dissolved methane concentration less than the solubility causes hydrate to dissociate if hydrate is present. The reaction rate constant \(R_h\) describes the time required to re-establish equilibrium when \(c_m \neq c_{eq}\). A value of \(R_h\) is adopted such that the adjustment to equilibrium is much faster than the mass transport processes. An analogous first-order model, with rate constant \(R_b\), is used to describe the rate of bubble growth below the HSZ.
CHAPTER 5. STEADY-STATE MODEL

The solubility of methane was derived in Chapter 2 based on the results of Zatsepina and Buffett [1997]. Phase equilibrium calculations show that the solubility of methane in seawater increases from the seafloor to the base of the HSZ. Within the HSZ, the solubility $c_{eq}$ is controlled mainly by the effects of temperature and can be expressed as

$$c_{eq}(T) = c_{eq}(T_3) \exp\left(\frac{(T - T_3)}{\tau}\right), \quad (5.7)$$

where $c_{eq}(T_3)$ is the solubility at the three-phase equilibrium temperature $T_3(P)$ and $\tau = 14.4^\circ C$ is obtained from a least-square fit of (5.7) to the results of Zatsepina and Buffett [1997]. Below the stability zone, the solubility is approximately constant and equal to the solubility at three-phase equilibrium

$$c_{eq}(z) = c_{eq}(T_3), \quad (5.8)$$

because increases in pressure and temperature have counter-acting effects on $c_{eq}$. The solubility within the HSZ is related to the depth $z$ by adopting a temperature profile that increases linearly with $z$ according to

$$T(z) = T(0) + Gz, \quad (5.9)$$

where $T(0)$ is the seafloor temperature and $G$ is the local geothermal gradient.

The concentration of dissolved methane in the pore fluid controls the volume and distribution of hydrate. Any methane in excess of the solubility causes hydrate formation according to (5.6). Growth of hydrate depletes the dissolved methane until equilibrium is re-established. Potential methane sources include biogenic production of methane from organic matter and the upward migration of methane from deeper sources. The rate of biogenic production of methane is denoted as $\Phi_m$, while the upward migration of methane from deeper sources is imposed as a methane flux at the base of the computational domain. The evolution of methane in pore fluid is described by

$$\phi(1 - h) \frac{\partial c_m}{\partial t} + \mathbf{u}_f \cdot \nabla c_m = \nabla \cdot [D_m \phi(1 - h) \nabla c_m] + \frac{\rho_h}{\rho_f} (c_m - c_h) \phi \mathbf{u}_f + \Phi_m, \quad (5.10)$$

where dissolved methane is transported by the effects of fluid advection and chemical diffusion.
in the pore fluid. The production of hydrate $\Phi_h$ removes methane from the pore fluid because the concentration $c_h$ of methane in hydrate greatly exceeds the dissolved concentration $c_m$. The biogenic production $\Phi_m$ appears as a methane source, which is related to the organic carbon in the sediments.

A representative reaction describing the biogenic production of methane is given by Paull et al. [1994] in which 2 mol of organic carbon (CH$_2$O) is converted to 2 mol of methane (CH$_4$)

$$2\text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2 \quad (5.11)$$

$$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}. \quad (5.12)$$

The amount of organic carbon available to methanogens is expressed as a weight percent of carbon relative to the dry weight of sediment. The available organic carbon is denoted by $\alpha$. The value of $\alpha$ is a fraction of the total organic carbon (TOC). The available carbon is buried with the sediments and depleted by the conversion to methane. The rate of conversion to methane is described by a rate constant $\lambda_m$, such that $\lambda_m^{-1}$ represents the time scale for conversion of the available organic carbon. The evolution of available organic carbon is described by

$$\frac{\partial \alpha}{\partial t} = -\mathbf{v_s} \cdot \nabla \alpha - \lambda_m \alpha. \quad (5.13)$$

Methane production is directly linked to the loss of organic carbon. Consequently, the rate of methane production can be written as

$$\Phi_m = \left(\frac{16\rho_s(1 - \phi)}{30\rho_f}\right)\lambda_m \alpha, \quad (5.14)$$

where the ratio of molar masses of CH$_4$ to CH$_2$O (i.e. 16/30) is needed to convert the units of $\Phi_m$ into a mass fraction of the liquid (per unit time).

Anomalous chlorine measurements are commonly associated with hydrate deposits [Hesse and Harrison, 1981; Kastner et al., 1995; Paull et al., 1996] and thus provide an important constraint on the model. The in situ chlorinity is altered by the combined effects of hydrate growth, fluid advection and chemical diffusion of chlorine ions through the pore fluid.
Hydrate growth excludes chlorine ions from the hydrate structure, causing an increased concentration of chlorine in the pore fluid. Conversely the dissociation of hydrate releases fresh water from its structure, resulting in a freshening of the pore fluid. The governing equation for the in situ chlorine concentration $c_c$ is given by

$$\phi(1-h) \frac{\partial c_c}{\partial t} + \mathbf{u} \cdot \nabla c_c = \nabla \cdot \left[ D_c \phi(1-h) \nabla c_c \right] + \frac{\rho_h}{\rho_f} c_c \phi \Phi_h. \quad (5.15)$$

Hesse and Harrison [1981] relate the observed chlorine concentration $c_{c}^{obs}$ from drill cores to the in situ concentration and the hydrate volume by

$$c_{c}^{obs} = (1-h) c_c, \quad (5.16)$$

where $h$ and $c_c$ are described by (5.1) and (5.15). The relationship in (5.16) provides the quantitative link between the model predictions and chlorinity observations.

Considerable simplifications to the governing equations are possible if the dependent variables $h$, $b$, $c_m$, $c_c$, and $\alpha$ do not vary laterally. Although this is not strictly true, lateral variations tend to be small compared with the vertical variations. Consequently, we adopt a one-dimensional approximation of the governing equations in which the spatial derivatives are restricted to vertical derivatives. The resulting governing equations were solved numerically in Chapter 3 to determine the evolution of the model variables below the seafloor.

An important finding of this study was that solutions approached steady states after approximately 5-10 Myrs, which indicates that the hydrate volume at a particular location is not dependent on the accumulation time after an initial transient interval. The model was applied at the Blake Ridge to show that chlorinity measurements and hydrate/free gas observations from Site 997 could be reproduced with an in situ biogenic methane source when 80% or more of the TOC is available for conversion. A subsequent investigation in Chapter 4 used chlorinity measurements and hydrate/free gas observations to show that upward migration of methane bearing fluid from a deeper source could also reproduce the measurements from the Blake Ridge. The current study distinguishes between these two mechanisms of methane supply at the Blake Ridge by including sulfate measurements in the
model. Existence of a steady state solution allows the time dependence of equations (5.1), (5.2), (5.10), (5.13), and (5.15) to be eliminated. The resulting equations are much more efficient to solve, especially when solutions on finely spaced grids are required. (This is the case when a narrow sulfate-reducing zone is included in the model).

5.3 Steady State Model

Time dependent solutions of the numerical model indicate that the hydrate volume and the associated chlorinity signature become independent of the accumulation time after several million years. By adopting a steady state assumption, the partial differential equations in section 5.2 are converted to ordinary differential equations with respect to depth $z$. The time scale needed to achieve the steady state is typically on the order of millions of years using initial conditions where no methane is initially present in the sediments. Somewhat shorter time scales are required to achieve a steady state when some initial distribution of methane is present in the sediments. In applying the steady state equations the processes causing hydrate formation are assumed to have operated consistently over several million years. Although this is not true at all hydrate locations, passive continental margins, such as the Blake Ridge, have been relatively stable over the last few million years.

The steady state approximation is obtained by setting $\partial/\partial t$ to 0 in equations (5.1), (5.2), (5.10), (5.13), and (5.15). This simplification yields a set of ordinary differential equations (with respect to $z$) to describe the process of hydrate formation below the seafloor. Solutions to these equations can be obtained on finely spaced grids without some of the attendant problems that occur in the time-dependent model (notably stiff equations and short time steps). As a result, computational time is significantly reduced from the time-dependent case. This increased computational efficiency facilitates the incorporation of a sulfate reducing zone, and makes it feasible to apply the model to the problem of global hydrate estimation, or data inversion using formal inverse methods.

Under steady state conditions, the production of hydrate balances the loss of hydrate due to burial and compaction according to (5.1). As a result, the steady state equation for
the hydrate distribution, which is obtained from (5.1), can be used to eliminate the hydrate production term \( \Phi_h \) from the equation for methane concentration in (5.10). The steady state equation for methane concentration can then be written as

\[
\frac{u_f}{D_m} \frac{\partial c_m}{\partial z} = \frac{\partial}{\partial z} \left[ D_m \phi (1 - h) \frac{\partial c_m}{\partial z} \right] + \frac{\rho_h}{\rho_f} (c_m - c_h) \frac{\partial}{\partial z} \left[ v_s \phi h \right] + \Phi_m. \tag{5.17}
\]

Because we eliminate the equation for the hydrate volume in deriving (5.17), we need an additional condition in order to solve (5.17) for the two unknown variables \( c_m \) and \( h \). This is done by imposing (local) thermodynamic equilibrium. When the dissolved methane concentration is less than the equilibrium solubility \( c_m < c_{eq} \), we set the hydrate volume to zero \( (h = 0) \) and solve equation (5.17) for the dissolved methane concentration. Alternatively, if the dissolved methane concentration is greater than the equilibrium solubility \( c_m > c_{eq} \), we impose equilibrium \( (c_m = c_{eq}) \) and solve equation (5.17) for the hydrate volume. An analogous expression for the methane concentration and bubble fraction is required below the HSZ. This equation is obtained by substituting the bubble fraction \( b \) for the hydrate fraction \( h \) and replacing the hydrate density \( \rho_h \) with the bubble density \( \rho_b \), calculated using the ideal gas law.

A similar substitution is made for the hydrate production \( \Phi_h \) in the chlorinity equation (5.15) under steady state conditions. The resulting chlorinity equation has the form

\[
\frac{u_f}{D_c} \frac{\partial c_c}{\partial z} = \frac{\partial}{\partial z} \left[ D_c \phi (1 - h) \frac{\partial c_c}{\partial z} \right] + \frac{\rho_h}{\rho_f} c_c \frac{\partial}{\partial z} \left[ v_s \phi h \right]. \tag{5.18}
\]

Below the hydrate stability zone, the bubble fraction \( b \) is substituted for the hydrate fraction \( h \) and the hydrate density \( \rho_h \) is replaced with bubble density \( \rho_b \).

Conversion of available organic carbon to methane does not occur until the sulfate concentration vanishes at the base of the SRZ. Below this depth, available organic carbon is buried along with the sediments and converted to methane at a rate \( \lambda_m \alpha \). The steady state version of (5.13), applicable below the SRZ, can be written as

\[
\frac{v_s}{\partial z} = -\lambda_m \alpha. \tag{5.19}
\]
Within the SRZ, organic carbon is depleted by the process of sulfate reduction. This process is incorporated in the model of the SRZ. Any available organic carbon that is transported by sedimentation through the base of the SRZ is converted to methane according to (5.19).

### 5.3.1 Sulfate Reducing Zone

The sulfate reducing zone extends from the seafloor to a depth where the sulfate concentration vanishes. This depth is typically on the order of centimetres in shallow marine sediments, and up to 100's of metres in the deep marine settings. Sulfate reducing zones associated with gas hydrate occurrences are commonly on the order of 5-20 metres and are characterized by a linear trend in the sulfate concentration. This feature is thought to be diagnostic of gas hydrate occurrences [Borowski et al., 1996, 1999]. To incorporate sulfate measurements into the hydrate model, two prevalent biogenic processes that affect the sulfate concentration within the SRZ are considered, namely anaerobic methane oxidation and bacterial sulfate reduction.

Microbial anaerobic methane oxidation has been proposed as the main diagenetic pathway for sulfate reduction associated with gas hydrate deposits and methane charged sediments [Borowski et al., 1996; Niewohner et al., 1998]. In fact Niewohner et al. [1998] argue that the sulfate profiles obtained off the coast of Namibia can be explained entirely by anaerobic methane oxidation due to an upward flux of methane into the SRZ. Although the specific mechanisms and the consortium of organisms involved in anaerobic methane oxidation are not well known [Boetius et al., 2000], the net reaction describing methane oxidation is widely accepted as

\[
\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}. \tag{5.20}
\]

This net reaction takes place at the sulfate-methane interface (SMI), which marks the boundary between the overlying sulfate reducing zone and the underlying zone of methanogenesis (see Figure 5.2). At this interface, a consortium of methanogens and sulfate reducers consume sulfate and methane in a one to one stoichiometric ratio. Recent work by Valentine and Reeburgh [2000] favour a set of reactions that yields a net methane oxidation reaction
involving twice the number of moles of the constituents, although their respective ratios remain unaltered. Previous studies [Borowski et al., 1996; Niewöhner et al., 1998] have used sulfate profiles to determine the molar fluxes of both sulfate and methane at the SMI according to (5.20). However, the sulfate and methane fluxes could not be related to the interstitial methane concentration or the corresponding hydrate distribution. In this study the methane concentration predicted by (5.17) is used to calculate the methane flux into the base of the SRZ. Because \( c_m \) and \( h \) vanish at the SMI, the mass flux of methane at the SMI is given by

\[
J_m = -D_{m\phi} \frac{\partial c_m}{\partial z},
\]

where \( \frac{\partial c_m}{\partial z} \) is evaluated immediately below the interface using the solution of (5.17) for \( c_m \). It is evident from the form of (5.17) that the solution for \( c_m \) depends on the distribution of hydrate \( h \) across the stability zone. This dependence should be reflected in the methane flux \( J_m \). The equality of the (molar) methane and sulfate fluxes at the SMI means that sulfate measurements provide indirect information about the distribution of hydrate. This information can be exploited using numerical models to obtain tighter constraints on the physical processes that operate within the HSZ.

A second sink of sulfate is distributed across the SRZ. Sulfate reducing bacteria consume organic carbon and sulfate in a two to one stoichiometric ratio to produce hydrogen sulfide according to

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^{-}. \tag{5.22}
\]

Although bacterial sulfate reduction may not be the dominant process of sulfate depletion in gas hydrate settings, some organic carbon is lost to sulfate reduction before it can be converted to methane. Incorporating the reaction in (5.22) into the model allows bounds to be placed on the amount of organic carbon available for methanogenesis. Boudreau and Westrich [1984] show that the rate of bacterial sulfate reduction is only weakly dependent on the concentration of sulfate in the pore fluid, and thus the abundance of organic carbon exerts the dominant control over sulfate reduction rates. Consequently, a model similar to Berner [1980] is adopted where the rate of sulfate depletion is proportional to the available
organic carbon \( \alpha \).

The organic carbon within the sediments is depleted by both bacterial sulfate reduction and methane production. The process of bacterial sulfate reduction operates within the SRZ, whereas methane production occurs at depths below the base of the SRZ. Equation (5.19) describes the distribution of organic carbon below the SRZ and an analogous equation for \( \alpha \) is adopted inside the SRZ

\[
v_s \frac{\partial \alpha}{\partial z} = -\lambda_s \alpha, \tag{5.23}
\]

where \( \lambda_s \) is the rate constant for the reaction of organic carbon with sulfate. The distribution of available organic carbon in the sediments is therefore described by (5.23) within the SRZ and (5.19) below. The available organic carbon is continuous across the interface between the SRZ and the zone of methanogenesis.

Sulfate reduction is determined by the loss of carbon in the SRZ in direct analogy with the methane production in (5.14). Consequently, we write the rate of sulfate reduction as

\[
\Phi_s = -\left( \frac{\rho_s(1 - \phi)}{60 \rho_f} \right) \lambda_s \alpha, \tag{5.24}
\]

where the ratio of molar masses of \( \text{SO}_4^{2-} \) to \( 2\text{CH}_2\text{O} \) (i.e. \( 96/60 \)) is needed to convert the units of \( \Phi_s \) into a mass fraction of the liquid (per unit time).

In summary, sulfate is reduced by conversion of organic carbon within the SRZ and by anaerobic methane oxidation at the base of the SRZ. The equation governing the steady state profile of the sulfate concentration \( c_s \) is analogous to the steady state equation for \( c_m \) in (5.17), although hydrate is absent from the SRZ. The resulting equation for \( c_s \) is

\[
u_f \frac{\partial c_s}{\partial z} = \frac{\partial}{\partial z} \left[ D_s \phi \frac{\partial c_s}{\partial z} \right] + \Phi_s, \tag{5.25}
\]

which includes the effects of sulfate transport by fluid flow \( u_f \) and chemical diffusion. Bacterial sulfate reduction, as described by (5.22), is represented by the source term \( \Phi_s \), while anaerobic methane oxidation (5.20) is imposed as a boundary condition on the sulfate flux at the base of the SRZ.

Incorporating a sulfate reducing zone into models for hydrate formation is important
for several reasons. Sulfate reduction causes $c_m$ to vanish in the near-surface sediments, which restricts methane production to depths below the SRZ. In addition, the available organic carbon is depleted by sulfate reduction throughout the SRZ, limiting the amount of organic carbon available for methanogenesis. Most importantly, the predicted methane flux at the base of the SRZ can be directly related to the sulfate profile by anaerobic methane oxidation (5.20). Comparison of observed sulfate measurements with the predicted sulfate profiles constrains $c_m$ and the associated hydrate distribution. The use of both sulfate and chlorinity measurements provide complementary data sets to better resolve the mechanism of methane supply at the Blake Ridge.

5.3.2 Method of Solution

We begin our description of the method of solution by summarizing the equations of the steady state model. Organic carbon ($\alpha$) is deposited at the seafloor and buried with the sediments at a velocity $v_s$. This organic carbon is depleted by sulfate reduction within the SRZ according to (5.23) and converted to methane below the SRZ according to (5.19). The corresponding rate of methane production (5.14) appears as a methane source $\Phi_m$ in equation (5.17), which describes the methane concentration $c_m$ and hydrate fraction $h$. When $c_m$ is below the solubility, thermodynamic equilibrium requires $h = 0$. On the other hand, when hydrate is present the methane concentration is fixed by the solubility ($c_m = c_{eq}$). Equation (5.18) describes the chlorine concentration throughout the HSZ, and can be related to drill core chlorinity measurements by (5.16). The sulfate concentration $c_s$ is governed by (5.25) within the SRZ, where $\Phi_s$ is the rate of sulfate reduction described by (5.24). The sulfate concentration is also influenced by the methane flux at the base of the SRZ (calculated according to (5.21)) through the process of anaerobic methane oxidation.

Below the HSZ, the methane bubble fraction $b$ and bubble density $\rho_b$ replace the hydrate fraction $h$ and hydrate density $\rho_h$ in (5.17) and (5.18). The variables $\alpha$, $h$, and $b$ are transported with the sediments at a velocity $v_s$, while $c_m$, $c_c$, and $c_s$ are mass fractions of dissolved components in the pore fluid, which are transported by the fluid velocity $u_f$ and
the effects of chemical diffusion.

All equations are solved using finite difference approximations for the spatial derivatives. A first-order upwinding scheme is used for advective terms of $\alpha$, $h$, and $b$, while second-order centered differences are used for the advective and diffusive terms of $c_m$, $c_c$, and $c_s$. I first solve for $\alpha$ using (5.23) within the SRZ and (5.19) below the SRZ. Next I solve (5.17) for either $c_m$ or $h$ by imposing the additional condition of thermodynamic equilibrium. For dissolved methane concentrations below the solubility, I set $h = 0$ and solve (5.17) for $c_m$. On the other hand, when the dissolved methane concentration is above the solubility, I set $c_m = c_{eq}$ and solve (5.17) for $h$. Equations (5.23), (5.19), and (5.17) are solved iteratively for $\alpha$, $h$, and $c_m$ using a relaxation technique [Press et al., 1988]. The solution for $h$ is used in equation (5.18) to determine the chlorine concentration. Because (5.18) is a linear equation for $c_c$ when $h$ is known, the finite difference approximations convert (5.18) into a linear system of equations, which is solved simultaneously for $c_c$. Finally, a finer grid is superimposed within the SRZ to solve (5.25) for $c_s$ using the relaxation technique.

5.3.3 Boundary and Interface Conditions

The computational domain is divided into three regions. The SRZ extends from the seafloor $z = 0$ to the sulfate-methane interface at $z = z_s$. The HSZ extends from $z = z_s$ to the base of the HSZ at $z = z_h$, which typically coincides with the BSR. The region below the HSZ extends to $z = z_n$, which we take to be twice the depth of the HSZ (i.e. $z_n = 2z_h$).

Two boundary conditions are required for the methane, chlorine and sulfate concentrations. The methane concentration is set to $c_m = 0$ at $z = z_s$ and the second condition is imposed at the base of the computational domain, which depends on the upward fluid velocity. In the absence of an upward fluid velocity, a no-flux condition $dc_m/dz = 0$ is imposed at $z = z_n$, which allows the composition of the pore fluid to freely adjust to the in situ generation of methane. When an upward fluid velocity is imposed, the concentration $c_m$ at $z = z_n$ is set to the composition of the incoming fluid. A similar approach is used to impose the boundary conditions of $c_c$. The chlorine concentration at the seafloor ($z = 0$) is set to
the present day value of seawater and the second condition is imposed at \( z = z_n \). A no-flux condition \( dc_c/dz = 0 \) is imposed at \( z = z_n \) in the absence of an upward fluid velocity, which allows the extent of the pore fluid freshening to be governed by hydrate recycling at the base of the HSZ. On the other hand, when the upward fluid velocity is prescribed, the composition of \( c_c \) at \( z = z_n \) is set to the value of the chlorine concentration measured at depth. The sulfate concentration is set to zero \( c_s = 0 \) at the base of the sulfate reducing zone \( z = z_s \), while the sulfate gradient is fixed by the methane gradient at \( z = z_s \). By equating the molar fluxes of sulfate and methane according to (5.20), the sulfate gradient can be expressed in the form of a mass fraction using

\[
\frac{dc_s}{dz} = \frac{96}{16} \frac{D_m}{D_s} \frac{dc_m}{dz}.
\]

The sulfate concentration at the seafloor \( z = 0 \) is allowed to adjust freely to satisfy the steady state equation and may therefore deviate from the seawater value. (Any deviation would represent a discrepancy between the model predictions and the observations).

Additional boundary conditions are required for the organic carbon \( \alpha \), hydrate \( h \), and bubble fraction \( b \). Each of these variables requires only one boundary condition because their governing equations contain only a first-order spatial derivative. The amount of available organic carbon is prescribed at the seafloor \( z = 0 \). The value is intended to represent a time average over the past few million years at a particular site. The hydrate fraction is set to zero at the seafloor, while the boundary condition on the bubble fraction is imposed at the base of the HSZ to enforce conservation of methane when \( h \) vanishes below the HSZ.

The base of the HSZ represents a thermodynamic boundary which separates hydrate in the overlying sediments from methane bubbles below. Consequently, gradients in hydrate and methane bubbles are not continuous at the interface and so the governing equations for \( c_m \) and \( c_c \) (which contain gradients in \( h \) and \( b \)) cannot be applied across this interface. Instead, conservation of methane and chlorinity is imposed by equating the fluxes across the HSZ interface. Two cases need to be distinguished according to the methane concentration in the pore fluid. When the methane concentration exceeds the solubility at the interface
both hydrate and bubbles will be present. The hydrate fraction $h$ at the interface is found by solving the steady state version of (5.1) in the absence of hydrate production ($\Phi_h = 0$). The equilibrium methane concentration is imposed and the methane conservation is used to determine the bubble fraction from

$$\frac{\rho_h}{\rho_f} h v_s (c_h - c_{eq}) - \frac{\rho_b}{\rho_f} b v_s (c_b - c_{eq}) = (1 - h) D_m \frac{dc^-}{dz} - (1 - b) D_m \frac{dc^+}{dz},$$

(5.27)

where $c_{eq}^-$ is taken to be the value of the equilibrium solubility above the interface and $c_{eq}^+$ is the equilibrium solubility below. The values $c_h$ and $c_b$ are the mass fractions of methane stored in the hydrate and bubbles respectively. (We take $c_b = 1$ when the gas is pure methane). When the dissolved methane is undersaturated at the interface, both $b$ and $h$ must vanish at the interface, so equation (5.27) reduces to

$$\frac{dc^-}{dz} = \frac{dc^+}{dz},$$

(5.28)

where $c_m^-$ and $c_m^+$ are no longer fixed by the solubility. A similar expression for the chlorinity interface condition is obtained by balancing the fluxes of chlorine across the HSZ interface. The chlorinity at the interface can be expressed as

$$\left( \frac{\rho_b}{\rho_f} b - \frac{\rho_h}{\rho_f} h \right) v_s c_c = (1 - h) D_c \frac{dc^-}{dz} - (1 - b) D_c \frac{dc^+}{dz},$$

(5.29)

when both hydrate and methane bubbles are present at the interface. This expression simplifies to

$$\frac{dc^-}{dz} = \frac{dc^+}{dz},$$

(5.30)

when hydrate and methane bubbles are absent at the interface.

5.4 Results: The Blake Ridge

The Blake Ridge is ideally suited for testing the steady state model because it is a well-studied hydrate location on a passive margin. Site 997 of ODP Leg 164 was drilled through a prominent BSR at the crest of the Blake Ridge. High-quality measurements of the sulfate
concentration were obtained in the near surface, while chlorinity measurements were collected from the seafloor to well below the base of the HSZ.

The mechanism of methane supply at the Blake Ridge is currently unresolved. Analysis of the carbon-isotopic compositions support a biogenic origin of the methane [Borowski et al., 1997; Matsumoto et al., 2000], but there is no clear consensus on the depth at which this methane was produced. A deep source of biogenic methane has been suggested on the basis of elevated bromide and iodide concentrations in the pore fluid [Egeberg and Barth, 1999]. Estimates of the age of the pore fluids are also significantly older than the surrounding sediments [Fehn et al., 2000]. Alternatively, numerical modelling has favoured a shallow in-situ source of methane in order to reproduce the chlorinity data [Egeberg and Dickens, 1999; Davie and Buffett, 2001]. However, the numerical models do not rule out other sources of methane. Results from Chapter 4 show that the chlorinity data at the Blake Ridge can be reproduced equally well with a deep source of methane. In order to distinguish between the two possible mechanisms, model parameters such as the velocity and composition of incoming fluids must be estimated independently or additional types of measurements must be introduced to constrain the model. Near surface sulfate profiles represent an additional measurement that can be related to the methane concentration and may thus be useful in resolving the mechanism of methane supply.

Use of a steady state model assumes that the parameters describing the geological conditions at the Blake Ridge represent average values over the last 5-10 Myrs. Values selected for these parameters are listed in Table 5.1. Several cases considered in Chapter 4 are investigated, but include predictions for sulfate profiles to better distinguish between the possible mechanisms of methane supply. Initially bacterial sulfate reduction is not allowed to operate within the sulfate reducing zone to isolate the effects of anaerobic methane oxidation on the predicted sulfate profile.

Results from Chapter 4 indicate that shallow in situ methane production is favoured at the Blake Ridge to explain the chlorinity measurements with a low upward fluid velocity of 0.08 mm yr\(^{-1}\), consistent with previous estimates from bromide and iodide profiles [Egeberg and
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<table>
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<tr>
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<td>m$^2$/s</td>
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Table 5.1: Site specific parameters for Site 997 at the Blake Ridge. * Values were increased to compensate for the discrepancy between the theoretical BSR depth (500 m salt water; 533 m pure water) and the observed depth (451 m). Diffusion coefficients of methane and sulfate are taken from Iversen and Jorgensen [1993] while chlorine is from Li and Gregory [1974].

Barth, 1999; Egeberg and Dickens, 1999]. Here we revisit these calculations, but incorporate the sulfate reducing zone and delay the onset of methane production until a depth of 40 m (about 20 m below the base of the SRZ). Model results yield a good fit to the chlorinity data (Figure 5.3A), while the estimates of hydrate and free gas agree well with inferences from several field studies. Hydrate occupies up to 4.5% of the pore volume from 70 m to the base of the HSZ (Figure 5.3C), which agrees well with the hydrate estimates of Paull et al. [1996] and Holbrook et al. [1996]. A deep layer of free gas which occupies up to 3% of the pore volume below the HSZ (Figure 5.3D) also agrees with previous estimates of free gas [Holbrook et al., 1996; Dickens et al., 1997]. However, the sulfate profile predicted by the model (Figure 5.3B) significantly over estimates the slope of the sulfate profile, implying a much larger methane flux into the SRZ than the sulfate measurements suggest. This large methane flux is related to the onset of in situ methane production at a shallow depth, which acts to steepen the near surface methane gradient. In addition, a large fraction
(≈ 50%) of the TOC must be converted at these shallow depths to compensate for the loss of methane through diffusion to the SRZ. In fact, the fit to the sulfate measurements becomes progressively worse and the fraction of metabolizable carbon must increase as the onset of methane production approaches the base of the SRZ. Therefore the constraint imposed by the sulfate measurements appears to rule out shallow in situ methane production immediately below the sulfate reducing zone.

An alternative mechanism of methane supply at the Blake Ridge is the upward migration of methane-bearing fluids from deeper within the sediment column. Fehn et al. [2000] suggest that this methane source is related to the diagenesis of organic material of early Tertiary age at depths of 1-3 km below the seafloor. To test this interpretation, a deep methane source is incorporated in the model by prescribing the composition and velocity of the incoming fluid. The fluid is assumed to be saturated with methane and an upward fluid velocity of 0.26 mm/yr is chosen to optimize the fit to the chlorinity measurements. (The fluid velocity is expressed as the interstitial velocity \( v_f \) at the seafloor). The resulting chlorinity profile is in good agreement with the measurements, although the predicted profile passes through the lower bounds of the chlorinity data (Figure 5.4A). Hydrate is predicted to occupy up to 3% of the pore volume from 175 m to the base of the HSZ (Figure 5.4C). A deep layer of methane bubbles occupying up to 2% of the pore volume forms below (Figure 5.4D). Both the hydrate and free gas volumes are slightly less than the estimates from previous field studies [Paull et al., 1996; Holbrook et al., 1996; Dickens et al., 1997], although they are within the uncertainty of these previous estimates. The sulfate profile predicted by the model yields a good fit to the sulfate measurements (Figure 5.4B) because the methane gradient at the base of the SRZ is not as large as that in the model with shallow methane production. A slight curvature in the predicted sulfate profile (Figure 5.4B) is observed due to the higher fluid velocities required to form hydrate with the deep methane source. The influence of fluid velocities is quantified using the ratio of advection to diffusion in the sulfate equation. This ratio defines a dimensionless number \( Pe \equiv v_f l / D_s \), called the Peclet number, which depends on the fluid velocity \( v_f \), the layer thickness \( l \), and the diffusivity \( D_s \). Using \( v_f = 0.26 \text{mm/yr} \),
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\( l = 22 \text{m} \) for the depth of the SRZ and \( D_s = 0.56 \times 10^{-9} \text{m}^2/\text{s} \), yields a Peclet number of \( Pe = 0.3 \), which indicates that transport by chemical diffusion is roughly 3 times larger than fluid advection. A purely linear profile occurs when \( Pe = 0 \), while substantial curvature appears in the sulfate profile as the fluid velocity is increased to values where \( Pe \approx 1 \).

Difficulties arise with a deep source of methane if the fluid migrating from depth is undersaturated with respect to methane. In order to form hydrate at the base of the HSZ a larger fluid velocity is required [Xu and Ruppel, 1999] and this results in a poor match to both the chlorinity and sulfate observations. For an incoming fluid with a methane concentration of 150 mM (75% saturation), a minimum fluid velocity of 0.70 mm/yr is required to form hydrate at the base of the HSZ. The resulting Peclet number is \( Pe = 0.8 \), which means that the associated sulfate profile would display substantially more curvature than the observations permit.

Chlorinity data at the Blake Ridge display an increase of measurement scatter from approximately 200 m to the base of the HSZ at approximately 464 mbsf. Paull et al. [1996] argued that the increased scatter is a result of the dissociation of discrete hydrate nodules during core recovery, causing localized freshening of the pore fluid. On the other hand, the steady-state model predicts a finely disseminated distribution of hydrate that varies smoothly through the sediment column. Pore scale processes are presumably responsible for aggregating finely disseminated hydrate into discrete nodules. Therefore, the predictions represent a spatial average of the discretely distributed nodules of hydrate. To recover the smoothly varying hydrate distribution, the measured chlorinity data from Site 997 are binned into 20 metre intervals as shown in Figure 5.5. The standard deviation of chlorinity measurements from each binned interval is plotted as an error bar on the averaged data. By binning the data into depth intervals, an increase in freshening between 200-464 metres becomes more evident as an excursion from the background chlorinity measurements above and below this zone. The chlorinity profile predicted by the deep source of methane yields a very good fit to the chlorinity data at shallow depths (0-200 m) and below the HSZ (Figure 5.5). However, between the 200-464 m the predicted chlorinity does not reproduce...
the increased freshening observed in the data. The inability of the deep methane source to reproduce the chlorinity observations between 200-464 m suggests that in situ methane production is required to complement the deep source. To explain the increased freshening observed between 200–464 m, we investigate the addition of an in situ methane source within the HSZ, but not immediately below the SRZ.

We incorporate a biogenic source of methane that begins at 180 m with the rate constant $\lambda_m$ given in Table 5.1. (This source is subsequently referred to as an intermediate methane source because it is neither deep nor shallow). Reasonable models require a small fraction of the TOC (~25%) be converted to methane. Figure 5.6 shows the predictions of an intermediate methane source together with a deeper source of methane saturated fluid migrating upward at a velocity of 0.23 mm/yr. The predicted chlorinity agrees well with the binned chlorinity data (Figure 5.6A). The intermediate source is able to reproduce the increased freshening between 200–464 m, while yielding a good match above and below this zone. The model also predicts a jump in freshening at the base of the HSZ, indicating that hydrate decomposition is causing localized freshening at the HSZ interface. In addition, the sulfate profile predicted by the intermediate source does the best job (of the methane sources considered) at reproducing the observations within the SRZ (Figure 5.6B). The slight curvature observed in the sulfate profile mimics the subtle curvature observed in the sulfate measurements. The hydrate fraction occupies up to 7% of the pore volume from 170 m to the base of the HSZ, while a deep layer of free gas occupying over 5% of the pore volume forms below (Figure 5.6C,D). The estimates of the hydrate and bubble volumes are larger than the deep source case, and are more in line with estimates from previous field studies [Paull et al., 1996; Holbrook et al., 1996; Dickens et al., 1997]. Importantly, the inclusion of the intermediate source allows undersaturated deep fluids to reproduce the chlorinity and sulfate measurements. As an experiment, the methane flux entering the base of the computational domain was lowered until hydrate no longer formed at the base of the HSZ. In one case the methane flux was lowered by decreasing the methane concentration of the incoming fluid, while keeping the fluid velocity constant. A minimum methane concentration of 150
mM (75% saturation) was able to reproduce both the chlorinity and sulfate measurements for a fluid velocity of 0.23 mm/yr. In a second case the methane flux was lowered by decreasing the upward fluid velocity of the saturated incoming fluid. Although reductions in the fluid velocity still allowed hydrate to form at the base of the HSZ, the agreement between the model predictions and chlorinity observations became progressively worse. Therefore, the addition of an in situ source at intermediate depths allows undersaturated fluids with a concentration as low as 150 mM and fluid velocity of 0.23 mm/yr to best reproduce the observations.

In summary, the introduction of sulfate measurements as an additional model constraint rules out shallow in situ methane production immediately below the SRZ. Sulfate profiles predicted by shallow in situ production yield a sulfate concentration of 70 mM at the seafloor, which is over a factor of 2 greater than value of seawater (28 mM) as shown in Figure 5.3B. On the other hand, a deep source of methane is able to reproduce sulfate data (Figure 5.4B). However, the chlorinity predicted by the deep source does not reproduce the amount of freshening observed between 200–464 m (Figure 5.5). The predicted chlorinity profile, along with smaller estimates of hydrate and bubble volumes than previous studies, suggest an in situ methane source at intermediate depth. In situ methane production commencing at an intermediate depth (180 m) was able to reproduce the chlorinity and sulfate measurements when 25% of the TOC was converted to methane. In particular, the increased freshening observed between 200–464 m was fit by the predicted chlorinity (Figure 5.6A). In addition, the hydrate and free gas volumes agree well with estimates from previous studies. While the upwelling fluids may be undersaturated, the methane concentration must be 150 mM or greater to reproduce the sulfate and chlorinity observations.

For the intermediate methane source, the sulfate profile associated with the best match of the chlorinity data displays slight curvature in the absence of bacterial sulfate reduction. This curvature is caused by the higher upward fluid velocity (0.23 mm/yr) required to reproduce the chlorinity observations. Therefore the assumption that the sulfate profiles are purely diffusive at the Blake Ridge is not strictly correct. Additional complications arise
by including the process of bacterial sulfate reduction within the SRZ. We investigate the effects of varying the sulfate reduction rate $\lambda_s$ on both the sulfate and chlorinity profiles. By including sulfate reduction, organic carbon is consumed within the SRZ and is not available for conversion to methane deeper in the sediments. Consequently, the volumes of hydrate and free gas decrease as less methane is produced by the in situ conversion of organic carbon below the SRZ. In addition, sulfate reduction appears as a sulfate sink in equation (5.25). Sulfate reduction depletes the sulfate concentration, causing concave curvature in the sulfate profile. The effects of sulfate reduction are shown in Figure 5.7 using rate constants $\lambda_s = 2 \times 10^{-13}$ s$^{-1}$ and $\lambda_s = 5 \times 10^{-13}$ s$^{-1}$. The available organic carbon at the seafloor $\alpha(0)$ is adjusted such that the amount of organic carbon exiting the SRZ is sufficient to reproduce the chlorinity measurements of Figure 5.6A. To do this we require $\alpha(0)$ to equal 0.6% dry weight of sediments (39% of TOC) for $\lambda_s = 2 \times 10^{-13}$ s$^{-1}$ and 1% dry weight of sediments (68% of TOC) for $\lambda_s = 5 \times 10^{-13}$ s$^{-1}$. The comparison of predicted sulfate profiles with the sulfate measurements show that the agreement between the predictions and observations becomes progressively worse as the rate of sulfate reduction increases (Figure 5.7). These results suggest that sulfate reduction at Site 997 is occurring at a slow rate such that the sulfate profile is minimally affected by sulfate reduction. It also means that only 25% of the TOC is needed for the intermediate methane source to explain both the sulfate and chlorinity observations at the Blake Ridge. The fact that the sulfate profile is reproduced entirely by the process of anaerobic methane oxidation argues that anaerobic methane oxidation is the dominant diagenetic pathway for sulfate at the Blake Ridge.
Figure 5.3: Results from the Blake Ridge calculated for shallow in situ production beginning at a depth of 40 m. An upward fluid velocity of 0.08 mm/yr (at the seafloor) is assumed on the basis of bromide and iodide profiles (0.08 mm yr\(^{-1}\)) [Egeberg and Barth, 1999; Egeberg and Dickens, 1999]. (A) The predicted chlorinity profile (solid) agrees well with the measured chlorinity (squares). (B) The predicted sulfate profile (solid) severely over-estimates the sulfate observations (squares) due to the large methane flux into the SRZ. (C) Hydrate occupies upwards of 4.5% of the pore volume from a depth of 70 m to the base of the HSZ. (D) A deep layer of free gas is present below the HSZ, occupying up to 3% of the porespace.
Figure 5.4: Results from the Blake Ridge for a deep methane source with a fluid velocity of 0.26 mm yr\(^{-1}\). (A) The predicted chlorinity profile (solid) agrees well with the measured chlorinity (squares), although the predicted profile passes through the lower bounds of the measured chlorinity. (B) The predicted sulfate profile (solid) yields a good fit to the sulfate measurements (squares) because the methane gradient at the base of the SRZ is not as large as that for the model with shallow methane production. (C) Hydrate occupies upwards of 3% of the pore volume from a depth of 180 m to the base of the HSZ. (D) A deep layer of free gas is present below the HSZ occupying up to 2% of the porespace.
Figure 5.5: Comparison of the predicted chlorinity profile for a deep source of methane and the spatially averaged chlorinity data. Chlorinity data were binned into 20 m intervals (standard deviation plotted as error bars) to represent the smoothly varying disseminated hydrate distribution predicted by the hydrate model. The predicted chlorinity profile (solid) agrees well with the averaged data (squares) in the upper 200 m and below the HSZ. Between 200–464 m the predicted chlorinity underestimates the freshening of the measured data.
Figure 5.6: Results from the Blake Ridge for an intermediate methane source (within the HSZ but not immediately below the SRZ) together with a deeper methane saturated fluid migrating upward at a velocity of 0.23 mm yr$^{-1}$. (A) The predicted chlorinity profile (solid) agrees well with the averaged measured chlorinity (squares). The predicted chlorinity yields a good match with the observed freshening between 200–464 m. (B) The predicted sulfate profile (solid) yields a good fit to the sulfate measurements (squares). (C) Hydrate occupies upwards of 7% of the pore volume from a depth of 180 m to the base of the HSZ. (D) A thick layer of free gas occupies 5% of the pore volume below the HSZ.
Figure 5.7: The effects of sulfate reduction on the sulfate profile are shown for $\lambda_s = 2 \times 10^{-13}$ s$^{-1}$ and $\lambda_s = 5 \times 10^{-13}$ s$^{-1}$. Agreement between the predicted sulfate profiles becomes progressively worse as the rate of sulfate reduction increases.
5.5 Results: The Cascadia Margin

The Cascadia Margin is another hydrate location where the steady state model may be applied. In contrast to the Blake Ridge, the Cascadia Margin is an active margin setting where the effects of fluid flow are thought to be important. We consider Site 889 that was drilled through a BSR approximately 18 km landward from the deformation front of the accretionary prism. Measurements of near surface sulfate concentration, in conjunction with chlorinity measurements collected from the seafloor to well below the base of the HSZ, provide complementary data constraints for the steady state model.

Upward focusing of biogenic methane from deeper sources has been proposed as the primary mechanism of methane supply at the Cascadia Margin [Hyndman and Davis, 1992]. Previous studies suggest that methane rich fluids are expelled from incoming sediments during accretionary thickening and focused into the HSZ by high fluid velocities in the range of 1–2 mm/yr [Wang et al., 1993]. Methane in excess of the solubility within the HSZ forms hydrate, which is inferred to occupy up to 30% of the pore volume based on seismic velocity modelling [Yuan et al., 1996]. On the other hand, results from Chapter 4 show that the chlorinity observations are reproduced equally well by either a deep source of methane or a shallow in situ methane source together with upward fluid flow. Both sources of methane require lower fluid velocities than previous accretionary thickening models [Wang et al., 1993], and predict much smaller volumes of hydrate (~2-5%) than previous estimates of 20–30% [Yuan et al., 1996]. (The smaller hydrate volumes predicted by the numerical models are consistent with drill core temperature measurements which infer that only 3% of the porespace is filled with hydrate [Kastner et al., 1995]). Near surface sulfate observations are introduced as an additional data constraint in the steady state model to resolve the mechanism of methane supply at the Cascadia margin. The linear nature of the sulfate measurements suggests that anaerobic methane oxidation is the main pathway for sulfate depletion at this site, although bacterial sulfate reduction is not ruled out. Initially bacterial sulfate reduction is not allowed to operate within the sulfate reducing zone to isolate the
CHAPTER 5. STEADY-STATE MODEL

effects of anaerobic methane oxidation on the predicted sulfate profile. A deep methane source in the absence of in situ production is considered first.

Results from Chapter 4 yielded the best match of the chlorinity observations for a saturated deep source with a fluid velocity of 0.42 mm/yr, which is only slightly higher than the critical velocity of 0.40 mm/yr. Incorporation of the SRZ into the steady state model causes a small increase (from 0.42 mm/yr to 0.51 mm/yr) in the critical fluid velocity that is required to maintain both hydrate and free gas at the base of the HSZ. (This increase is in response to setting \( c_m = 0 \) at the base of the SRZ, which increases the loss of methane to the seafloor). The chlorinity profile predicted by the model agrees well with the chlorinity observations (Figure 5.8A). Hydrate occupies upwards of 2.5% of the pore volume from 100 m to the base of the HSZ (Figure 5.8C) which is in good agreement with hydrate volumes inferred from drill core temperature measurements [Kastner et al., 1995]. In addition, a layer of free gas occupying just over 2% forms below the HSZ (Figure 5.8D). However, the predicted sulfate profile underestimates the sulfate observations by approximately a factor of two (Figure 5.8B).

The discrepancy between the predicted sulfate profile and observations implies that either sulfate is being consumed by bacterial sulfate reduction within the SRZ or that a larger methane gradient into the SRZ is required by anaerobic methane oxidation. We first investigate the addition of bacterial sulfate reduction within the SRZ. Figure 5.9 shows the sulfate predictions for varying amounts of organic carbon available to react with sulfate according to equation (5.22). We set \( \lambda_s = 20 \times 10^{-13} \text{ s}^{-1} \) to ensure that the available organic carbon is consumed within the SRZ. Increasing the organic carbon for bacterial sulfate reduction causes increased curvature of the predicted sulfate profile, resulting in poor agreement with observations (Figure 5.9). The fact that the sulfate observations do not display the curvature characteristic of bacterial sulfate reduction, indicates that sulfate reduction is not the main process of sulfate depletion at Site 889.

Alternatively, the discrepancy between the sulfate predictions and measurements can be explained by anaerobic methane oxidation with a steepened methane gradient at the base
of the SRZ. An increased methane gradient can be caused by either a larger upward fluid velocity or the addition of a methane source at shallow depth. A larger upward fluid velocity of 1.25 mm/yr steepens the methane gradient at the base of the SRZ and results in good agreement between the predicted sulfate profile and sulfate measurements (Figure 5.10B). However, this larger fluid velocity results in a poor match of the predicted chlorinity profile with the observations because the steep curvature of the predicted chlorinity profile poorly reproduces the chlorinity observations (Figure 5.10A). On the basis of this poor match, larger fluid velocities are ruled out and an additional methane source at shallow depth is considered in order to explain the sulfate measurements.

Shallow in situ production of methane requiring 50% conversion of TOC, together with a methane saturated fluid migrating upward at a velocity of 0.35 mm/yr was found to reproduce the chlorinity observations at Site 889. This scenario is investigated using the sulfate measurements as an additional data constraint. Models requiring 60% conversion of TOC commencing at depths of 10 m (5 metres below the SRZ), in conjunction with methane saturated fluids migrating at 0.36 mm/yr, are able to reproduce both the chlorinity and sulfate observations (Figure 5.11A, B). The shallow in situ production steepens the methane gradient at the base of the HSZ, resulting in a steeper sulfate gradient and providing a good match to the sulfate measurements. Hydrate is predicted to occupy up to 4% of the pore volume from 50 m to the base of the HSZ (Figure 5.11C), in good agreement with hydrate volumes inferred from temperature measurements [Kastner et al., 1995]. Below the HSZ, free gas is predicted to occupy 6% of the pore volume (Figure 5.11D). In addition, undersaturated fluids with a minimum methane concentration of 95 mM are able to reproduce the chlorinity and sulfate observations. The hydrate and free gas distributions are very similar to the saturated case, but the free gas layer has a distinct base at a depth of 440 m.
Figure 5.8: Results from the Cascadia Margin for a deep methane source with a fluid velocity of 0.51 mm/yr. (A) The predicted chlorinity profile (solid) agrees well with the measured chlorinity (squares). (B) The predicted sulfate profile (solid) underestimates the sulfate measurements (squares) by over a factor of two. (C) Hydrate occupies upwards of 2.5% of the pore volume from 100 m to the base of the HSZ, in good agreement with hydrate volumes inferred from drill core temperatures [Kastner et al., 1995]. (D) A layer of free gas is present below the HSZ occupying up to 2% of the pore volume.
Figure 5.9: Effects of increasing bacterial sulfate reduction on the sulfate profile. Increased organic carbon available to react with sulfate (e.g. increased $\alpha$) causes curvature in the predicted sulfate profile, which poorly matches the observations.
Figure 5.10: Results from the Cascadia Margin for a deep methane source with a fluid velocity of 1.25 mm/yr. (A) The predicted chlorinity profile (solid) poorly reproduces the measured chlorinity (squares) due to the high fluid velocities. (B) The predicted sulfate profile (solid) yields a good fit to the sulfate measurements (squares) because the methane gradient at the base of the SRZ is steepened.
Figure 5.11: Results from the Cascadia Margin for shallow in situ production beginning at a depth of 10 m, together with a fluid velocity of 0.36 mm/yr. (A) The predicted chlorinity profile (solid) agrees well with the measured chlorinity (squares). (B) The predicted sulfate profile (solid) yields a good fit to the sulfate measurements (squares). (C) Hydrate occupies upwards of 4% of the pore volume from 100 m to the base of the HSZ, in good agreement with hydrate volumes inferred from drill core temperatures [Kastner et al., 1995]. (D) A layer of free gas is present below the HSZ occupying up to 6% of the pore volume.
5.6 Summary

A steady state model is developed to predict the volume and distribution of hydrate in marine sediments. Time-dependent equations describing the formation of hydrate below the seafloor are reduced to steady-state approximations by assuming that the marine environment has reached the state where hydrate growth is balanced by hydrate losses. The steady state representation is amenable to solutions on finely-spaced grids which facilitates the incorporation of the sulfate reducing zone into the model. The model for sulfate concentration is coupled to the available organic carbon and the interstitial methane concentration through the processes of sulfate reduction and anaerobic methane oxidation. Measured sulfate and chlorinity profiles provide two separate constraints on the mechanism of methane supply and the quantity and distribution of hydrate and free gas in the sediments.

Model predictions for conditions representative of the Blake Ridge are compared with chlorinity and sulfate measurements from Site 997. Compared with previous studies that use only chlorinity measurements, the additional constraint imposed by sulfate measurements allows the mechanism of methane supply at this site to be identified. A shallow in situ methane source is ruled out by the poor match to the sulfate observations (even though chlorinity observations were adequately explained). The shallow in situ methane source steepens the methane gradient to the base of the SRZ, resulting in a corresponding increase in sulfate predictions towards the seafloor and a predicted concentration at the seafloor which is over 2 times that of measured seawater. On the other hand, a saturated deep methane source is able to reproduce both the chlorinity and sulfate measurements for an upward fluid velocity of 0.25 mm/yr. However, comparison of the predicted chlorinity with spatially averaged observations (intended to simulate the disseminated distribution predicted by the model) shows that increased freshening observed between 200-450 m cannot be reproduced solely by a deep methane source. In addition, undersaturated methane bearing fluids require larger upward velocities to form hydrate to the base of the HSZ, resulting in poor agreement between the model predictions and chlorinity/sulfate observations. The preferred interpretation of
the mechanism of methane supply at Site 997 involves an intermediate source of methane coupled with a deeper fluid velocity of 0.23 mm/yr. The intermediate methane source still lies within the HSZ (commencing at 180 m), but it is not permitted immediately below the SRZ. This intermediate source results in good agreement between the predicted chlorinity profile and observations, while the predicted sulfate profile yields the best match to the measurements of the three sources considered in this study.

Increasing the rate of bacterial sulfate reduction within the SRZ causes the agreement between the model predictions and sulfate measurements to become progressively worse. Bacterial sulfate reduction introduces an addition sulfate sink, resulting in increased curvature of the sulfate profile. The slight curvature in the sulfate profile at the Blake Ridge suggests that anaerobic methane oxidation is the dominant diagenetic process for sulfate depletion at Site 997.

The steady state model is also applied at the Cascadia Margin to resolve the mechanism of methane supply at Site 889. Methane supplied solely from a deep methane source underestimates the methane flux at the base of the SRZ, resulting in a poor match with the sulfate measurements. A shallow in situ methane source together with a deep saturated fluid migrating upward at a velocity of 0.36 mm/yr is required to reproduce both the sulfate and chlorine measurements. Hydrate is predicted to occupy up to 4% of the pore volume from 50 m to the base of the HSZ, in good agreement with hydrate volumes inferred from temperature measurements [Kastner et al., 1995]. The addition of sulfate reduction within the SRZ results in increased curvature of the predicted sulfate profile and yields a poor match to the sulfate measurements. This result along with the linear nature of the sulfate measurements indicates that anaerobic sulfate reduction is the main diagenetic process for sulfate depletion at Site 889.
CHAPTER 6

Conclusions

In this thesis, quantitative models are developed for predicting the volume and distribution of gas hydrate in marine sediments. The comparison of model results (chlorinity, sulfate, hydrate and free gas volumes) with observations from hydrate locations allows postulated sources of methane to be evaluated on a quantitative basis. In particular, the hydrate model is applied at both the Blake Ridge and Cascadia Margin to resolve the source and mechanism of methane supply at these locations. The main findings of this work are summarized below.

Chapter 1 provides a brief background discussion of gas hydrates and highlights the need for numerical models to resolve the important processes that contribute to hydrate formation at different tectonic settings. In particular, there is a lack of quantitative evidence to support various hypotheses concerning the source of methane for marine gas hydrate and the mechanism of methane supply at the Blake Ridge and Cascadia Margin.

Chapter 2 presents a practical method of predicting the methane solubility in a marine setting. The equilibrium methane solubility is important as it determines the minimum methane concentration needed for hydrate stability and influences the distribution and volume of hydrate in marine sediments. By providing the water depth, seafloor temperature, and geothermal gradient at a specific location, we are able to calculate the pressure and temperature conditions at the base of the HSZ. The methane solubility is then calculated at the conditions of three-phase equilibrium using the results of Zatsepina and Buffett [1997]. Simple parametric models are used to extend the results into the regions above and below the
HSZ. Solubility profiles at four hydrate locations were examined to qualitatively interpret possible mechanisms of methane supply. It was found that sites with steep solubility profiles and low TOC (i.e., Cascadia Margin and Chile Triple Junction) favored the focusing of deep methane sources as the main mechanism of methane supply, while sites with a smaller slope of the solubility profile within the HSZ and higher TOC (Blake Ridge and Peruvian Margin) suggest that biogenic production of methane may be important at these locations.

Chapter 3 describes the derivation of a time-dependent model to describe the formation of gas hydrate below the seafloor. A conceptual model describes the important processes for hydrate formation at conditions representative of the deep continental margin. This conceptual model is translated to a set of governing equations describing the evolution and distribution of marine hydrate. Initial, boundary, and interface conditions are applied, allowing the equations to be solved numerically, and yielding time evolution sequences for hydrate formation. An important finding of this chapter was that solutions approached steady states after approximately 5–10 Myrs, which indicates that the hydrate volume at a particular location is not dependent on the accumulation time after an initial transient interval. A typical evolution sequence for methane production by biogenic conversion of organic carbon is examined, and the key physical parameters that influence the model results are identified. In particular, the organic carbon deposited at the seafloor ($a(0)$), sedimentation rate ($\dot{S}$), and reaction rate ($\lambda_m$) have the greatest influence on the numerical predictions. The model is applied at the Blake Ridge to show that chlorinity measurements and hydrate/free gas observations from Site 997 can be reproduced with an in situ biogenic methane source when 80% or more of the TOC is available for conversion.

Chapter 4 describes the use of numerical models for the formation of gas hydrate to assess the influence of methane supply on observable features of hydrate occurrences. In particular, we explore alternative mechanisms of methane supply at the Blake Ridge and Cascadia Margin to draw inferences about the specific source of methane at these two locales. Observations of chlorinity, hydrate and free gas from Site 997 at the Blake Ridge can be explained by a deep source with an upward fluid velocity of 0.26 mm yr$^{-1}$ or by an in situ
source with 50% conversion of organic carbon and an upward fluid velocity of 0.08 mm yr\(^{-1}\). In a similar manner, observations of chlorinity from Site 889 at the Cascadia Margin can be explained by either a deep source with a fluid velocity of 0.42 mm yr\(^{-1}\) or by an in situ source with 50% conversion of organic carbon together with an upward fluid velocity of 0.35 mm yr\(^{-1}\). A method for resolving the mechanism of methane supply is suggested by the difference in methane fluxes at the seafloor between the competing methane sources (i.e. Table 4.2). By relating the methane flux to the sulfate flux at the base of the sulfate reducing zone, sulfate measurements may be used in conjunction with chlorinity observations to distinguish between methane sources. An important finding at the Cascadia Margin is that the predicted volume of hydrate is significantly lower than the hydrate volumes estimated from seismic velocity analysis and interpretation of resistivity measurements [Yuan et al., 1996; Hyndman et al., 1999]. Interestingly, the hydrate volumes predicted by the model agree well with hydrate volumes of 3%, which have been reported at Site 889 from temperature measurements of drill core upon recovery [Kastner et al., 1995].

Chapter 5 develops a steady state model to describe the formation of hydrate below the seafloor. Time-dependent equations describing the formation of hydrate below the seafloor are reduced to steady-state approximations by assuming that the marine environment has reached the state where hydrate growth is balanced by hydrate losses. The model includes the sulfate reducing zone (SRZ), which allows the sulfate concentration to be coupled to the available organic carbon and the interstitial methane concentration through the processes of sulfate reduction and anaerobic methane oxidation. Measured sulfate and chlorinity profiles provide two separate constraints on the mechanism of methane supply and the quantity and distribution of hydrate and free gas in the sediments. The steady state model is applied at both the Blake Ridge and Cascadia Margin to resolve the mechanism of methane supply at these two locales. Model predictions for conditions representative of the Blake Ridge are compared with chlorinity and sulfate measurements from Site 997. Sulfate measurements rule out a shallow source of methane directly below the SRZ because the predicted sulfate profile overestimates the measurements by a factor of 2 or more. Although a deep source of
methane reproduces the main features of the sulfate and chlorinity data when the upward fluid velocity is 0.25 mm/yr, the deep source fails to reproduce the increased freshening observed between 200–450 mbsf. We find that an in situ methane source (located in the lower part of the HSZ) together with an incoming methane bearing fluid at 0.23 mm/yr gives the best fit to both the sulfate and chlorinity data. In addition, the predicted sulfate profile indicates that the process of anaerobic methane oxidation is the primary pathway of sulfate depletion at the Blake Ridge. Model predictions for conditions representative of the Cascadia Margin are also compared with chlorinity and sulfate measurements from Site 889. Methane supplied solely from a deep methane source underestimates the methane flux at the base of the SRZ, resulting in a poor match with the sulfate measurements. The favoured interpretation of the methane supply at Site 889 involves a shallow in situ methane source together with a deep methane bearing fluid migrating upward at a velocity of 0.36 mm/yr in order to reproduce both the sulfate and chlorine measurements.

The development of numerical models describing hydrate formation (both time-dependent and steady state) and the success at applying the models to known hydrate settings opens the possibility to numerous future applications. The most interesting of these applications is the use of the steady state model to estimate the geographic distribution of hydrate if the required model parameters are known. Parameters required by the model include the fluid flow, organic matter accumulation, sedimentation rates, porosity, water depth, temperature at the seafloor, and geothermal gradient. Since many of these parameters are available in global databases, it is feasible to use our steady state model to refine estimates of the global hydrate inventory, or apply the model in regional studies. The ability of the model to provide estimates of the chlorinity and sulfate profiles along with hydrate and free gas volumes allows for model calibration at known hydrate occurrences and would provide testable predictions of observables at undiscovered locations of large hydrate accumulations.

Incorporation of the steady state model into global carbon cycle models would be of significant interest as hydrate represents a large sink/source of carbon in the shallow geosphere. Consideration of methane hydrate in the carbon cycle in the form of a hydrate capacitor is
conceptually presented in Dickens [2001a]. Inclusion of the hydrate model into carbon cycle models would allow for the interaction/contribution of marine hydrates to the global carbon cycle to be evaluated on a quantitative basis.

Another application would link model predictions for the hydrate and free gas volumes and chlorine concentrations to seismic velocity models and resistivity borehole measurements using rock physics models. The experimental and modelling study of Helgerud [2001] examines the influence of hydrate distribution in marine sediments on seismic velocities. Using the seismic velocity models of Helgerud [2001], the results from our hydrate model can be used to predict seismic velocities at known hydrate locations. In addition, model predictions of hydrate volumes and the in situ chlorine concentration can be related to borehole resistivity measurements through the application of Archie's law. As a result, both seismic velocity models and resistivity measurements from locations of hydrate occurrence would provide additional data constraints on our hydrate model.

Numerous additional opportunities for the application of quantitative models to study important questions relevant to marine gas hydrates exist, they just need to be identified. The ultimate success of this thesis will be measured by the future use of the hydrate model by others to address some of these outstanding issues concerning marine gas hydrates.
A.1 Material Derivative of a Volume Integral

In deriving the governing equations in Chapter 3, we were required to evaluate how a given quantity \( A(\vec{x}, t) \), where \( A \) represented some fluid property per unit volume (i.e. chlorinity, methane concentration), changes with respect to time as the material volume deforms. The material volume is defined as an arbitrarily chosen control volume of fluid whose surface moves at the particle velocity as shown in Figure A.1. The significance of the volume moving at the same rate as the particle velocity is that no mass is transported across the chosen control surface that encloses the control volume.

Consider a property \( I(t) \) defined as the integral of some fluid property \( A(\vec{x}, t) \) over a deforming material volume \( V(t) \) as shown in Figure A.2. We define

\[
I(t) = \int_{V(t)} A(\vec{x}, t) \, dV,
\]

where the integral is over a given set of particles. The corresponding surface \( S \) is fixed and the volume deforms as the fluid is transported at the local velocity \( v \). To evaluate how the property \( I(t) \) changes with time, we take the derivative \( dI(t)/dt \). However, the time derivative operator may not be taken directly inside the integral as the volume over which we are integrating is also dependent on time. Consequently we express the derivative in terms of a limit as
Figure A.1: The control volume is defined as a volume of fluid whose surface moves with an identified group of particles (A, B, C in this example). At a later time $t + dt$, the control volume has changed but still encloses the same particles.

Figure A.2: The control volume deforms as the fluid is transported at the local velocity $v$. Consequently the volume $V$ at time $t$ is not necessarily equal to the volume $V + \Delta V$ at time $t + dt$. The change in volume depends on the volume swept out by the surface $S$ due to the local velocity field (see inset).
\[ \frac{dI}{dt} = \lim_{dt \to 0} \frac{1}{dt} \left[ I(t + dt) - I(t) \right], \quad (A.2) \]

\[ = \lim_{dt \to 0} \frac{1}{dt} \left[ \int_{V(t+dt)} A(\vec{x}, t + dt) dV - \int_{V(t)} A(\vec{x}, t) dV \right]. \quad (A.3) \]

We let the volume at time \( t \) be expressed as \( V \), while the volume at time \( t + dt \) may written as the sum of the original volume and the change in volume \( V + \Delta V \). Substituting for the volumes

\[ \frac{dI}{dt} = \lim_{dt \to 0} \frac{1}{dt} \left[ \int_{V} A(\vec{x}, t + dt) dV + \int_{\Delta V} A(\vec{x}, t + dt) d\Delta V - \int_{V} A(\vec{x}, t) dV \right]. \quad (A.4) \]

Gathering the integrands taken over the same volume \( V \) we find

\[ \frac{dI}{dt} = \lim_{dt \to 0} \frac{1}{dt} \left[ \int_{V} A(\vec{x}, t + dt) - A(\vec{x}, t) dV + \frac{1}{dt} \int_{\Delta V} A(\vec{x}, t + dt) d\Delta V \right]. \quad (A.5) \]

The first term is the normal expression for the derivative, so we can simplify

\[ \frac{dI}{dt} = \int_{V} \frac{\partial A(\vec{x}, t)}{\partial t} dV + \lim_{dt \to 0} \frac{1}{dt} \int_{\Delta V} A(\vec{x}, t + dt) d\Delta V. \quad (A.6) \]

Consider the surface of the volume \( V \) as shown in Figure A.2. The rate at which the volume \( \Delta V \) deforms is equal to the rate at which the volume is swept out by the surface \( dS \)

\[ \frac{d\Delta V}{dt} = \vec{v} \cdot \hat{n} dS, \quad (A.7) \]

where \( \vec{v} \) is the local particle velocity and \( \hat{n} \) is the outward normal to the surface \( dS \) as shown in Figure A.2. If we focus on the second term of equation (A.6), substitution of \( d\Delta V \) and simplification yields

\[ \lim_{dt \to 0} \frac{1}{dt} \int_{S} A(\vec{x}, t + dt) \vec{v} dt \cdot \hat{n} dS, \quad (A.8) \]

\[ \lim_{dt \to 0} \int_{S} A(\vec{x}, t + dt) \vec{v} \cdot \hat{n} dS, \quad (A.9) \]

\[ \int_{S} A(\vec{x}, t) \vec{v} \cdot \hat{n} dS. \quad (A.10) \]
Therefore the change in $I$ within the volume is due to the rate of change of $I$ at a point and the net flow of $I$ across the surface $S$

$$\frac{dI}{dt} = \int_V \frac{\partial A(\vec{x}, t)}{\partial t} dV + \int_S A(\vec{x}, t) \hat{v} \cdot \hat{n} dS. \quad (A.11)$$

The final simplification is to convert the surface integral to a volume integral through the application of Gauss' theorem. Further simplification yields the final form of the material derivative of a volume integral

$$\frac{dI}{dt} = \int_V \frac{\partial A}{\partial t} + \nabla \cdot [A \vec{v}] \, dV. \quad (A.12)$$
A.2 Definition of Model symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_m )</td>
<td>mass fraction of methane</td>
</tr>
<tr>
<td>( c_{eq} )</td>
<td>equilibrium mass fraction of methane</td>
</tr>
<tr>
<td>( c_c )</td>
<td>mass fraction of chlorine</td>
</tr>
<tr>
<td>( c_s )</td>
<td>mass fraction of sulfate</td>
</tr>
<tr>
<td>( c_b )</td>
<td>mass fraction of methane in bubbles</td>
</tr>
<tr>
<td>( c_h )</td>
<td>mass fraction of methane in hydrate</td>
</tr>
<tr>
<td>( D_c )</td>
<td>chemical dispersion, diffusion coefficient of chlorine (m(^2) s(^{-1}))</td>
</tr>
<tr>
<td>( D_m )</td>
<td>chemical dispersion, diffusion coefficient of methane (m(^2) s(^{-1}))</td>
</tr>
<tr>
<td>( D_s )</td>
<td>chemical dispersion, diffusion coefficient of sulfate (m(^2) s(^{-1}))</td>
</tr>
<tr>
<td>( b )</td>
<td>fractional volume of methane gas bubbles in pores</td>
</tr>
<tr>
<td>( h )</td>
<td>fractional volume of hydrate in pores</td>
</tr>
<tr>
<td>( \phi )</td>
<td>sediment porosity</td>
</tr>
<tr>
<td>( \Phi_m )</td>
<td>rate of methane production (s(^{-1}))</td>
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<tr>
<td>( \Phi_s )</td>
<td>rate of sulfate reduction (s(^{-1}))</td>
</tr>
<tr>
<td>( \Phi_h )</td>
<td>rate of hydrate production (s(^{-1}))</td>
</tr>
<tr>
<td>( \Phi_b )</td>
<td>rate of bubble production (s(^{-1}))</td>
</tr>
<tr>
<td>( \dot{S} )</td>
<td>sedimentation rate (m s(^{-1}))</td>
</tr>
<tr>
<td>( u_f )</td>
<td>fluid transport velocity (m s(^{-1}))</td>
</tr>
<tr>
<td>( v_f )</td>
<td>interstitial fluid velocity (m s(^{-1}))</td>
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<td>( v_s )</td>
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<tr>
<td>( \rho )</td>
<td>density (kg m(^{-3}))</td>
</tr>
<tr>
<td>( \lambda_m )</td>
<td>rate constant for methanogenesis (s(^{-1}))</td>
</tr>
<tr>
<td>( \lambda_s )</td>
<td>rate constant for sulfate reduction (s(^{-1}))</td>
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<tr>
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<td>rate constant for hydrate formation (s(^{-1}))</td>
</tr>
<tr>
<td>( \mathcal{R}_b )</td>
<td>rate constant for methane bubble formation (s(^{-1}))</td>
</tr>
</tbody>
</table>

Subscripts

- \( s \) sediment
- \( f \) fluid
- \( h \) hydrate
- \( b \) bubbles
- \( B \) bulk

Table A.1: Notation for model parameters
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