To the Graduate Council:

I am submitting herewith a thesis written by David Riestenberg entitled "Sediment Surface Effects on Methane and Natural Gas Hydrate Formation and Dissociation." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

Claudia Mora, Major Professor

We have read this thesis
And recommend its acceptance:

Accepted for the Council:

Vice Provost and Dean of Graduate Studies

Sediment Surface Effects on Methane and Natural Gas Hydrate Formation and Dissociation

A Thesis
Presented for the
Master of Science Degree
The University of Tennessee, Knoxville

David Edward Riestenberg
December 2001

Acknowledgements

I would like to thank Dr.s Tommy Phelps and Libby West in guiding me through this research. Their patience in teaching me scientific method, helping me generate ideas, and devising experimental procedures is greatly appreciated. I never had any doubt that they had my best interests at heart during our many discussions on the direction of the research and my future. I would like to acknowledge the efforts of David Peters and Jim Blencoe in ORNL SPS operations, Dr. Sangyong Lee provided in experimental preparation and interpretation of the data, and Dr. Yul Roh for performing X-ray diffraction analysis of the particles used in this study. I also thank Dr.s Claudia Mora and Maria Uhle for serving on my committee and putting up with my general lack of preparation.

I am forever indebted to my parents Ron and Dr. Mary Riestenberg for supporting me financially and emotionally during my pursuit of this degree. My mom taught me the love of learning that inspired my return to school for a degree in Geology. My many, and often lengthy, hikes with my dad taught me that there are few problems in life that aren't belittled by the inspiration and exhaustion derived after miles of following his long stride and even longer whistlin' tunes on the trail.

This research was supported by a grant from the Laboratory Director's Research and Development Fund of Oak Ridge National Laboratory and by the Gas Hydrates program through the Office of Fossil Energy, U.S. Dept. of Energy. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under Contract No. DE-AC05-00OR22725.

Abstract

The effects of sediment surfaces on methane hydrate formation and dissociation were investigated using colloidal suspensions and new experimental methods developed for a large volume (72-L), temperature-controlled pressure vessel. Hydrates were formed by bubbling methane gas through test solutions at temperatures and pressures within the hydrate stability field. Hydrate formation was visually detected by the accumulation of hydrate-encrusted gas bubbles. To measure hydrate dissociation conditions, the pressure vessel was warmed while temperature was monitored within a zone of previously-formed hydrate-encrusted gas bubbles. Hydrate dissociation was indicated by a distinct plateau in temperature within the hydrate zone, at the same time that temperatures of the gas and liquid phases within the vessel continued to rise. The "dissociation plateau" appears to be a phenomenon that is unique to the large volume pressure vessel used for the experiments. In experiments where hydrates were formed in pure water, temperature and pressure conditions for the temperature plateau matched model-predicted values for hydrate stability in water, confirming the validity of this new method for measuring hydrate dissociation conditions. Formation and dissociation conditions were measured for methane hydrates in colloidal suspensions containing bentonite. Hydrate formation experiments indicated that the presence of 200 mg/L bentonite in water significantly decreased pressures required for hydrate formation relative to formation in pure water. On the other hand, hydrate dissociation conditions measured in 34 g/L bentonite, silica, and calcium carbonate suspensions and a humic acid suspension with a concentration of 1g/L did not differ significantly from that of water. Dissociation experiments in a 3.4%

sodium chloride solution showed a 2 °C negative effect in hydrate stability. Dissociation conditions in natural gas hydrates in a 34 g/L bentonite suspension matched model predictions of stability in pure water. These results are relevant to the origin and stability of natural gas hydrate deposits known to exist in deep permafrost and marine sediments, where the effects of sediment surfaces are largely unknown.

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction to Gas Hydrates and Research Hypothesis.

1.1 Introduction to Natural Gas Hydrates

Gas hydrates are solid crystalline compounds that belong to a group called clathrates, consisting of a host cage of hydrogen bonded water molecules, which act to trap low molecular weight gases within their framework (Clarke et al., 1999). Hydrates share many of the characteristics of ice, including their translucent appearance and similar density (Sloan, 1998). Hydrates can exist at temperatures above the melting point of ice as long as there is sufficiently high pressure in the system (>20 bar). Hydrates concentrate their host gases (one volume of water per 207 volumes of methane in methane hydrates) (Makogon, 1997) and thus can support their own combustion if the gas is flammable.

Hydrates were first discovered in the laboratory in 1778, but they did not receive much attention until the 1930's when it was discovered that they could form in and clog natural gas lines (Sloan, 1998). There are two types of hydrate cage structures that commonly capture and trap gases (Buffett, 2000). *Structure I hydrates* are made up of 46 hydrogen bonded water molecules that form 8 cages. Structure I hydrates can only trap low molecular weight (MW) hydrocarbons, such as CH_4. In the presence of higher MW gases (propane and larger), *Structure II hydrates* will form which are made up of 136 water molecules and 24 cages (Sloan, 1998). A *Structure H hydrate* has been created in the

laboratory that can capture even larger MW hydrocarbons including those with ring structures (Makogon, 1997). The presence of the larger MW gases lends more stability to Structure II hydrates than methane gives to Structure I, so they are stable at significantly higher temperatures (up to 10 °C) or lower pressures (Makogon, 1997).

In the 1970's it was determined that vast amounts of gas hydrates occur naturally. Most naturally occurring gas hydrates are in the form of methane hydrates (Structure I). Methane hydrates occur beneath permafrost in the arctic regions and globally in sub-seafloor sediments at cold temperatures (~5 °C) and high pressures (>3 Mpa or >300m water depth). Greater than 99% of known methane hydrate deposits occur in ocean sediments (Kvenvolden, 1999). Smaller amounts of hydrates may occur within the sub-bottom sediments of large lakes (Kuzmin et al., 2000). Hydrates may also occur extraterrestrially in comets, and on other planets, such as within the Martian polar ice caps (Buffett, 2000). Methane hydrates will only form if there is sufficient natural gas in the system to initiate and continue to stabilize formation. They can potentially remain stable for long periods of time, provided there is sufficient pressure, and sufficient flux of dissolved gas into the surrounding pore waters to keep the trapped hydrate gases from dissolving (Zatsepina and Buffett, 1997). For this reason, most large hydrate deposits occur in association with a geologic structure that provides a channel for the continual renewal of gas in the system, such as faults, vents, diapirs, and mud volcanoes (Booth et al., 1996). If local gas production is extremely high or recent transport conduits have opened (such as the Gulf of Mexico), hydrates can outcrop at the water-seafloor interface. (Sassen et al., 2001), however most hydrates occur in sediment pore spaces. Within the

hydrate P/T stability zone in sediments, hydrates can occur as laminae in fine-grained sediment, more massive nodules in any sediment grain size, or as a cement which occurs predominantly in coarser-grained sediments (Booth et al., 1996). Overall however, larger amounts of hydrates appear to occur more often in coarse-grained sediments (Ginsburg et al., 2000). Recently, it has been discovered that seafloor gas seeps associated with hydrates support dynamic methanotrophic communities of organisms (Sassen et al., 1999).

Estimates of the amount of methane trapped in natural hydrates are enormous (estimates range from 1 to 46 x 10^{15} m^3 of methane; Kvenvolden, 1999; Dickens, 2001), potentially exceeding the mass of known petroleum reserves. The estimates are based on very incomplete data since hydrates are extremely difficult to sample directly. Seafloor seismic data often show a reflection at the hydrate-free gas boundary below hydrate-laden sediment. This seismic reflection is called the bottom-simulating reflector (BSR) because it follows the contours of the seafloor surface, often crosscutting sedimentary layering. A second method of estimating the global hydrate mass is based on projected estimates of the volume of seafloor sediments that are in the hydrate stability zone (HSZ), which is based on laboratory determined pressure /temperature conditions for hydrate stability (Dickens, 2001). Finally, the degree of sediment pore water freshening caused by release of salt free water when hydrates dissociate in drilled cores is used as a means to estimate total mass.

The source of the methane for seafloor hydrates is either biogenic or thermogenic. Methanogenic bacteria produce biogenic methane within anoxic conditions. Biogenic methane typically produces almost pure methane hydrates (Structure I) with a lighter carbon isotopic ($\delta^{13}C$) composition ($\delta^{13}C$ = -55 to –70‰ PDB; Kvenvolden, 1995). Thermogenic sources produce hydrates of methane plus higher MW gases (typically Structure II) (Martens, 1991) with a heavier isotopic carbon content relative to biogenic hydrates ($\delta^{13}C$ = -35 to –45‰ PDB; Kvenvolden, 1995).

Kvenvolden (1999) stated there are 3 main concerns with hydrates as they relate to human welfare: hydrates as a natural gas resource, hydrates as an agent for global climate change, and seafloor hydrates as a geological hazard. Because they are deposited predominantly in low permeability sediments (clays and fine silts) recovery of hydrates as an energy resource is currently difficult and uninviting (Kvenvolden, 1999; Ginsburg, 2000). Regardless of the degree of variability in the estimates of methane trapped in hydrates, the amount is enormous. Hydrates trap gas at up to 6 times the concentration of conventional natural gas deposits (Kvenvolden, 1999). Total estimates are 2 to 5 times the amount of currently recoverable conventional natural gas (Kvenvolden, 1999) and 300 times the amount in the total recoverable amount of natural gases in the United States (Sloan, 1998). Even if gas production from hydrates is currently unfeasable, the position of the BSR can be a useful for oil and gas exploration as a direct thermal indicator, and prominent hydrate deposits can signify active gas production in deeper sediments (Sassen et al., 2001; Grauls, 2001).

If it can reach the atmosphere without being oxidized to CO_2, methane is a very powerful greenhouse gas It is 20-30 times more effective, molecule for molecule released, in trapping heat than CO_2 (Manahan, 2000). Small releases of methane into the ocean from the seafloor, such as from a methane vent, appear to be oxidized to CO_2 prior to its release into the atmosphere. Only large releases of gas (a "burp") typically cause significant amounts of methane to reach the atmosphere (Lerche and Bagirov, 1998). Even after oxidation to CO_2, a large release of methane could change the global CO_2:O_2 ratio significantly, potentially affecting biological systems (Jahren et al., 2001). Warming of the seafloor water, potentially caused by global warming, may alter seafloor P/T conditions and cause gas release from hydrate bearing ocean sediments (Paull et al., 1996). Offshore slumping of hydrate-bearing sediments, a potential result of altered ocean currents, may also rapidly release free gas trapped beneath the hydrates. Some studies correlate methane releases to climate change and even biological extinctions in the geologic past. (Hesselbo et al., 2000; Katz et al., 1999; Padden et al., 2001). The lowering of sea-level accompanying a glacial event would lower the overburden on hydrate-bearing sediments, causing the HSZ to shift downward and methane to be released. Finally, a negative feedback to warming may occur, with an increase in sea level causing the HSZ to shift upward and global hydrate levels may thus increase again.

Dissociation of hydrates releases free gas which acts to weaken and destabilize the sediments it has formed in. This can occur if the sediment overburden is lowered (such as a sea level drop), or if the temperature of the sediment is increased by seawater warming (Paull et al., 1996; Kvenvolden, 1999). Seismic disturbances caused by drilling through

the HSZ present a risk to offshore oil-rigs or other manmade structure built on hydrate bearing sediments by initiating sediment failure. There are also explosion hazards related to offshore platform installation over hydrate-laden sediment if released gas concentration is at an explosive level.

1.2 Mineral Surface Effects on Hydrates

1.2.1 *Hydrate Formation*

Most previous laboratory studies of hydrate formation and stability have examined pure water and gas systems. Little is known of the effects of sediments (mineral surfaces) on hydrate behavior. It is extremely difficult to sample hydrates *in situ* due to their rapid dissociation when depressurized, although the limited amount of studies of hydrates in their sediments suggest a sediment grain size influence on hydrate occurrence (Ginsburg et al., 2000).

In pure water, a significant amount of subcooling or overpressurization is necessary to initiate methane hydrate formation (Blackwell, 1988; Tohidi, 2001). Mineral surfaces are known to lower the kinetic energy barrier for initiating the formation and growth of most crystal structures (Stumm, 1992) and are predicted to be effective hydrate nucleators (Cha et al., 1988; Englezos and Hall, 1994). Mineral surfaces that closely mimic the crystal structure of water ice show the greatest degree of kinetic promotion (Blackwell, 1998). Al_2O_3, $CaCO_3$, and SiO_2 particles were studied for their effect on the supercooling (i.e., actual formation temperature minus equilibrium temperature at a given pressure)

necessary to initiate hydrate formation. Both Al_2O_3 and $CaCO_3$ at 1 g/l concentrations lowered the supercooling by over 2°C compared to bulk water experiments. Crystal structure, particle shape, surface area, charge and functional groups were compared, and a crystal structure similar to ice was found to be the most important determinant of an effective nucleator. The addition of particles has been hypothesized to pre-order surface bonded water molecules in a structure similar to hydrate cages or nucleation sites (Cha et al. 1988) that could thermodynamically and/or kinetically promote hydrate nucleation. Because nearly all natural gas hydrates occur within the pores of marine or permafrost sediment, it is important to determine whether sediment surfaces significantly impact hydrate formation.

1.2.2 *Hydrate Stability*

The dissociation point for methane hydrate is an indicator of thermodynamic instability and is important when considering hydrates in a natural system. Dissociation points have been determined experimentally mainly using two techniques, depressurization and thermal stimulation of the hydrates (Sloan, 1998). In depressurization experiments, the pressure on the hydrate system is lowered below hydrate stability P/T (Kim et al., 1987). Studies using the thermal stimulation method can be done in two ways. Hydrates can be heated by adding warm fluids to the system (Kamath et al., 1984; Kamath and Holder, 1987) or hydrates can be warmed without adding warm fluids. The latter method has been used to measure hydrate equilibrium in a variety of systems, including seawater (Dickens and Quimby-Hunt, 1994; Maekawa et al., 1995), in the presence of third surfaces (Cha et al., 1988), and in soils and restricted pore spaces. (Handa and Stupin,

1992; Wright et al., 1999; Ostergaard et al., 2000). In warming experiments, hydrate dissociation can be identified and measured by a pressure increase upon release of the trapped gas, or the absorption of latent heat by the dissociating hydrates. In this study, we use the method of warming the hydrate mass to measure the dissociation point because this method can be very precisely controlled in our pressure vessel.

The first report of a mineral surface effect on hydrate stability was by Cha et al. (1988) who reported that suspensions of bentonite, a major component of drilling mud, lowered the pressure of hydrate stability at a given temperature with respect to pure water alone. Hydrates of a natural gas mixture (typical of those produced in the Gulf of Mexico) were formed by cooling a pressurized system containing the gas mixture with water and bentonite to well below the hydrate stability P/T. Hydrate formation was indicated by a sharp decrease in the vessel pressure caused by inclusion of the gases into hydrate cages. The vessel was then allowed to warm, and the vessel pressure increased as hydrates dissociated. When the pressure isochore during vessel heating met the cooling isochore, it was assumed that all hydrates had dissociated and those pressure/temperature conditions were taken to be the stability point. The presence of a 34 g/l bentonite suspension increased the hydrate stability by ~2°C. Cha et al. (1988) speculated on two possible mechanisms for the increased hydrate stability. Thermodynamic promotion of hydrates may have occured if bentonite surfaces acted as a nucleating agent to stabilize the hydrate. Kinetic promotion may have occurred if the water adsorbed to bentonite surfaces acted to pre-order water and begin hydrate lattice formation. It should be noted that these experiments were conducted in suspensions of bentonite, thus eliminating the effects of

restricted pore sizes which may also influence hydrate stability. These experiments were repeated with similar results by Ouar et al. (1992).

Englezos and Hall (1994) conducted experiments on the equilibrium conditions of CO_2 hydrate in the presence of montmorillonite. This condition was determined by forming hydrates in the presence of the clay particles well within the known P/T stability field, and then decreasing the pressure and observing the visual growth of the hydrate crystals until the threshold where growth began to occur was determined. They demonstrated that a 5g/l suspension of montmorillonite had no discernable effect on CO_2 hydrate equilibrium, however, the hydrate mass did grow more rapidly in the presence of the particles than in bulk water.

Recently, Tohidi et al. (2001) visualized hydrate growth in pore spaces of glass micromodels. Methane hydrates were formed from nucleation on the surface of gas bubbles trapped in the pores. Formation was rapid since the system was subcooled by ~11°C. After the system was allowed to equilibrate for several hours, the crystals coalesced, but a thin film of water always remained between the hydrates and the glass pore surfaces, suggesting a minimal effect of the quartz glass surface on stability.

1.3 Research Hypothesis and Objectives

The overall hypothesis of this research is that hydrates will have different formation and stability conditions in colloidal suspensions as compared to bulk water conditions.

Colloids are particles of less than 10 μm that remain suspended in fluids due to Brownian motion. For this reason, colloids are ideal for the study of surface chemistry effects on hydrate formation and stability, without the additional effects of restricted pore spaces. The surfaces of colloidal sediments will have a kinetic effect on hydrate nucleation by adsorbing and ordering water molecules via hydrogen bonding, providing nucleation surfaces for the formation of methane hydrates (Cha et al., 1988; Blackwell, 1998). Kinetic promotion of hydrate formation is measured by a drop in the overpressure necessary for hydrate formation to begin versus the overpressure necessary in bulk water alone.

Colloidal sediments may be hypothesized to cause an increase in the hydrate stability pressure/temperature as compared to bulk water conditions. This will occur because, as sediment-bound water molecules form hydrate cages, they remain bonded to the sediment surfaces, forming an absorbed hydrate and increasing stability (Cha et al., 1988). Stability is measured by determining the hydrate dissociation pressure/temperature. A goal of this research was to quantify changes in methane and natural gas hydrate stability as measured by a change in the dissociation pressure at a given temperature. Experiments were conducted using 3 different types of colloids: bentonite, microcrystalline silica (SiO_2), and calcium carbonate ($CaCO_3$), as well as a humic acid suspension. Sediment surfaces were found to be efficient at lowering the kinetic threshold for initiating methane hydrate formation. Hydrates formed in a 200 mg/l suspension of bentonite showed a significant decrease in formation pressure versus experiments conducted in water alone. However, none of the sediments tested showed significant changes in hydrate stability

versus hydrate stability in pure water. This result suggests that sediment surfaces have little effect on the thermodynamic stability of hydrates.

The major chapters of this thesis are briefly outlined below.

Chapter 2 - *Sediment Surface Effects on Methane Hydrate Formation and Dissociation*: The primary objective of this chapter was to describe our equipment and techniques used to measure hydrate formation and dissociation conditions in the presence of colloidal sediments. Results of methane hydrate formation experiments in a 200 mg/l bentonite are presented as well as hydrate stability experiments in 34 g/l suspensions of bentonite and microcrystalline silica. This chapter was submitted as a manuscript to Marine Geology in October 2001 by David Riestenberg, Olivia West, Sangyong Lee, Scott McCallum, and Tommy J. Phelps.

Chapter 3 - *Additional Experiments on Hydrate Formation and Stability*: The objective of this chapter was to provide the remaining hydrate formation and stability data for experiments not described in Chapter 2. A methane hydrate formation experiment conducted in a 10 mg/l ferrichydrite suspension showed a minimal reduction in the overpressure necessary for hydrate formation. Methane hydrate dissociation experiments were performed in a 34 g/l CaCO3 suspension, a 1 g/l humic acid suspension, and a 100 g/l microcrystalline silica suspension. Methane hydrate stability was also investigated in a fine-grained quartz sand and quartz gravel to investigate the effect of variable pore spaces on hydrate stability. Methane hydrate dissociation experiments performed in a 3.5% NaCl

solution matched literature stability values, suggesting that our hydrate dissociation technique is effective at investigating stability under a variety of conditions. Finally, stability experiments were performed with natural gas hydrates in a 34 g/l bentonite suspension.

Chapter 4 - *Discussion and Conclusions:* The purpose of this chapter was to provide an overall discussion of the data from Chapters 2 and 3 and a comparison to previous published studies on hydrate formation and stability.

Chapter 2

Sediment Surface Effects on Methane Hydrate Formation and Dissociation.

2.1 Abstract

The effects of sediment surfaces on methane hydrate formation and dissociation were investigated using colloidal suspensions and new experimental methods developed for a large volume (72 liters), temperature-controlled pressure vessel. Hydrates were formed by bubbling methane gas through test solutions at temperatures and pressures within the hydrate stability field. Hydrate formation was visually detected by the accumulation of hydrate-encrusted gas bubbles. To measure hydrate dissociation conditions, the pressure vessel was warmed while temperature was monitored within a zone of previously formed hydrate-encrusted gas bubbles. Hydrate dissociation was indicated by a distinct plateau in temperature within the hydrate zone then indicated hydrate dissociation at the same time that temperatures of the gas and liquid phases within the vessel continued to rise. The "dissociation plateau" appears to be a phenomenon that is unique to the large volume of the pressure vessel used for the experiments. In experiments where hydrates were formed in pure water, temperature and pressure conditions for the temperature plateau matched model-predicted values for hydrate stability in water, confirming the validity of this new method for measuring hydrate dissociation conditions. Formation and dissociation conditions were measured for methane hydrates in colloidal suspensions containing bentonite. Hydrate formation experiments indicated that the presence of 200

mg/l of bentonite in water significantly decreased pressures required for hydrate formation relative to formation in pure water alone. On the other hand, hydrate dissociation conditions measured suspensions of 34 g/L bentonite and silica did not differ significantly from that of water. These results are relevant to the origin and stability of natural gas hydrate deposits known to exist in deep permafrost and marine sediments, where the effects of sediment surfaces are largely unknown.

2.2 Introduction

Gas hydrates are solid crystalline compounds that consist of low-molecular weight gases trapped in a framework of hydrogen-bonded water molecules (Clarcke et al., 1999). Because they are stable at low temperatures (< 10 °C) and high pressures (>500 bar), methane hydrates naturally occur in the seafloor and permafrost sediment at thicknesses possibly exceeding 1 km (Milkov and Sassen, 2000). These deposits are considered a potential energy resource, containing 2 – 5 times the amount of methane in conventional gas sources (Kvenvolden, 1999). More recently, researchers have found evidence for rapid and massive hydrate dissociation in the geologic past that may be have been associated with global climate change (Hesselbo et al., 1999; Katz et al., 1999). Hydrate-bearing sediments may also be prone to slumping (Kvenvolden, 1999), therefore hydrates may represent a geotechnical hazard to offshore oil-rigs and platforms located in areas where sediment lies within the hydrate pressure-temperature (P-T) stability field.

Hydrate formation and equilibrium conditions in methane/water and methane/salt water systems are fairly well characterized (Sloan, 1998). However, there is a dearth of experimental data on hydrates formed in the presence of sediments where the pore structure and surface chemistry may influence equilibrium conditions (Clennell et al., 1999). A number of experiments on the influence of particle surface chemistry on hydrate formation have been reported in the literature. Blackwell (1998), for example, found that mineral surfaces that more closely mimic the crystal structure of water ice were effective hydrate nucleators, showing the greatest degree of kinetic promotion. Cha et al. (1988) and Oaur et al. (1992) observed a significant shift in the P-T stability curve of natural gas hydrate in bentonite (34 g/L) suspensions, suggesting the bentonite has a thermodynamic effect. Englezos et al. (1998) observed that CO_2 hydrate stability was unaffected by the presence of 5 g/L bentonite in water. Clearly the effects of sediment surface chemistry are still largely unknown.

We address the necessity for experimental data on sediment surface effects by investigating methane hydrate formation and dissociation in suspensions of colloidal sediment minerals. These studies were conducted using new techniques in the Seafloor Process Simulator (SPS), a large-volume, high-pressure vessel designed for research on gas hydrates under natural ocean conditions (Phelps et al., 2001).

2.3 Methods and Materials

The Seafloor Process Simulator (SPS) is a large volume, temperature-controlled high-pressure vessel capable of simulating deep seafloor pressures and temperatures where hydrates are stable (**Fig. 2.1**; Phelps et al., 2001). Details regarding the SPS (**Fig. 2.1**) can be found in Phelps et al. (2001). For the experiments reported here, the vessel pressure was measured using a series of piezoelectric transducers (Precise Sensors, model 9112) with a working range of 0-200 bar (0-2900 psi). The vessel was cooled to experimental temperatures (2 °C to 7 °C) in an explosion-proof cold room. Temperatures within the vessel were measured using Hastelloy-sheathed type K thermocouples (ARI Industries, Inc., Addison, IL) which were calibrated to an accuracy of +/- 0.2 °C. Thermocouples were placed in the gas phase, water phase, and at the gas/water interface where hydrates collected upon formation (**Fig. 2.1B**). Temperature and pressure data were collected in time sequence using a data acquisition system consisting of National Instruments Fieldpoint modules connected to a personal computer that logged data at 10 to 30 sec time intervals using LabView v5.1.

Colloidal suspensions were prepared by premixing the colloids with a small amount of distilled water. These concentrated suspensions were then diluted to the experimental concentration using distilled water. The types of colloids used in the experiments include bentonite (Avocado, Ward Hill, MA, USA product # 15795) and microcrystalline silica powder (Unimin, IMSIL microcrystalline silica A-8, Elco, Il, USA), both with a median grain size of 3 –5 μm.

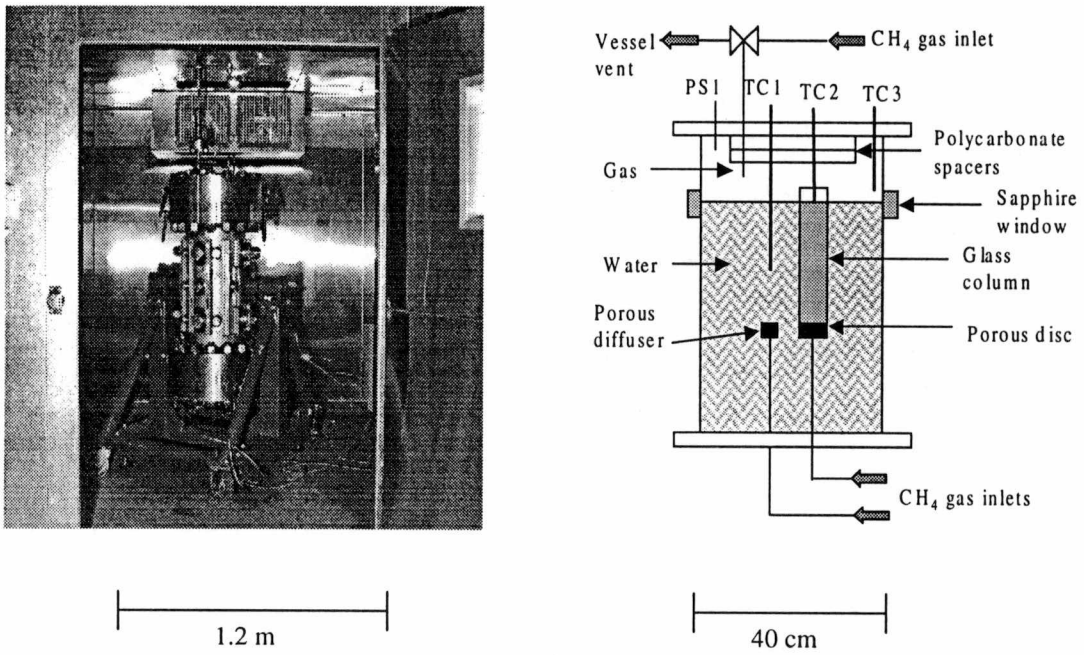

Figure 2.1 The Seafloor Process Simulator 70 (SPS) at Oak Ridge National Laboratory.
A. Photograph of the 41 port SPS and wheeled trunion mount within an explosion-proof temperature controlled environmental chamber.
B. Schematic of the SPS indicating the location of sapphire windows, water phase, gas diffuser, experimental column, thermocouples (TC1 – 3), pressure transducer (PS1), and gas inlets and outlets.

Measurement of hydrate formation conditions was as follows. The vessel was filled with 55 – 57 liters of water/colloid suspension leaving 15 – 20 liters of gas headspace (**Fig. 2.1b**). In some experiments, polycarbonate spacer disks were attached to the vessel's top lid to lower the headspace volume to about 10 liters. The vessel was then pressurized with 99.9% pure methane gas to about 34 bars and cooled to ~5 °C for at least 12 hours to allow the system to equilibrate outside of the bulk hydrate formation P-T conditions. After equilibration, and with the vessel vent closed, methane gas was injected through a stainless steel porous diffuser at the bottom of the vessel. Alternatively, methane gas was injected through a 4.8 cm-diameter, 60 cm-long glass column containing the colloid/water suspension (**Fig 2.1**). The glass column was used to ensure that the more concentrated colloidal suspensions were well homogenized during the gas injection. Gas was injected at a flow rate that caused vessel pressure to increase at 0.41- 0.48 bar/min. Prior to methane hydrate formation, gas bubbles would rise through the water and burst at the gas-water interface. Eventually, gas bubbles became encrusted with a methane hydrate film and began to accumulate at the gas-water interface (**Fig. 2.2**); the vessel pressure at this point was taken as the hydrate formation pressure. The vessel was depressurized to atmospheric conditions and flushed with nitrogen gas for a minimum of 2 hours between each experiment to minimize memory effects (Sloan, 1998). No more than two experiments were performed without emptying the water from the vessel.

Hydrate dissociation equilibrium conditions were measured by warming the vessel after a mass of hydrates was produced following the procedure described above. After a mass of hydrate was formed, methane gas was either added or vented from the vessel headspace

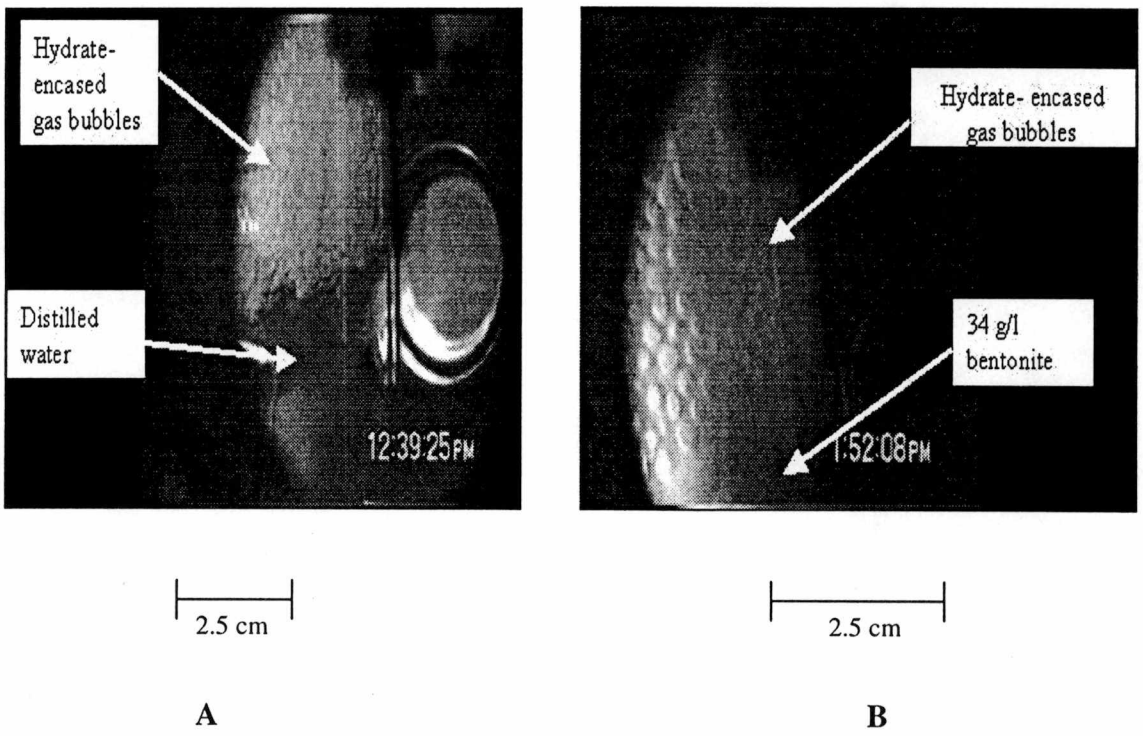

Figure 2.2 Photograph of hydrate encased CH_4 collecting at the gas/water interface in a 4.8 cm-diameter column as seen through the sapphire windows of the SPS.
A) Hydrates formed at the gas/water interface in distilled water.
B) Hydrates formed in an aqueous suspension containing 34 g/L bentonite.

to achieve the target experimental pressure. The vessel vent was then closed and the vessel was warmed by turning the cold room refrigeration off, causing the gas and liquid in the vessel to warm at a rate less than 0.5 °C/hr. During this warming, the thermocouple in the hydrate zone at the gas/water interface would increase with time, but would eventually register a near constant value (a plateau) while the temperature of the vessel headspace continued to climb. The hydrate zone temperature plateau was considered an indication of hydrate dissociation; the plateau temperature and vessel pressure were taken as the hydrate stability point.

2.4 Results and Discussion

2.4.1 Formation

Hydrate formation during vessel pressurization was detected visually through the sapphire windows by the appearance of gas bubbles encrusted by a hydrate shell, which collected at the gas/water interface (**Fig. 2.1B**). **Figure 2.2** shows two views of hydrate formation in which semi-translucent bubbles can be seen collecting at the interface within the glass column. The bubble size for the water and colloid/water experiments ranged from 3 – 5 mm in diameter, which is similar to the 2 - 6 mm bubble size created by Brewer et al. (1998) in their in situ ocean methane injection experiments. As the bulk volume of hydrate-encrusted gas bubbles increased, it would build downward into the water column and occasionally the mass would migrate abruptly upward due to its buoyancy. Buoyancy differences between suspension and water-derived hydrates have

not been quantified, although suspension-derived hydrates tended to exhibit less upward migration (data not shown).

Visual detection of hydrate formation was usually accompanied by a sharp increase in the gas/water interface temperature. This temperature jump was due to the exothermic nature of hydrate formation. The magnitude of the temperature increase ranged from 0.5 °C for a small amount of hydrates up to 3 °C if a large amount of hydrate was formed (data not shown).

It has been noted that in order to form hydrates, a system must be either overpressurized or subcooled to initiate hydrate formation (Sloan, 1998; Morgan et al., 1999; Englezos et al., 1994; Blackwell, 1988). In our experiments, the overpressurization necessary for hydrate formation dramatically decreased with the addition of colloids into the system (**Table 2.1**). The estimated formation overpressurization is the difference between actual vessel pressure upon hydrate formation and the model-calculated (CSMHYD, Sloan 1998) hydrate equilibrium pressure for pure water at the measured vessel temperature. The estimated formation subcooling is the difference between the actual vessel temperature and the model-calculated hydrate equilibrium temperature for pure water at the measured vessel pressure during hydrate formation. At 4 – 6 °C, an overpressurization greater than 40 bars was required to initiate hydrate nucleation in water (**Table 2.1**). By comparison, experiments with bentonite suspensions (200 mg/L) showed an average overpressurization of 6.6 bars at temperatures similar to the water

Table 2.1 Observed hydrate formation pressures and estimated overpressurization and subcooling in water and bentonite (200 mg/L) suspensions.

Description of Experiment	Experimental hydrate formation pressure (bar)	Vessel temperature (°C) (+/- 0.2 °C)	Calculated hydrate formation overpressure (bar)	Calculated hydrate formation subcooling (°C)
Water only	89.6	4.0	53.7	8.4
Water only	86.1	6.0	41.3	6.2
Bentonoite 200 mg/L	46.9	4.5	7.58	2.1
Bentonite 200 mg/L	45.3	4.6	6.89	1.7
Bentonite 200 mg/L	44.1	4.5	6.13	1.5
Bentonite 200 mg/L	43.8	4.5	5.79	1.5
Bentonite averages (n=4)	45.0+/- 1.4		6.60 +/- 0.80	1.7+/-0.28

experiments. The small standard deviation between the repetition of these experiments (0.8 bars) suggests that this phenomenon is highly reproducible.

Other researchers have noted a reduction of overpressurization or subcooling from pure water conditions for hydrate formation (Cha et al., 1988; Morgan et al., 1999; Blackwell, 1998). Our results suggest that even a relatively low (200 mg/L) concentration of suspended particulates has a significant effect on the kinetics of hydrate formation.

2.4.2 Dissociation

During the warming experiments, the temperature of the hydrates (at the interface) initially increased at the same rate as the water and headspace gas until it reached a point at which the gas/liquid interface temperature diverged from the gas temperature (**Fig. 2.3**, time ~10 hrs) and plateaued at a near constant value (**Fig. 2.3**, time ~12.5 hrs). The interface/hydrate zone temperature held steady over time as the temperature of the gas and liquid continued to rise. The near-constant temperature of the hydrate zone was interpreted as an indication of hydrate dissociation and absorption of the latent heat of hydrate formation. Over time, the interface temperature would rapidly join with the gas phase temperature, presumably when hydrate dissociation was complete (**Fig. 2.3**, time ~20 hrs). Hydrate dissociation experiments were conducted in a closed vessel so, as expected, gas phase pressures measured in the vessel headspace initially increased with the gas phase temperature at a relatively constant rate (e.g., **Fig. 2.3**, time < 10 hrs). Shortly after the hydrate zone temperature started to plateau, vessel pressure rose more

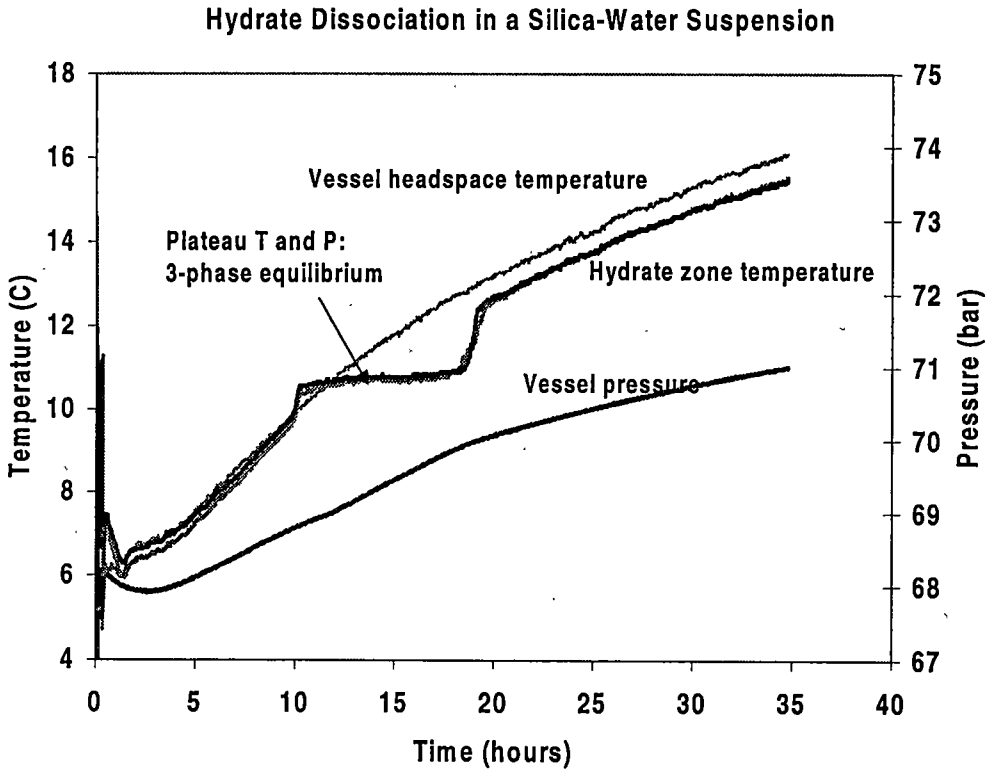

Figure 2.3 Hydrate zone and gas phase temperatures and vessel pressure during vessel warming. Note that the interface/hydrate zone temperature plateaued for ~6 hours while the gas phase temperature increased by 2 °C during the same time period. The temperature plateau was attributed to the absorption of latent heat during hydrate dissociation.

rapidly with time, probably from gas released during hydrate dissociation (**Fig. 2.3**, time ~12.5 hrs). After the temperature plateau (**Fig. 2.3**, time ~20 hrs), the rate of increase vessel pressure markedly slowed, likely due to the end of hydrate dissociation such that subsequent pressure increase was from gas heating alone. The overall pressure change during a warming experiment was typically less than 10 bars, with the pressure change during the temperature plateau on the order of 1 bar. Thus, pressure was nearly constant during hydrate dissociation.

In all dissociation experiments a distinct plateau of the gas/water interface or hydrate temperature was evident, with the duration of the plateau ranging from 0.7 hours to as long as 9.5 hours (**Table 2.2**). There were no distinct trends in the duration of the plateau with any of the experimental parameters. The duration of the plateau was probably affected by hydrate dissociation kinetics, the mass of hydrates produced, and the vessel heating rate. Because there was a limited degree of control in the amount of hydrates formed in our experiments, it is difficult to interpret the duration of the temperature plateaus listed in **Table 2.2**, although there appears to be a general trend of shorter plateau intervals at higher dissociation temperatures.

The long duration of the temperature plateaus seen in our experiments is probably a consequence of the large thermal mass of the vessel and its contents, which allow for gradual temperature increases and slow heat transfer as the vessel and its contents are

Table 2.2 Characteristics of hydrate dissociation experiments and measured hydrate equilibrium pressures and temperatures.

experiment/ test solution	dissociation temperature (°C)	dissociation pressure (bar)	duration of hydrate zone temperature plateau/hyd rate dissociation (hrs)	rate of temperature increase in hydrate zone during dissociation (°C /hr)	rate of temperature increase in gas phase during hydrate dissociation (°C /hr)
Water	10.0	69.7	5.8	0.03	0.24
	10.2	70.4			
Water	10.1	70.6	2.55	0.06	0.23
	10.3	70.8			
Water	11.8	85.8	9.5	0.03	0.18
	12.0	86.8			
Water	12.0	86.8	5.7	0.04	0.23
	12.2	87.3			
Water	14.2	105.6	1.4	0.21	0.44
	14.5	106.1			
Water + 34 g/L Bentonite	8.5	57.0	1.7	0.17	0.42
	8.8	57.2			
Water + 34 g/L Bentonite	12.4	89.6	2.0	0.03	0.35
	12.5	89.9			
Water + 34 g/L Bentonite	14.1	105.5	1.8	0.07	0.29
	14.3	105.8			
Water + 34 g/L Silica	3.6	35.5	1.76	0.01	0.61
	3.6	35.6			
Water + 34 g/L Silica	9.2	57.9	3.3	0.00	0.33
	9.2	58.3			
Water + 34 g/L Silica	9.6	68.7	1.49	0.15	0.25
	9.9	68.9			
Water + 34 g/L Silica	10.6	69.0	6.0	0.04	0.34
	10.9	70.0			
Water + 34 g/L Silica	11.73	82.3	2.38	0.05	0.21
	11.85	82.6			
Water + 34 g/L Silica	13.7	95.6	5.0	0.06	0.30
	14.0	96.7			
Water + 34 g/L Silica	14.7	107.4	0.74	0.04	0.20
	14.8	107.5			

warmed. Furthermore, the relatively high volume of gas headspace in the vessel (>10 L) allows for near-constant pressure conditions (change of < 1 bar) even while gas is released from hydrates during dissociation. Thus, it is possible to achieve quasi-equilibrium between the hydrate, gas and liquid phases in the SPS during vessel warming. The endpoints of the temperature plateau and corresponding pressures were taken as hydrate-liquid-gas equilibrium conditions. We considered a plateau as occurring when the temperature of the hydrates increased at a rate of ≤ 0.2 °C/hour and when the rate of temperature increase of the hydrates differed visibly from that of the headspace gas. Measuring hydrate P-T equilibrium conditions during hydrate dissociation is an accepted technique used by several researchers, including Cha et al. (1988) and Maekawa et al. (1995). Wright et al. (1999), conducting warming experiments in a pressure vessel containing 100 – 140 cm^3 hydrate bearing soil samples also found that the hydrate temperatures deviated from the vessel temperature for a period of 5 – 6 hours, but the deviation did not approach a plateau.

Figure 2.4 and **Table 2.2** show P-T equilibrium measurements in distilled water, bentonite, and silica suspensions. Experiments with pure water gave equilibrium values consistent with model predictions for bulk water conditions (CSMHYD, Sloan 1998). The CSMHYD model is a statistical thermodynamic model used to calculate hydrate equilibrium P/T conditions. There are three steps in calculating the model equilibrium pressure at a given temperature (described in Sloan, 1988). First, the chemical potential of the gas hydrate (chemical potential difference between gas hydrate and an empty hydrate cage) is calculated using the van der Waals model at a given temperaure and

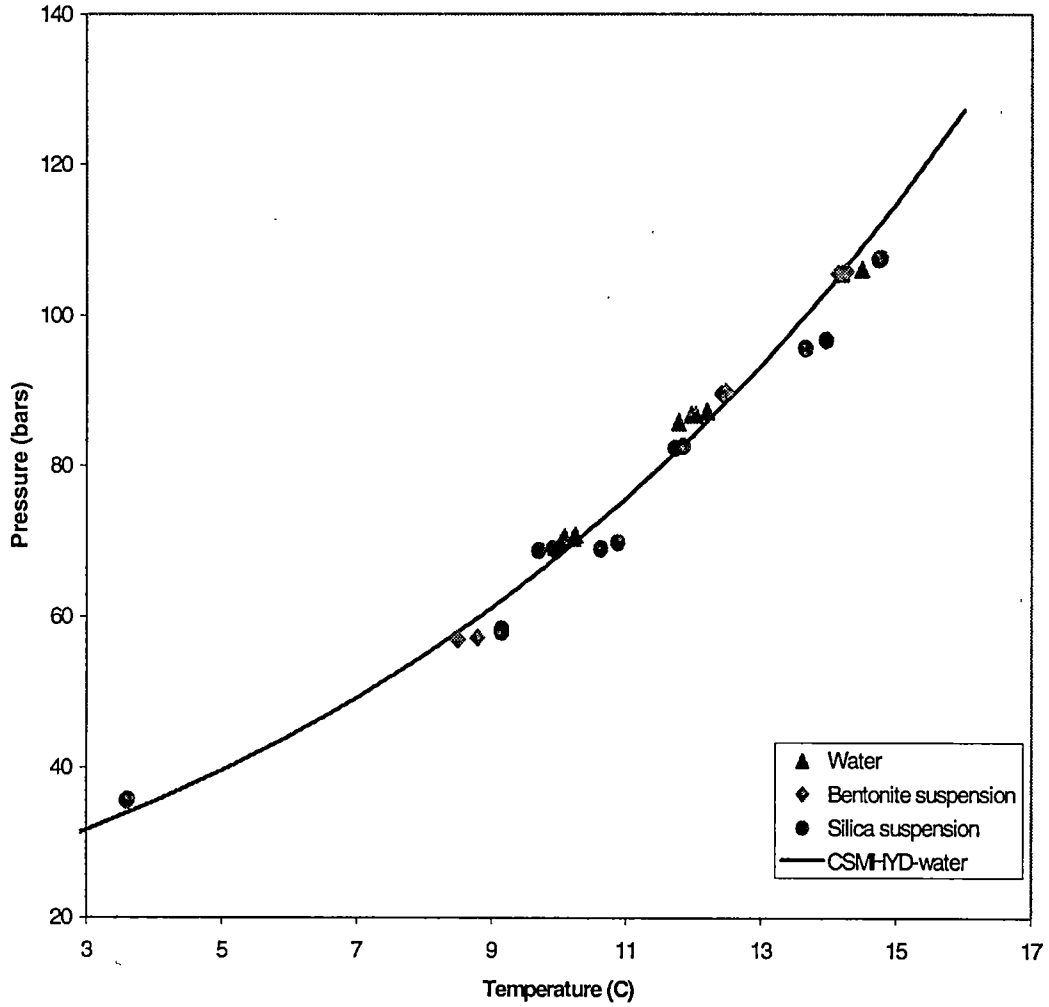

Figure 2.4 Comparison of CSMHYD model (Sloan, 1998) predictions with SPS methane hydrate equilibrium measurements.

assumed pressure. The optimized chemical potential of the empty cage is fit to hydrate equilibrium data. Second, the chemical potental for water is calculated (chemical potential difference between water and an empty hydrate cage). If the calculated potentials are equal, the given temperature and assumed pressure is equal to the equilibrium point. If they are not equal, the assumed pressure is updated and the chemical potentials are re-calculated until an equal value is determined.

The bentonite and silica data as plotted in **Figure 2.4** did not show a significant effect on hydrate stability when compared to the experimental and CSMHYD-calculated equilibrium conditions for water. The shift in equilibrium for a 34 g/L bentonite suspension reported by Cha et al. (1988) and Oaur et al. (1992) was over 2 °C versus experiments conducted in pure water. They were using a natural gas mixture which contained >10% higher molecular weight hydrocarbons. Englezos et al. (1994) reported that a 5 g/L bentonite suspension had little or no significant effect on CO_2 hydrate stability. P-T equlibrium conditions for the three test fluids are plotted in **Figure 2.5** on a semi-logarithmic graph with ln(P) and 1/T(K) on the y and x-axes, respectively. The slopes of the fitted lines in **Figure 2.5** correspond to the heats of hydrate formation (ΔH_f) for each of the test fluids through the Clausius-Clapeyron equation (Cha et al., 1988). The slopes of the fitted lines (with 95% confidence intervals) in Fig. 4b are -7985 ± 582, -9049 ± 698, and -7910 ± 474 K^{-1} for water, bentonite and silica suspensions respectively. The 95% confidence intervals were estimated as twice the standard error of the regressed slope. Using $d(\ln(P))/d(1/T) = -\Delta H_f/R$ where R is the gas constant, measured ΔH_f values are 66.4 ± 4.8, 75.2 ± 5.8, 65.8 ± 4.0 kJ/mol for water, bentonite

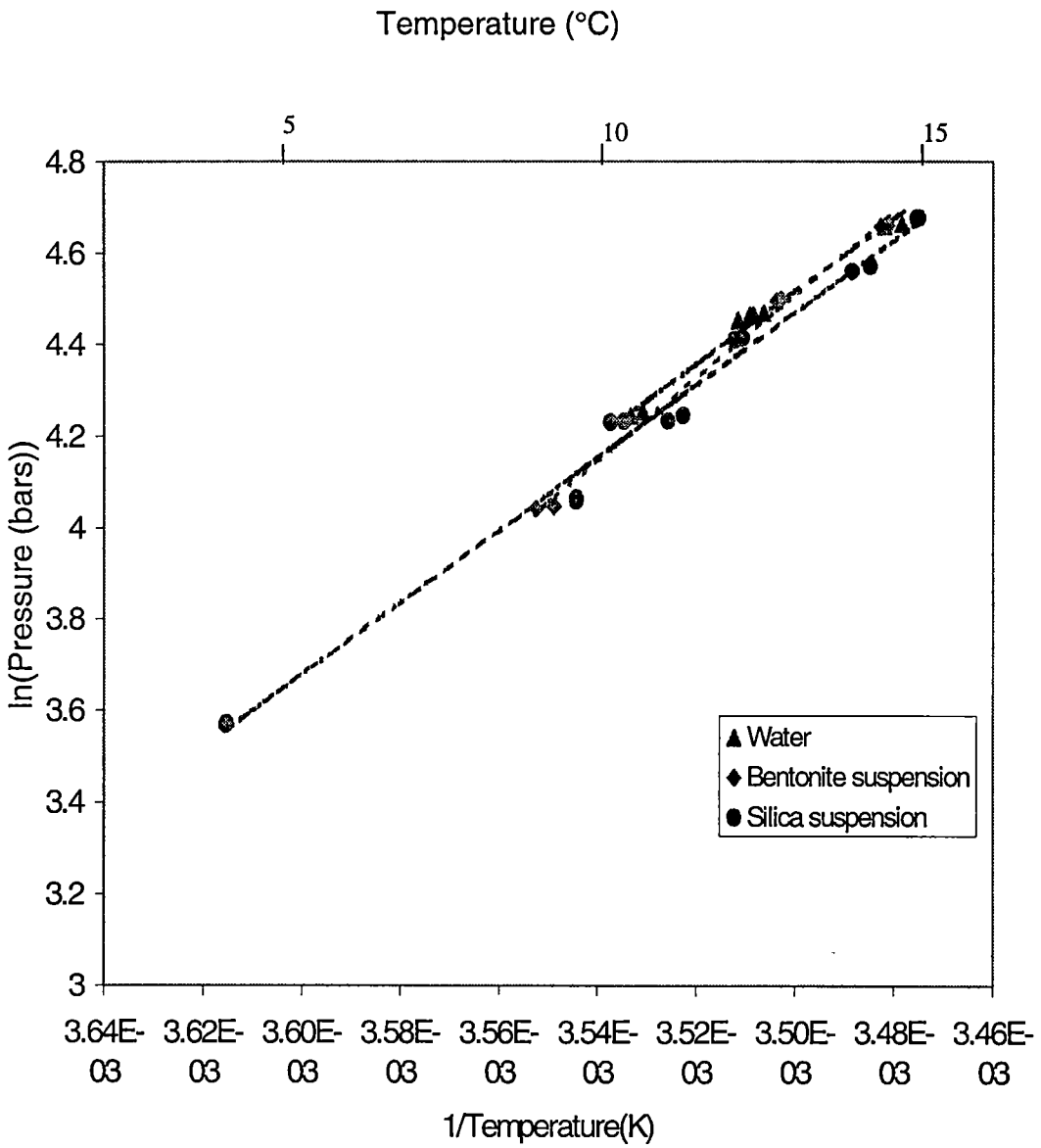

Figure 2.5 Semi-logarithmic plot of P vs 1/T (K) using same data in Figure 2.4.

and silica suspensions, respectively. ΔH_f values in the bentonite and silica suspensions are comparable to that of water alone. The difference between the water, bentonite and silica ΔH_f estimates is not statistically significant because their respective 95% confidence intervals overlap.

Equilibrium P-T conditions measured in early silica suspensions showed a deviation from the experimental and model-calculated hydrate equilibrium data in water (**Fig. 2.4**, 4 data pairs below CSMHYD line), with a temperature shift of ~0.5°C throughout the pressure range used in the experiments (**Fig. 2.4**). Subsequent silica experiments run three months after these first data showed little or no effect by the silica. There are several possible reasons for this change in the silica's activity and the overall effect of the combined data was statistically insignificant (**Figs. 2.4** and **2.5**). First, there may be some aging effect of the silica particles themselves, either through surface chemical reactions or re-crystallization. Second, minor changes in the dissolved species in the water used may have caused a decrease in the silica's surface reactivity. We have observed increases the silica's coagulation when suspensions were made in water with a higher mineral content (data not shown).

The fitted line through the silica data in **Figure 2.5** is shifted slightly relative to both the bentonite and water data. The relative shift between the bentonite and silica P-T curves may be interpreted as an increased ordering effect in the silica suspensions when compared to the bentonite suspensions. The silica powder consists of 98.5% quartz (analysis provided by supplier) while x-ray diffraction analysis of the bentonite showed a

mixed mineral composition including smectite, illite, opal, quartz and plagioclase. Because water interacts differently with different mineral surfaces, our results suggest that there may be some interaction between water molecules and the near-pure crystalline silica particles and the heterogeneous bentonite, and that the ordering on these surfaces may favor hydrate formation at higher temperatures or lower pressures. With respect to dissociation, the effect of sediment surface chemistry appears to be statistically insignificant. Additional research is being conducted using a more purified water source as well as a simulated natural gas for hydrate formation and stability studies.

2.5 Summary

In summary, we have developed a technique to examine the effects of particle concentration, type, and surface chemistry on hydrate formation and equilibrium conditions. Hydrate formation in water and colloidal suspensions were induced by bubbling methane gas through test solutions, and visually detected by the accumulation of hydrate-encased gas bubbles and the gas-water interface. The collected hydrate formation data shows a dramatic impact of suspended particles, lowering the overpressure necessary for the onset of hydrate formation even at a relatively low solid concentration. Decreasing the required overpressurization could aid attempts to produce anthropogenic gas hydrates such as in ocean CO_2 sequestration or desalinization applications. To measure hydrate dissociation conditions, the pressure vessel containing previously formed hydrates was warmed while temperature was monitored within the

zone of hydrate-encrusted gas bubbles. Hydrate dissociation was then indicated by a distinct plateau in temperature within the hydrate zone, while temperatures of the gas and liquid phases within the vessel continued to rise. The latter appears to be a phenomenon that is unique to the large volume of the pressure vessel used for the experiments. The data collected suggest that some particle surfaces, even at high concentrations, have statistically insignificant impacts on methane hydrate stability. Initial silica experiments showed an increase in hydrate equilibrium temperature but this effect disappeared in later experiments. These results are in contrast to previously reported studies where bentonite was shown to significantly lower equilibrium pressure for a simulated natural gas which contained >10% higher molecular weight hydrocarbons (Cha et al. 1988, Ouar et al. 1992). Thus, for natural gas hydrate deposits that consist of nearly pure methane, stability may be little affected by sediment surface chemistries, whereas they may significantly decrease the overpressure required for hydrate formation.

Chapter 3

Additional Experiments on Hydrate Formation and Stability.

3.1 Introduction

In this chapter, the results of hydrate formation and stability experiments which were not included in Chapter 2 will be presented. A methane hydrate formation experiment conducted in a 10 mg/l ferrichydrite suspension showed a minimal reduction in the overpressure necessary for hydrate formation. Methane hydrate dissociation experiments were performed in a 34 g/L CaCO3 suspension, a 1 g/L humic acid suspension, and a 100 g/L microcrystalline silica suspension. Methane hydrate stability was also investigated in a fine-grained quartz sand and quartz gravel to investigate the effect of variable pore spaces on hydrate stability. These results, along with the 34 g/L microcrystalline silica and bentonite experiments presented in Chapter 2 (plus one additional low temperature bentonite experiment presented here), provide evidence that sediment surfaces appear to have little effect on methane hydrate thermodynamic stability. Methane hydrate dissociation experiments performed in a 3.5% NaCl solution matched literature stability values, suggesting that our hydrate dissociation technique is effective at investigating stability under a variety of conditions.

3.2 Experimental Results

3.2.1 Hydrate formation in a 10 mg/l ferrichydrite suspension

In order to investigate the effects of a very low particle concentration on hydrate formation, a 10 mg/l ferrichydrite were suspended on water in the vessel and one nucleation experiment was conducted using the same bubbling procedure as the bentonite and water formation experiments as described in Chapter 2. The results of this experiment are presented in **Table 3.1**. At 3.7°C, the observed overpressure necessary for hydrate formation was 41.1 bars. This result is similar to the observed overpressures for the water experiments (53.7 and 41.3 bars) and is significantly higher than the 6.6 average overpressure from the 200 mg/L bentonite experiments. Morgan et al. (1999) and Blackwell (1998) also observed minimal decreases in hydrate (both methane and CO_2) formation overpressure using various solids at lower concentrations. This result suggests that either the lower concentration or the differences in mineralogy between the bentonite and ferrichydrite may eliminate the hydrate formation promotion effect. More experiments with a low concentration of bentonite would aid in determining which is the case.

Table 3.1 Observed hydrate formation pressure and estimated overpressurization and subcooling in a 10 mg/l ferrichydrite suspension.

Description of Experiment	Experimental hydrate formation pressure (bar)	Vessel temperature (°C) (+/- 0.2 °C)	Estimated hydrate formation overpressure (bar)	Calculated hydrate formation subcooling (°C)
Water + 10 mg/l ferrichydrite	75.79	3.7	41.1	7.0

3.2.2 Hydrate stability in a 34 g/l $CaCO_3$ suspension.

$CaCO_3$ deposits are common in shallow ocean settings. In order to determine what effect these mineral grains may have on hydrate stability, experiments were run in a 34 g/L suspension of ground carbonate powder derived from ooids (predominantly aragonite and calcite). The results of these experiments are presented in **Table 3.2** and in **Figure 3.1**. These results may have been complicated by the presence of dissolved CO_2 in the vessel from a previously run CO_2 hydrates experiment. Water containing a high level of carbon dioxide readily dissolves calcium carbonate minerals (Manahan, 2000) so the actual concentration of calcium carbonate in the test solution may have been lower than expected. Likewise, the ionic concentration of the test fluid may have been increased. During the dissociation plateau, temperatures of the gas phase fluctuated parallel to the interface temperatures, suggesting that CO_2 hydrates may have been forming and dissociating during the warming of the vessel. Overall, the dissociation P/T conditions matched experimental and literature values for bulk water (**Figure 3.1**). This suggests that natural carbonate sediments may not have any significant effect on the stability of hydrates within their pore spaces. After these experiments, the vessel water was changed between CO_2 and methane hydrate experiments.

3.2.3 Hydrate stability in 1 g/l of humic acid.

Humic substances are known to interact with and sorb hydrophobic organic compounds (Manahan, 2000). Although the solubility of methane is low (about 10% that of CO_2), hydrates were formed in a humic acid suspension in order to determine whether these

Table 3.2 Characteristics of methane hydrate dissociation experiments and measured hydrate equilibrium pressures and temperatures in a 34 g/l $CaCO_3$ suspension.

Experiment/ Test solution	Dissociation temperature (°C)	Dissociation pressure (bar)	Duration of hydrate zone temperature plateau/hydrate dissociation (hrs)	Rate of temperature increase in hydrate zone during dissociation (°C /hr)	Rate of temperature increase in gas phase during hydrate dissociation (°C /hr)
Water + 34 g/L $CaCO_3$	7.9	55.6	5.47	0.16	0.27
	8.8	56.3			
Water + 34 g/L $CaCO_3$	10.2	72.9	16.96	0.07	0.14
	11.4	74.6			
Water + 34 g/L $CaCO_3$	12.7	87.9	2.36	0.05	0.08
	12.8	88.5			
Water + 34 g/L $CaCO_3$	12.7	89.5	1.10	0.16	0.23
	12.9	89.6			
Water + 34 g/L $CaCO_3$	13.9	105.2	3.36	1.12	0.47
	14.3	106.0			

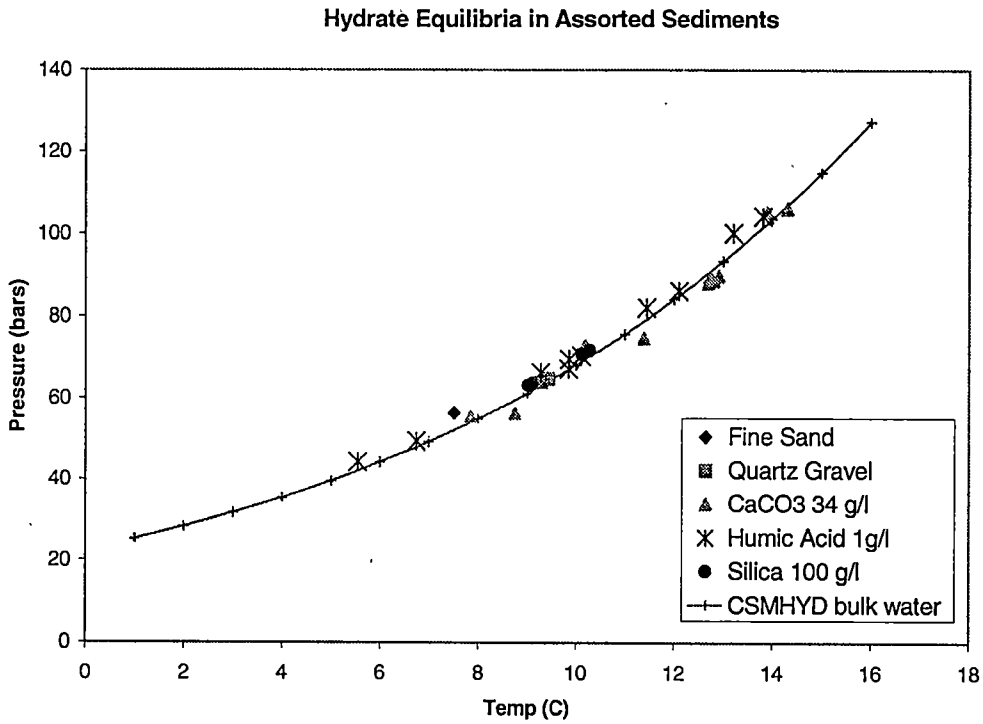

Figure 3.1 Methane hydrate equilibrium conditions in the presence of coarse-grained sediments and in assorted concentrations of colloidal minerals.

compound's interaction with dissolved phase methane might effect hydrate stability. A 1 g/L suspension of humic acid was made in distilled water and hydrates were formed and dissociated by the same procedure for the stability experiments outlined in Chapter 2. The results of these experiments are presented in **Table 3.3** and **Figure 3.1**. The dissociation P/T conditions were similar to experimental and literature values for bulk water. This result suggests that any interactions between methane or water and the humic biomolecules does not have any apparent effect on methane hydrate stability. Therefor it is not expected that hydrates formed in organic rich sediments will have significantly different stability characteristics than those formed in sediments with low organic levels.

3.2.4 Hydrate stability in a 100 g/l microcrystalline silica suspension.

In order to determine if there was a concentration dependent effect of colloidal surfaces on hydrate stability, methane hydrates were formed and allowed to dissociate in a 100 g/L suspension of microcrystalline silica in distilled water. This was the same microcrystalline silica that was used at a 34 g/L concentration for the experiments discussed in Chapter 2. These results are presented in **Table 3.4** and **Figure 3.1**. The dissociation P/T conditions for these experiments were similar to those of experimental pure water and the 34 g/l microcrystalline silica suspensions. This suggests that if there is indeed an effect of silica surfaces on hydrate stability, it remains minimal even at high concentrations.

Table 3.3 Characteristics of methane hydrate dissociation experiments and measured hydrate equilibrium pressures and temperatures in a 1 g/l humic acid suspension.

Experiment/ Test solution	Dissociation temperature (°C)	Dissociation pressure (bar)	Duration of hydrate zone temperature plateau/hydrate dissociation (hrs)	Rate of temperature increase in hydrate zone during dissociation (°C /hr)	Rate of temperature increase in gas phase during hydrate dissociation (°C /hr)
Water + 1g/L Humic Acid	5.5	44.2	6.22	0.19	0.34
	5.7	49.3			
Water + 1g/L Humic Acid	9.3	66.2	5.17	0.11	0.39
	9.9	67.2			
Water + 1g/L Humic Acid	9.9	69.6	4.47	0.06	0.23
	10.1	70.3			
Water + 1g/L Humic Acid	11.4	82.0	13.87	0.05	0.18
	12.1	86.0			
Water + 1g/L Humic Acid	13.2	100.2	25.65	0.02	0.13
	13.8	104.1			

Table 3.4 Characteristics of methane hydrate dissociation experiments and measured hydrate equilibrium pressures and temperatures in a 100 g/l microcrystalline silica suspension.

Experiment/ Test solution	Dissociation temperature (°C)	Dissociation pressure (bar)	Duration of hydrate zone temperature plateau/hydrate dissociation (hrs)	Rate of temperature increase in hydrate zone during dissociation (°C /hr)	Rate of temperature increase in gas phase during hydrate dissociation (°C /hr)
Water + Silica 100 g/L	9.0	63.08	4.44	0.02	0.32
	9.1	63.61			
Water + Silica 100 g/L	10.1	70.76	7.04	0.02	0.31
	10.3	71.61			

3.2.5 Hydrate stability in coarse-grained sediments

Two experiments were conducted on the stability of hydrates formed in coarser grained sediments (non-colloidal), one in a >1mm grain-size quartz gravel, and the other in a 200 μm grain-size quartz sand. The 4.8 x 60 cm column used was filled with the sediments and then water was added until the water level was above the top of the sediments and visible through the saphire window. In both experiments hydrates were made in the pore spaces of sediments, in contrast to the hydrates made in colloidal suspensions, as in the other formation and stability experiments. These were the first stability experiments performed and during the warming of the vessel the coldroom door warm was opened, which heated the vessel more rapidly than during the closed door experiments (all colloidal suspension stability experiments). After these experiments it was determined that optimal hydrate equilibrium conditions were best achieved by slower warming of the vessel. These experiments were conducted to determine whether the surface chemistry of the mineral grains or the restricted pore spaces would effect hydrate stability. A thermocouple was placed within the sediments at approximately the level of the gas/water interface within the sediments to measure the temperature of the hydrates.

The same bubbling technique used to make the hydrates in the Chapter 2 studies was used to make hydrates in the gravel experiment. However, gas flowed through channels formed in the fine sand when methane was bubbled through the column, eliminating the pore space effect on stability we were attempting to observe. Therefore, hydrates were formed by rapid partial depressurization of the vessel after it had been pressurized well

beyond hydrate stability P/T with methane. This technique promotes hydrate formation in two ways. First, the Joule-Thompson cooling that occurred in the gas phase significantly lowered the temperature of the gas/water interface, thus enhancing hydrate formation. Also, rapid depressurization of the water phase led to evolution of methane gas from the dissolved phase, and the formation of methane gas micro-bubbles. Hydrates then formed on the surfaces of these bubbles. This rapid depressurization technique produces a smaller mass of hydrates than the bubbling technique so only a very brief dissociation plateau occurred and only one dissociation point could be recorded.

The results of these experiments are presented in **Table 3.5** and in **Figure 3.1**. The dissociation points of these two experiments roughly match experimental and literature P/T conditions for dissociation in bulk water. This result was expected since pore size effects are not thought to effect hydrate stability until they are extremely small (Ostergaard et al., 2000). It should be noted that these experiments were preformed

Table 3.5 Characteristics of methane hydrate dissociation experiments and measured hydrate equilibrium pressures and temperatures in larger grain-size sediments.

Experiment/ Test solution	Dissociation temperature (°C)	Dissociation pressure (bar)	Duration of hydrate zone temperature plateau/hydrate dissociation (hrs)	Rate of temperature increase in hydrate zone during dissociation (°C /hr)	Rate of temperature increase in gas phase during hydrate dissociation (°C /hr)
Water + 200 μm sand	7.5	56.3	-	-	-
	-	-	-	-	-
Water + 1-2 mm gravel	9.3	64.4	4.90	0.03	0.31
	9.4	64.8			

before the thermocouples were calibrated to +/- 0.2°C so their precision may have been questionable.

3.2.6 Hydrate Stability in a 34 g/l bentonite suspension at a low temperature.

The data from Chapter 2 suggested that the effects of bentonite on hydrate stability may have been more pronounced at low temperatures. To investigate that finding, we conducted an experiment on hydrate stability in a 34 g/L bentonite suspension at ~35 bar. The result of this experiment is presented in **Table 3.6**. The dissociation P/T for this experiment matched model predictions for pure water stability. When this point is combined with the bentonite data from Chapter 2, it suggests that bentonite has little effect on hydrate stability over a large range of temperatures (3 – 14°C) and pressures (35 – 106 bars). This is equivalent to pressures from between about 350 – 1100 m ocean depth.

Table 3.6 Characteristics of methane hydrate dissociation experiments and measured hydrate equilibrium pressures and temperatures in a 34 g/l bentonite suspension.

Experiment/ Test solution	Dissociation temperature (°C)	Dissociation pressure (bar)	Duration of hydrate zone temperature plateau/hydrate dissociation (hrs)	Rate of temperature increase in hydrate zone during dissociation (°C /hr)	Rate of temperature increase in gas phase during hydrate dissociation (°C /hr)
Water + 34 g/l Bentonite	3.2	35.1	3.10	0.06	0.59
	3.4	35.4			

3.2.7 Hydrate stability in a 3.5% NaCl solution

Hydrates were formed in 3 whole vessel experiments within a 3.5 % NaCl (by weight) solution in an attempt to investigate hydrate stability in salinity similar to that of seawater. The data are presented in **Table 3.7** and **Figure 3.2**. These experiments were not conducted in a column and instead used the entire vessel volume (about 57 liters of water). The procedure for making the hydrates was similar to bubbling technique outlined in Chapter 2. A thermocouple was placed at approximately the level of the gas/water interface in the vessel to measure the temperature of the hydrates. During the warming experiments, the coldroom door was opened, creating a greater warming rate in the vessel as can be seen in the increased warming rates of the gas phase in **Table 3.7** versus the lower warming rates in the later experiments (see Chapter 2 **Table 2.2**). The decreased activity of water in the presence of dissolved ions has been shown to lower the stability of methane hydrates (Dickens and Quimby-Hunt, 1994) and our data agree with their results (**Fig. 3.2**).

3.2.8 Natural gas hydrate stability in a 34 g/l bentonite suspension.

Hydrates of natural gas are common in sediments associated with a geologic structure that allows upward migration of deep, geothermally-produced gasses (Booth and Rowe, 1996). The composition of the natural gas used in these experiments was 87.4% methane, 8% ethane, 3.1% propane, 1% butane, 0.5% n-pentane, and .04% nitrogen. This composition is typical for natural gas from the Gulf of Mexico. Since natural gases contain higher MW hydrocarbons, they will produce Structure II hydrates (Sloan, 1998). It is possible that this cage structure will interact in different ways with sediment surfaces

Table 3.7 Characteristics of methane hydrate dissociation experiments and measured hydrate equilibrium pressures and temperatures in a 3.5 % NaCl solution.

Experiment/ Test solution	Dissociation temperature (°C)	Dissociation pressure (bar)	Duration of hydrate zone temperature plateau/hydrate dissociation (hrs)	Rate of temperature increase in hydrate zone during dissociation (°C /hr)	Rate of temperature increase in gas phase during hydrate dissociation (°C /hr)
Water + 3.5%NaCl	6.7	58.1	3.51	0.28	1.2
	7.7	60.9			
Water + 3.5%NaCl	9.4	77.8	2.08	0.12	0.38
	9.6	78.5			
Water + 3.5%NaCl	11.9	103.8	5.69	0.09	0.27
	12.4	105.6			

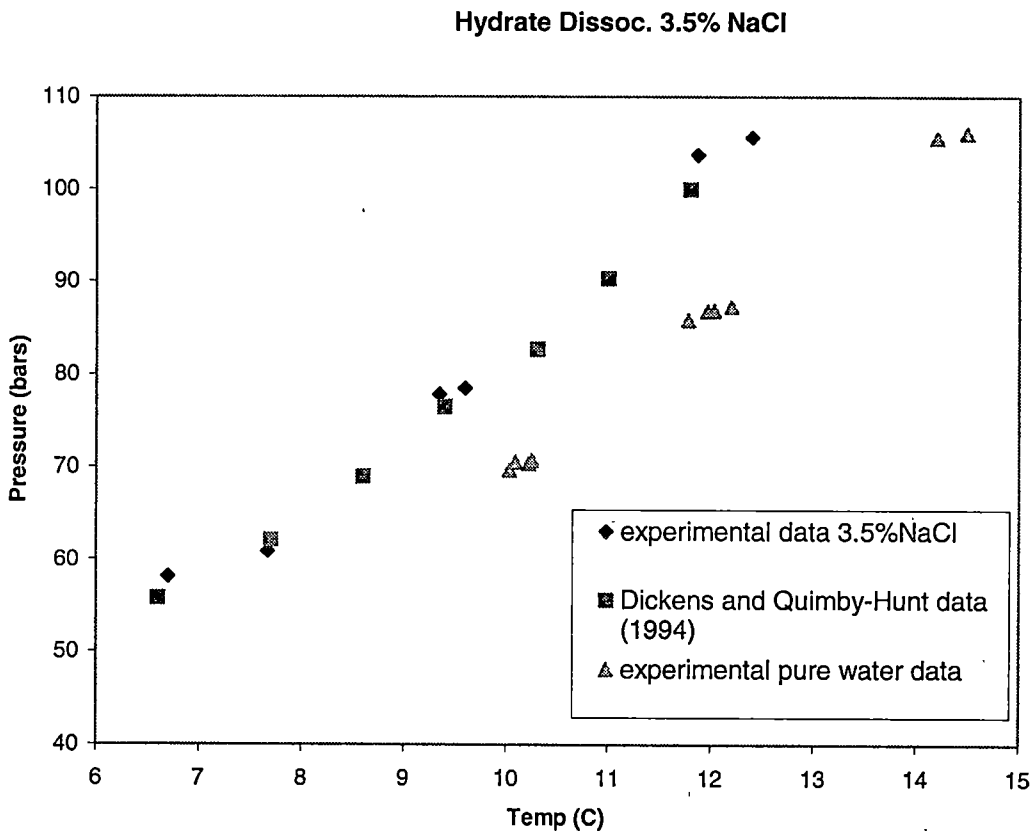

Figure 3.2 Methane hydrate equilibrium conditions in a 3.5% salt solution.

than Structure I pure methane hydrates and the effect on their stability will be altered. Natural gas hydrate stability was investigated in a 34 g/l suspension of bentonite by using the same dissociation procedure as the methane hydrate column experiments. The results of these experiments are presented in **Table 3.8** and **Figure 3.3**. In contrast to the methane hydrate experiments, there was no distinct plateau observed during the natural gas experiments. A deviation in the hydrate temperature was observed in all cases and this was assumed to mark the onset of hydrate dissociation. Associated with this temperature deviation, the pressure of the vessel would begin to increase at a greater rate, also suggesting hydrate dissociation. Since no true dissociation plateau was observed, the end of the dissociation period was recorded as the point at which the rate of vessel pressure increase slowed and increased only due to gas expansion. In two cases, it was not possible to observe this temperature change so only one dissociation point was recorded.

The results of these experiments indicated that dissociation P/T values for natural gas in a 34 g/l bentonite suspension matched CSMHYD (Sloan, 1998) model predictions (see **Fig. 3.3**) for natural gas stability in bulk water. This was the same natural gas compostion and bentonite concentration used by Cha et al. (1988) and Ouar et al. (1992) in hydrate stability experiments. They observed more vigorous formation and a 1-2°C shift toward stability at higher temperatures when hydrates were formed in the bentonite slurry versus their bulk water experiments. In their experiments, however, the vessel warming rate was

Table 3.8 Characteristics of natural gas hydrate dissociation experiments and measured hydrate equilibrium pressures and temperatures in a 34 g/l bentonite suspension.

Experiment/ Test solution	Dissociation temperature (°C)	Dissociation pressure (bar)	Estimated duration of hydrate dissociation period (hrs)	Rate of temperature increase in hydrate zone during dissociation (°C /hr)	Rate of temperature increase in gas phase during hydrate dissociation (°C /hr)
Water + 34 g/l Bentonite	9.5	22.2	-	-	-
Water + 34 g/l Bentonite	11.1	27.6	-	-	-
	-	-			
Water + 34 g/l Bentonite	10.7	27.7	2.76	0.18	0.32
	11.7	27.8			
Water + 34 g/l Bentonite	14.6	40.1	10.05	0.08	0.08
	15.2	40.4			

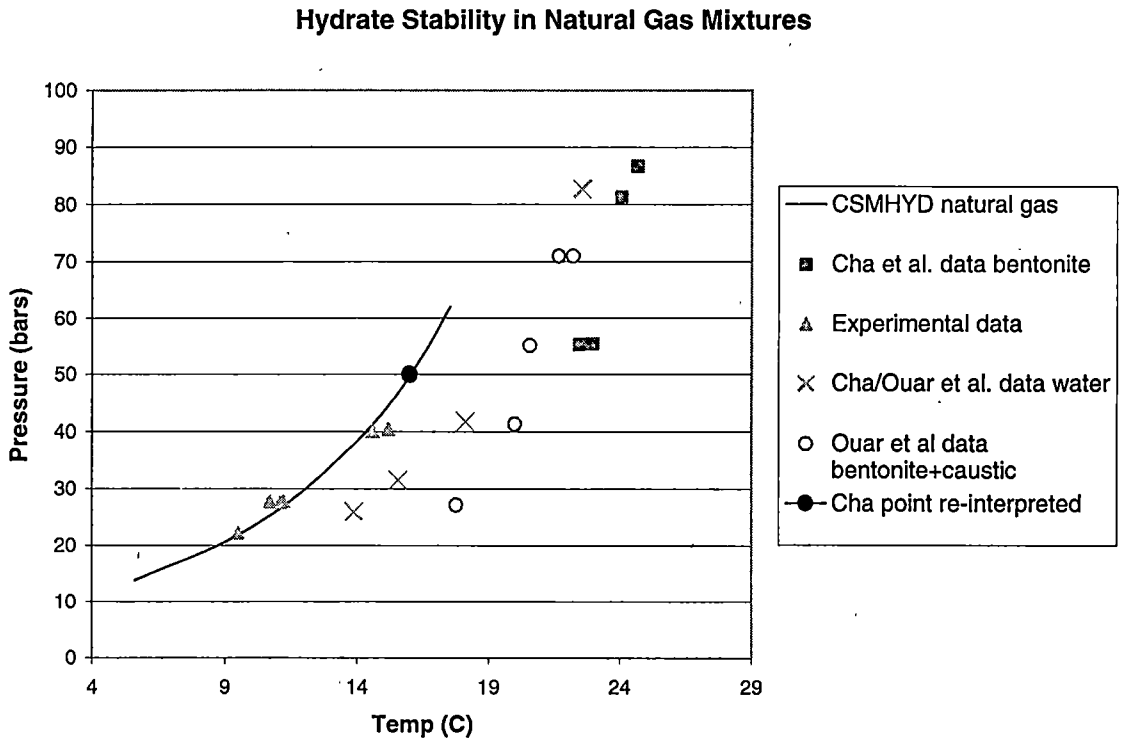

Figure 3.3 Natural gas hydrate equilibrium conditions in 34 g/l bentonite suspensions.

between 1 and 2.5°C/hr and it is possible that the bentonite did not necessarily effect hydrate stability but could have an effect on hydrate dissociation kinetics. This would be consistent with our observation of no distinct temperature plateau upon hydrate dissociation and the visual presence of hydrates after the interface temperature deviation had ended. Experiments investigating natural gas hydrate stability in bulk water are currently being conducted and may help to further investigate this hypothesis.

3.2.9 Summary Tables

Table 3.9 provides a summary of the calculated slopes and ΔH_f values along with their 95% confidence intervals for all of the fluids used in the pure methane hydrate dissociation experiments. The 95% confidence intervals were estimated as twice the standard error of the regressed slope. **Table 3.10** provides a summary of characteristics for each of the colloidal sediments studied for hydrate stability. The mineralogical content was determined by using XRD analysis (performed by Yul Roh).

Table 3.9 Calculated Slopes and heats of formation for the methane hydrate stability experiments.

Experiment	Slope +/- 95% confidence interval (K^{-1})	ΔH_f +/- 95% confidence interval (kJ/mol)
Bulk water	-7985 +/- 582	66.4 +/- 4.8
34 g/l Silica	-7910 +/- 474	65.8 +/- 4.0
34 g/l Bentonite	-8070 +/- 561	67.1 +/- 4.6
34 g/l $CaCO_3$	-8398 +/- 936	62.0 +/- 7.8
1 g/l Humic Acid	-8397 +/- 337	69.8 +/- 2.8
3.5 % NaCl	-8970 +/- 915	74.6 +/- 7.6

Table 3.10 Characteristics of the sediments studied.

Sediment	**34 g/l Silica**	**34 g/l Bentonite**	**34 g/l $CaCO_3$**	**1 g/l Humic Acid**
Composition	98.5 % Microcrystalline Quartz	Illite, Smectite, Opal, Quartz, Plagioclase	Calcite, Aragonite	Complex Biomolecules
Grain Size	3 – 5 um	3 – 5 um	3 – 10 um	-
Suspension* surface tension (dynes/cm)	74	74	75	Not performed
Suspension pH	6.3	9.4	9.0	8.1

*the measured surface tension for the bulk water was 74 dynes/cm

Chapter 4

Discussion and Conclusions.

4.1 Methane Hydrate Formation

The 200 mg/l bentonite hydrate formation experiments presented in Chapter 2 (**Table 2.1**), suggested that even a relatively low concentration of suspended particles will significantly lower the overpressure necessary for the onset of hydrate formation. Hydrate formation in a 10 mg/l ferrichydrite suspension, however, did not show a significant reduction in formation overpressure. Possible reasons for this include the low concentration of the ferrichydrite as compared to the bentonite (20 times lower), as well as possible surface chemistry differences between the two minerals.

Cha et al. (1988) noted that when natural gas hydrates were formed in a 34 g/l bentonite suspension, hydrates formed "faster, and more hydrates are formed" versus formation in pure water. Blackwell (1998) determined that low concentrations of some minerals could significantly lower methane hydrate formation "supercooling", which is synonomous with the term subcooling (formation temperature with particles present – stability temperature in pure water at a given pressure). She suggests the reason for this reduction is the increased hydrogen bonding between surface hydroxyl groups and water molecules, which produces a structure layer of water molecules that promotes hydrate cage

formation in the presence of methane. The most sensitive mineral they studied was $CaCO_3$ in which methane hydrate formation supercooling drops were apparent at 20-40 mg/l, and were statistically significant at 100 mg/l. However, even at 600 mg/l, the $CaCO_3$ particles lowered only to subcooling to 2.67 +/- 0.17°C. In our experiments, the subcooling for 200 mg/l bentonite was decreased to 1.7 +/- 0.28°C, suggesting that it may be an even stronger nucleating agent than $CaCO_3$. Bentonite contains a suite of clay minerals such as illites and smectites (**Table 3.10**) which are known to form strong H-bonds with water (Dixon and Weed, 1989) and may pre-order the surface sorbed water molecules for hydrate cage formation.

In summary, the bubbling technique used to sediment effects on hydrate formation provides reproducible results. The presence of 200 mg/l of bentonite decreased the supercooling necessary to form hydrates form in bulk water by >40 bars to 6.6 +/- 0.1 bar. Put another way, the presence of bentonite lowered the supercooling necessary to form methane hydrates to 1.7°C from >6°C in bulk water. This dramatic decrease in the kinetic barrier to hydrate formation may be valuable to development of applications, which utilize hydrate production such as desalinization and natural gas transport.

4.2 Methane and Natural Gas Hydrate Stability

As discussed in Chapter 2, some researchers have suggested that bentonite provides thermodynamic stability to hydrates (of natural gas) (Cha et al., 1988; Ouar et al., 1992) while Englezos and Hall (1994) found that montmorillonite had no discernable effect on

hydrate equilibrium. With the addition of the low temperature bentonite stability experiment described in Chapter 3 (Table 7), the calculated heat of hydrate formation (ΔH_f) using the Clausius-Clapeyron equation (Cha et al., 1988) is changed to –8070 ± 561 from -9049 ± 698 K^{-1} as presented in the Chapter 2 manuscript. This slope is very similar to the –7910 ± 474 K^{-1} slope calculated for water alone, further suggesting that in our experiments, bentonite has little effect on stability. Using $d(\ln(P))/d(1/T) = -\Delta H_f/R$ where R is the gas constant, the measured ΔH_f value for bentonite changes from 75.2 ± 5.8 to 67.1 ± 4.6 kJ/mol. This value is similar to the 66.4 ± 4.8 kJ/mol calculated for water, suggesting bentonite has little effect on the heat of hydrate formation. The calculated slopes and ΔH_f values along with their 95% confidence intervals for all of the fluids studied are presented in **Table 3.9**.

The 3.5% NaCl solution data are presented graphically in **Figure 3.2** along with our water data. Also presented are the data of Dickens and Quimby-Hunt (1994), who studied hydrate stability in 3.35% filtered seawater. Our results closely those of Dickens and Quimby-Hunt (1994) and show a >1 °C shift in hydrate stability in the presence of a high salinity solution. The results of these experiments were evidence that our hydrate equilibrium technique generates results that match literature values for conditions outside of those of pure water. Interestingly, the ΔH_f for the salt solution was the highest for any of the fluids studies and the furthest from bulk water (**Table 3.9**), suggesting that the effects of NaCl are more temperature dependant than those of the other fluids. However, it should be stressed that there are these experiments were conducted outside of the

column in the whole vessel, with a more rapid vessel heating rate, and conducted before the thermocouples were calibrated.

Two stability experiments were conducted in sediments with grain-sizes larger than colloidal, one with a quartz gravel and one with a fine-grained quartz sand. In both cases the hydrate dissociation conditions were similar to those conducted in bulk water (Chapter 3, **Table 3** and **Fig. 1**). Like the NaCl solutions, these experiments were conducted with the coldroom door open causing more rapid vessel warming using uncalibrated thermocouples. In both experiments, hydrates were made in the pore spaces of sediments, in contrast to hydrates made in a colloidal suspension as in other stability experiments. Very small pore spaces may cause lower stability temperatures due to high interfacial tension (Clennell et al., 1999). The results were expected since restricted pore spaces are not thought to affect hydrate stability until they are on a very fine-scale (pore diameters of < 250 Å (Ostergaard et al., 2000)). However, the technique of rapid depressurization used to form hydrates in the fine sand could be useful for producing hydrates in fine-grained sediments or in highly concentrated suspensions.

Humic acid is a complex mix of biopolymer which are the resulting stable products of microbial breakdown of soil biomass (Sposito, 1989). Many organic substances may interact with humic material through hydrogen bonding or weak van der Waals interactions. Methane has a relatively low solubility, between 0.06 – 0.16 mol/L in fresh water at the experimental pressures in which these experiments were conducted (Duan et al., 1992). However, it is possible that dissolved methane interacted with a complex

organic substance, such as humic acid, to introduce some effect on the stability of methane hydrates. Hydrates formed in a 1 g/l suspension of humic acid, however, showed a similar stability curve as that of bulk water (Chapter 3, Figure 1). This result suggests that if any interactions between methane and the humic acid is occuring, the effect is insignificant in the stability of methane hydrates.

Carbonate deposits are common in ocean sediments. The average carbonate compensation depth in the modern ocean is about 4500 m (Boggs, 1995). Since hydrates commonly form in sediments much shallower than that depth, it is possible for hydrates to form in carbonate deposits. Powdered ooid carbonates composed primarily of calcite and aragonite were used to simulate natural carbonate sediments. Overall, the dissociation of methane hydrates was similar to that of bulk water (Chapter 2, Table 5 and Figure 1). However, the flatlines during dissociation during these experiments were different than during any of the other experiments. The flatlines were quite erratic, fluctuating by as much as 0.5 °C. Also, the temperature of the gas phase would often show the same curious erratic plateau. There are at least two hypotheses for this behavior. First, when the ground carbonates were suspended in water at high pressures and low temperatures, they could be quite soluble releasing Ca^{+} and CO_3^{-} ions into the water phase increasing the overall the ionic strength. More likely, however, is the possibility that CO_2 that was dissolved in the surrounding vessel water formed CO_2 hydrates both in the gas phase as well as in the column. This possibility would help explain the gas phase temperature paralleling that of the interface temperature.

Experiments were conducted on a 100 g/l suspension of silica to determine whether a more concentration of solids might contribute to hydrate stability. The dissociation conditions of these experiments matched those obtained for pure water (Chapter 3, Table 6 and Figure 1), suggesting that even a concentration of sediment surfaces may not effect methane hydrate stability.

Natural gas hydrates formed in a 34 g/l bentonite suspension had dissociation P/T values similar to natural gas stability model predictions (CSMHYD Sloan, 1998). In contrast to experiments conducted with pure methane hydrates, natural gas hydrates did not display an equilibrium dissociation plateau. This may be due to the fact that as the natural gas components were released upon dissociation, the higher MW gasses (such as propane and ethane) may have re-formed hydrates which would have higher stability P/T's than the mixed gas (Sloan, 1998).

The natural gas composition used was the same natural gas compostion and bentonite concentration used by Cha et al. (1988) and Ouar et al. (1992) in hydrate formation and stability experiments. They observed more vigorous formation and a 1-2°C shift toward stability at higher temperatures when hydrates were formed in the bentonite slurry versus their bulk water experiments. In their experiments, however, the vessel warming rate was between 1 and 2.5°C/hr and it is possible that the bentonite did not necessarily effect hydrate stability but could have had an effect on hydrate dissociation kinetics. This would be consistent with our observation of no distinct temperature plateau upon hydrate dissociation and the visual presence of hydrates after the interface temperature deviation

had terminated. Another possibility is that their technique of taking the P/T at the last point of pressure increase as the equilibrium point may not give a true representation of hydrate stability under those conditions. In **Figure 3.3**, their P/T points for bulk water do not match up with model predictions and are indeed >1 °C too far into the stability zone. This may be a consequence of the rapid warming rate employed in their technique. In their paper, an example hydrate formation/dissociation run in 34 g/l bentonite is shown. If the point halfway between the onset of hydrate dissociation (marked by an increase in vessel pressure) and the end of the dissociation period (marked by the end of the pressure increase, the point taken as the equilibrium point) is marked, it plots very near the bulk water equilibrium point. This point is plotted in **Figure 3.3**. While this method was valuable for predicting the effects of bentonite in drilling muds on hydrate formation and dissociation in pipelines where temperature changes are more rapid, it may not reflect the role of mineral surfaces on natural hydrate stability where temperature fluctuations are generally slower. Experiments investigating natural gas hydrate stability in bulk water are currently being conducted and may help to further delineate the role of bentonite on natural gas hydrate dissociation thermodynamics and kinetics.

Very recently, Tohidi et al. (2001) observed gas hydrate growth in pore spaces within glass micromodels. They noted that methane hydrates only grew on the surfaces of gas bubbles (i.e. from gas phase methane) and not from dissolved methane. After hydrates had grown and stabilized for several hours, they filled most of the pore spaces but a thin layer of liquid water was always present between the hydrate mass and the pore walls. A significant subcooling (~11°C) was necessary to instigate hydrate formation. They

suggested that the presence of nucleation seeds could have decreased the subcooling necessary for formation and could possibly have facilitated hydrate formation from dissolved phase methane. Our data suggests that bentonite is a powerful seed for hydrate formation which significantly lowers the subcooling/overpressure necessary for hydrate formation and could be useful in studies such as this. They attribute the lack of hydrate contact with the quartz-like glass pore walls to the stronger wettability of water to quartz than gas to quartz. They speculate that in natural system, the presence of non-silicate minerals and organic matter may change the behavior of hydrate growth. While lacking the ability to visualize hydrate growth on mineral surfaces, our results suggest that after hydrates have formed, they may not significantly interact with non-silicate minerals (bentonite and carbonate) or organic matter (humic acid).

In conclusion, none of the sediments studied demonstrated a significant effect on methane hydrate stability. While bentonite did display a dramatic effect on the kinetics of hydrate formation, it, along with the other minerals studied, did not seem to effect stability thermodynamics. Thus it seems that mineral surfaces may provide a nucleation surface to aid in the initialization of hydrate formation, but they do not appear to interact with the hydrate structure after formation. Therefore, the mineralogy of seafloor and permafrost deposits may not be a significant determinant of the presence or absence of natural gas or pure methane hydrates.

References

Boggs, S. Jr., 1995. Principles of Sedimentology and Stratigraphy. Prentice Hall, Inc. Upper Saddle River, NJ.

Booth, J. S., Rowe, M. M., Fischer, K. M., 1996. Offshore Gas Hydrate Sample Database with an Overview and Preliminary Analysis. U. S. Geological Survey Open File Report 96-272

Brewer, P. G., Orr, Jr. F. M., Friedrich, G., Kvenvolden, K. A., Orange, D. L., 1998. Gas Hydrate Formation in the Deep Sea: In Situ Experiments with Controlled Release of Methane, Natural Gas, and Carbon Dioxide. Energy and Fuels 12:183 – 188

Blackwell, V. R., 1998. Formation Processes of Clathrate Hydrates of Carbon Dioxide and Methane. PhD Thesis. California Institute of Technology, California.

Buffett, B. A., 2000. Clathrate Hydrates. Annual Reviews on Earth and Planetary Science. 28:477-507

Cha, S. B., Ouar, H., Wildeman, T.R., Sloan, E.D., 1988. A Third Surface Effect on Hydrate Formation. Journal of Physical Chemistry. 92:6492-6494

Clennell, M. B., Hovland, M., Booth, J. S. Henry, P., Winter, W. J., 1999. Formation of Natural Gas Hydrates in Marine Sediments. 1. Cenceptual Model of Gas Hydrate Growth Conditioned by Host Sediment Properties. Journal of Geophysical Research. 104:22,985-23,303

Clarke, M.A., Pooladi-Darvish M., Bishnoi, P. R., 1999. A Method to Predict Equilibrium Conditions of Gas Hydrate Formation in Porous Media. Indian Engineering Chemistry Research. 38:2458-2490

Dickens, G., 2001. The Potential Volume of Oceanic Methane Hydrates with Variable External Conditions. Organic Geochemistry. 32:1179-1193

Dickens, G. R., Quimby-Hunt, M. S., 1994. Methane Hydrate Stability in Seawater. Geophysical Research Letters. 19: 2115-2118

Dixon, J. B., Weed, S. B., 1989. Minerals in Soil Environments. SSSA Book Series 1. Soil Science Society of America. Madison, WI, USA

Duan, Z. H., Moller, N., Greenberg, J., Weare, J. H., 1992. The Prediction of Methane Solubility in Natural-Waters to High Ionic-Strength from 0 degrees C to 250 Degrees C and from 0 to 1600 Bar. Geochimica et Cosmochimica Acta 56:1451-1460

Englezos, P., Hall, S., 1994. Phase Equilibrium Data on Carbon Dioxide Hydrate in the Presence of Electrolytes, Water Soluble Polymers and Montmorillonite. Canadian Journal of Chemical Engineering. 72, 887–893

Englezos, P., and Ngan, Y. T., 1994. Effect of Polyethylene Oxide on Gas Hydrate Equilibria. Fluid Phase Equilibria.. 92:271-288

Ginsburg G., Soloviev V., Matveena T., Andreeva I., 2000. Sediment Grain-Size Controlon Hydrate Presence, Sites 994, 995, and 997. Proceedings of The Ocean Drilling Program, Scientific Results. 164.

Grauls, D., 2001. Gas Hydrates: Importance and Applications in Petroleum Exploration. Marine and Petroleum Geology. 18: 519-523

Handa, Y. P., Stupin, D., 1992. Thermodynamic Properties and Dissolution Characteristics of Methane and Propane Hydrates in 70-Å-Radius Silica Gel Pores. Journal of Physical Chemistry. 90: 8599-8605

Hesselbo, S.P., Grocke, D.R., Jenkyns, H.P., Bjerrum, C.J., Farrimond, P., H.S, Morgans-Bell, Green, O.R., 2000. Massive Dissociation of Gas Hydrate during a Jurassic oceanic anoxic event. Nature. 406:392-395

Jahren, A., Arens, N., Sarmiento, G., Guerro, J., Amundson, R., 2001. Terrestrial Record of Methane Hydrate Dissociation in the Early Cretaceous. Geology. 29:159-162

Kamath, V. A., Holder, G. D., 1987. Dissociation Heat Transfer Characteristics of Methane Hydrates. AIChE Journal 33: 347-350

Kamath, V. A., Holder, G. D., Angert, P. F., 1984. Three Phase Heat Transfer During the Dissociation of Propane Hydrate. Chemical Engineering Science 39: 1435-1442

Katz, M. E., Pak, D.K., Dickens, G. R., Miller, K. G., 1999. The Source and Fate of Massive Carbon Input During the Latest Paleocene Thermal Maximum. Science. 286:1531-1533

Kim, H. C., Bishnoi, P. R., Heideman, R. A., Rizvi, S. H., 1987. Kinetics of Methane Hydrate Decomposition. Chemical Engineering Science. 42:1645-1653

Kvenvolden, K. A., 1999. Potential Effects of Gas Hydrate on Human Welfare. Proceedings of the National Academy of Science. 96:3420-3426

Kvenvolden, K., 1995. A Review of the Geochemistry of Methane in Natural Gas Hydrate. Organic Geochemistry. 23: 997-1008

Kuzmin, M. A., Geletiy, V. F., Kalmychkov, G., Kuznetsov, F. A., Larionov, E. G., Manakov, A. Yu., Mironov, Yu. I., Smoljakov, B. S., Dyadin, Yu. A., Duchkov, A. D., Bazin, N. M., Mahov, G. M., 2000. The First Discovery of the Gas Hydrates in the Sediments of the Lake Baikal. In *Gas Hydrates. Challenges for the Future*. New York Academy of Sciences. New York, NY. 112-116

Lerche, I., Bagirov E., 1998. Guide to Hydrate Stability in Various Geologicical Settings. Marine and Petroleum Geology. 15:427-437

Maekawa, T., Itoh, S., Sakata, S., Igari, S-I., Imai, N., 1995. Pressure and Temperature Conditions for Methane Dissociation in Sodium Chloride Solutions. Geochemical Journal 29:325-329

Makogon Y. F., 1997. Hydrates of Hydrocarbons. PennWell Books. Tulsa, OK.

Manahan, S. E. 2000 Environmental Chemistry. Lewis Publishers. New York, NY.

Martens C. S., Chanton J. P., Paull C. K., 1991. Biogenic methane from abyssal brine seeps at the base of the Florida Escarpment. Geology. 19:851-854

Milkov, A. V., Sassen, R., 2000. Thickness of the Gas Hydrate Stability Zone, Gulf of Mexico Continental Slope. Marine and Petroleum Geology 17:981–991

Morgan, J. J., Blackwell, V. R., Johnson, D. E., Spencer, D. F. North, W. J., 1999. Hydrate Formation from gasseous CO_2 and Water. Environmental Science and Technology. 33:1448 – 1452

Ouar, H., Cha, S. B., Wildeman, T. R., Sloan, E. D., 1992. The Formation of Natural Gas Hydrates in Water-Based Drilling Fluids. Transactions of IchemE. 70 Part A.

Ostergaard, K. K. Llamedo, M. Burgass, R. W., Tohidi, B., 2000. On Hydrate Equilibria in Porous Media. Presented at AGU. Fall 2000 meeting.

Padden, M., Weissert, H., de Rafelis, M., 2001. Evidence for Late Jurassic Release of Methane from Gas Hydrate. Geology. 29: 223-226

Paull, C. K., Buellow, W. J., Ussler, W., Borowski, W. S., 1996. Increased Continental-Margin Slumping Frequency During Sea-Level Lowstands Above Gas Hydrate-Bearing Sediments. Geology 24:143-146

Phelps, T. J., Peters, D. J., Marshall, S.L., West, O. L., Liang, L., Blencoe, J. G., Alexiades, V., Jacobs, G. K., Naney, M. T., Heck Jr., J. L., 2001. A New Experimental Facility for Investigating the Formation and Properties of Gas Hydrates under Simulated Seafloor Conditions. Reviews of Scientific Instruments. 72:1514-1521

Sassen, R., Losh, S., Cathles III, L., Roberts, H., Whelan, J., Milkov, A., Sweet, S., DeFreitas, D., 2001. Massive Vein-Filling Gas Hydrate: Relation to Ongoing gas Migration from the Deep Subsurface in the Gulf of Mexico. Marine and Petroleum Geology. 18: 551-560

Sassen, R., Joye, S., Sweet, S., DeFreitas, D., Milkov, A., MacDonald, I., 1999. Thermogenic Gas Hydrates and Hydrocarbon Gasses in Complex Chemosynthetic Communities, Gulf of Mexico Continental Slope. Organic Geochemistry. 30: 485-497

Sloan E. D.,1998. Clathrate Hydrates of Natural Gases, 2nd ed. Marcel Dekker, New York, NY.

Sposito, G., 1989. The Chemistry of Soils. Oxford University Press. New York, NY.

Stumm, W., 1992. Chemistry of the solid-water interface Wiley-Interscience, New York.

Tohidi, B., Anderson, R., Clennell, M.B., Burgass, R., Biderkab, A., 2001. Visual Observation of Gas-Hydrate Formation and Dissociation in Synthetic Porous Media by Means of Glass Micromodels. Geology. 29: 867-870

Wright, J. F., Dallimore, S. R., Nixon, F. M., 1999. Influences of Grain Size and Salinity on Pressure-Temperature Thresholds for Methane Hydrate Stability in JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research-Well Sediments; in Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research-Well, Mackenzie Delta, Northwest Territories, Canada. GSC Bulletin 544:229-240

Zatsepina, O. Ye., Buffett, B. A., 1997. Phase Equilibrium of Gas Hydrate: Implications for the Formation of Hydrate in the Deep Sea Floor. Geophysical Research Letters. 24:1567-1570

Vita

David Edward Riestenberg was born and raised in Cincinnati, Ohio. He attended St. Teresa of Avila grade school and Covington Latin High School (minus one year at Elder High School) where he played basketball for teams that went a combined 6-39, give or take a few losses. He attended the College of Mount St. Joseph and majored in Biology, graduating Magna cum Laude in 1996. Dave decided to take a few years off of school and held several interesting jobs such as swim club pass checker and hotel valet. In 1998 he accepted a one year position at the University of Cincinnati Department of Cell Biology in Dr. Sohaib Khan's cancer research lab. During that time, David began to consider graduate school, but he wanted to learn as much as possible during his studies, so he decided to change fields from his undergrad major and he went into Geology, the subject in which his mother received her PhD. He was accepted at the University of Tennessee and began the pursuit of an MS in the fall of 1999. His initial interest was in the subject of paleontology, but none of the possible projects at UT piqued his interest, so he looked into alternative projects. In the winter of 2000, David met Dr. Tommy Phelps at Oak Ridge National Laboratory where he was introduced to the field of gas hydrate research. They agreed to a project studying the effects of sediments on hydrate formation. This thesis is the result of that research. Also during his tenure at UT, David learned to love the outdoor escapes in which Tennessee abounds. He also acquired an undying love of the color orange.

Like many Cincinnatians, Dave is a mixture of German and Irish heritage and so he enjoys nearly all forms of beer.