

Origin and character of gaseous hydrocarbons in the hydrate and non-hydrate charged sediments on the Norway - Svalbard margins

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# Preface

The work of this PhD thesis was carried out at the Department of Chemistry at the University of Bergen. The thesis consists of an introductory part, a synthesis of the main results and a third part, which consists of one published and two submitted papers. It is a contribution to the Norwegian Research Council PETROMAKS project Gas hydrates on the Norwegian - Svalbard margins (GANS, Norwegian Research Council project no. 175969/S30). The GANS project is an academia-industry collaborative, financed by the Norwegian Research Council (NFR) and a consortium of private investors (oil companies). The GANS project is an interdisciplinary venture combining geochemistry, geology, geophysics and geo-microbiology in the investigation of hydrate bearing margins on Norwegian territory. The scope of the project is well out of measure for this dissertation, which concentrates on the GANS subtask; Identify the origin of gaseous hydrocarbons in hydrate and non-hydrate charged sediments.

During the four years of research, I have participated at four international conferences, been on four research cruises and contributed to the GANS' official and intern meetings and workshops. The great variety of tasks and the fascinating nature of the topic made it possible for me to publish a popular science article in Klassekampen, and be interviewed by Dagens Næringsliv.

To some extent the GANS project has been a pioneer in gas hydrate research in the Norwegian science community, and in the pursuit of monitoring geochemical aspects of hydrate bearing sediment I have had to employ a set of sampling methods including techniques both common and uncommon to the geochemical research community. In addition, the thesis also includes gas hydrate laboratory experiments making me the fortunate candidate of a versatile submitting.

## Acknowledgements

To build this house called a dissertation, I would not have made it without my main architect of chemistry; Professor Tanja Barth. Numerous times I have stepped into my architectures office depressed thinking the house was missing a room, a staircase or a toilet, only to find she had a new blueprint of the building in her drawer helping me to see how things could be arranged. Of course I also benefitted from the skilled contractor of geology, Professor Haffidi Haffidason, guiding me through the building materials. Without him I believe it would be built on sand.

In the early but crucial process of raising the house skeleton Anna, Kristin and Guro was help of essence. Notes and templates of how to do specifics and a good push in the back now and then are much obliged. Throughout the building process various expertise has been provided, and I am grateful for Shiva and Djurdjica's calculations in the 'kitchen area', Vibeke and Elin for analysis of 'air quality' and Berit for being like the kind of colleague of Haffidi's who knows more about his own back yard than him self. Of course I want to give the whole group of individuals in Tanjas party a hand for all being cooperative and good humoured. Of the workers on the building site and encountered during the building process to whom I could generally contemplate the subject of building houses, I would like to name Inge, Bergithe, Sylvi and Rhiannon.

To all of my friends and acquaintances who either have helped with carrying, measuring and feeding me, or just have kept me happy off the construction site; thank you.

And finally to my family: You are the land of which this house was founded on.

# Abstract

Gas incubated in clathrate water-structures, stabilizes the hydrogen bonded substance termed gas hydrate. In the marine environment vast amount of carbon is stored as gas hydrates within the temperature and pressure zone these ice-like structures are stable. Natural gas hydrate mapping and characterization is important basic research that brings about critical knowledge concerning various topics. Natural gas hydrates is a vital part of the carbon cycle, it is a potential energy resource (and thereby a potential climate agent) and it is a potential geo-hazard.

One of the goals the GANS initiative aimed at exploring, was the hydrate bearing sediment of the Norway -Svalbard margins, to investigate the character and expansion of natural gas hydrates. Part of the investigation was to define how the gas in the hydrated sediment was produced and where it came from. As a result this thesis addresses the matter of light hydrocarbon characterization and origin in two Norwegian hydrate deposits.

On cruises to Vestnesa on the Svalbard margin and to Nyegga in the mid-Norwegian margin, samples of hydrate charged and non-hydrate charged sediments were obtained and analyzed. Through compositional and isotopic analyses the origin of the hydrate bound gas in the fluid escape feature G11 at Nyegga was determined. The hydrate incubated methane is microbial produced as well as parts of the hydrate bound ethane. The compositional analysis in both the Nyegga area and at the Vestnesa Ridge points at thermogenic contributions in the sediment interstitials and pore water.

The two hydrate bearing margins show large differences in hydrocarbon content and microbial activity in the pockmarks investigated. The gravity cores from the penetrated pockmark at Vestnesa showed low hydrocarbon content and thus suggest ceased or periodic venting. The fluid flow escape

features at Nyegga show large variety of flux rates based on ROV monitoring and headspace analysis of the sediment and pore water. The light hydrocarbon content varies largely both between the pockmarks and within a single pockmark.

Laboratory experiments have been performed to consider the carbon isotope fractionation effect of hydrate formation. The experiments display minor fractionation with contrasting fractionation effects of carbon isotopes when forming methane hydrates and structure two hydrates of methane, ethane and propane. This does not conflict with the interpretation of the isotopic signature of the hydrated deposits at Nyegga. Thus the proposed microbial carbon circulation in the free gas zone beneath the gas hydrate stability zone is withheld as the probable root of the light isotopic signature.

# List of Papers

**Paper I:** The geochemical characteristics of the hydrate-bound gases from the Nyegga pockmark field, Norwegian Sea. E. Vaular, T. Barth and H. Hafliðason. *Org. Geochem.* 41 (2010), pp. 437-444.

**Paper II:** Comparison of Vestnesa and Nyegga Pockmark Fields using light hydrocarbon parameters for geochemical profiling. E. Vaular, H. Hafliðason and T. Barth. Submitted to *Marine Geology*.

**Paper III:** Carbon isotope fractionation during hydrate formation at Nyegga-Norwegian Sea, a case study. E. Vaular, T. Barth and D. Corak. Submitted to *Chemical Geology*.

## Abbreviations

BGHS	Base of Gas Hydrate Stability
BSR	Bottom Simulating Reflector
CN03	A fluid escape feature at Nyegga
DOC	Dissolved Organic Carbon
FGZ	Free Gas Zone
FID	Flame Ionization Detector
GANS	Gas Hydrates on the Norway- Barents Sea- Svalbard Margin
G11	A pockmark/seep mound at Nyegga
GC	Gravity Core
GC	Gas Chromatography
GDF	Glacigenic Debris Formation
GH	Gas Hydrate
GHZ	Gas Hydrate Zone
GHOZ	Gas Hydrate Occurance Zone
GHS	Gas Hydrate Stability
GHSZ	Gas Hydrate Stability Zone
HC	Hydrocarbon
HGF	High Gas Flux
HSZ	Hydrate Stability Zone
IETM	Initial Eocene Thermal Maximum
IRMS	Infrared Mass Spectroscopy
ITP	Isothacophoresis
LGF	Low gas flux
MDAC	Methane Derived Authigenic Carbonate
msbf	meters below sea floor
PDB	Pee Dee Belemnite
PC	Piston Core
PT	Pressure and Temperature
ROV	Remotely Operated Vehicle
SMOW	Standard Mean Ocean Water
SMT	Sulfate Methane Transition zone
TCD	Thermal Conductivity Detector
TOC	Total Organic Carbon
VFA	Volatile Fatty Acids
VPDB	Vienna Pee Dee Belemnite
VOA	Volatile Organic Acids



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# Part I

## Introduction



# Chapter 1

## Outline

The thesis consists of three parts denoted Part I-III.

In Part I, an introduction to the topics of the PhD work is presented. The basics of gas hydrates are covered in Chapter 2, with sections elaborating on the history, their properties and their role in the marine environment.

The two research areas of interest are located north-west of Svalbard and in the south-east Norwegian Sea. These are shortly introduced in Chapter 3. A brief outline on the GANS project related to this thesis is given in Chapter 4.

The fundamental methods and analytic measurements are also described in this Part. Chapter 5 present the procedures from sampling and containing samples offshore, to analysis and experimental work performed in the laboratory onshore. In Part II, an introduction to gas hydrate research is given in Chapter 6.2, with the main results summarized and discussed in the following chapter. The third part of this thesis includes the three papers given in the list of publications (see page vii).





# Chapter 2

## Gas Hydrates

A solid water phase that encloses gas is termed gas hydrate or a clathrate hydrate of gas. The water lattice in such a substance is oriented in cage-like structures, which can be stabilized by relatively small gas molecules. It looks like packed snow or ice.

### 2.1 Background and history

Gas hydrates were accidentally encountered by an unaware Joseph Priestley in 1790 [1], but were formally discovered by Sir Humphrey David in 1810 [2]. In terms of hydrate research, the rest of the 19th century passed in sole curiosity study, attempting to find out which gas molecules that could fit inside the clathrate structure of water molecules. In 1888, Villard was the first to measure methane hydrates and other light hydrocarbon hydrates, some 40 years before they were discovered blocking gas transmission lines in the mid-1930's [3]. The detection of hydrate plugging pipelines marked a serious upscale in the hydrate research, due to the sudden change in interest from a rarity to an important factor for economy and safety in the petroleum indus-

try. However, natural gas hydrates were first recognized to form wherever the pressure and temperature conditions were favourable as late as 1970 [4, 5]. But from the first discovery of naturally occurring natural gas hydrate in the permafrost, findings of natural gas hydrate have been reported from the sub-surface sediments along the continental slopes of the Pacific and the Atlantic, and have been recovered from near-surface environments along continental margins worldwide [6, 7]. In the last 30 years, serious interest has been directed to studies of natural gas hydrate and its postulated societal relevance on resource, climate and geohazards [8].

## 2.2 The properties of gas hydrates

### 2.2.1 Structures

The guest gas molecules are a requirement to stabilize the clathrate structure called gas hydrate. Gas hydrates are non-stoichiometric, solid compounds similar to ice crystals [9], and have been found to occur in three different crystal structures built up by five types of known hydrate cages (Fig. 2.1).

Structure I is the most common in nature environments; Structure II mainly occurs in manmade environments; while structure H is the rarest and may occur in both environments but only in mixtures of large and small gas molecules [10]. In principle, the occupied hydrate cage is a function of the size ratio between the guest molecule and the host cavity (Fig. 2.2).

In the sediments, most natural gas hydrate are methane hydrates and form structure I cavities. Thermogenic gases like propane and i-butane are too big for structure I hydrates, and form structure II hydrates. In such cases methane will occur in both cage sizes of the structure II hydrate.

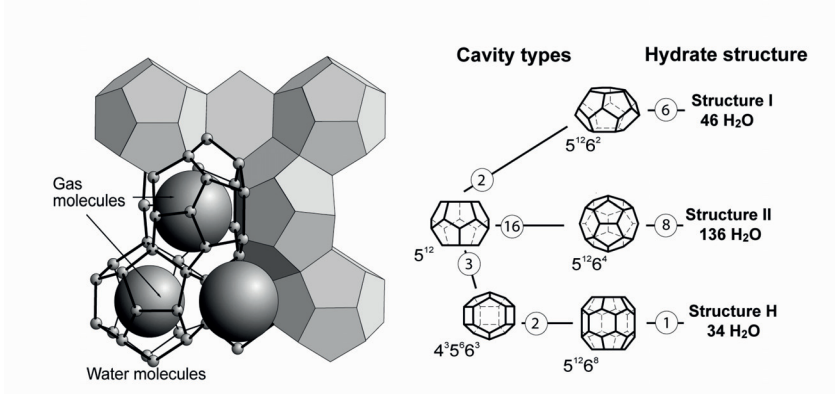


Figure 2.1: The figure shows the three common hydrate unit structures. Enlarged to the left; the unit structure of structure I. To the right, the five cavity types, which, when combined as given, can form three different hydrate structures (sI, sII and sH). All structures include the smallest cavity,  $5^{12}$ . Nomenclature; e.g.  $5^{12}6^2$  indicates a water cage composed of 12 pentagonal and 2 hexagonal faces [4].

## 2.2.2 Stability

When the physical conditions are present and the concentrations of light hydrocarbon gases exceed pore water saturation, gas hydrate can form naturally. The sediment zone that possess the properties of holding gas hydrate stable, are called the Gas Hydrate Stability Zone (GHSZ), or the Gas Hydrate Zone (Fig.2.3). The stability is influenced by various parameters such as water temperature, geothermal gradient, depth below the sea surface (pressure), pore water salinity, the composition of the guest molecules e.g. [11], ionic strength of the water [1] and heat flow [12]. However, like in the laboratory, the phase boundary of solid hydrate and liquid water and gas are ultimately controlled by temperature and pressure.

As shown in Figure 2.3, also the water column could possess the pressure and temperature conditions for hydrate stability, but due to gas hy-

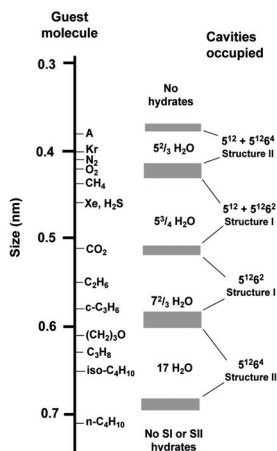


Figure 2.2: Size of occupants versus size of hydrate cavities. The molecules are related to the structure types as single hydrate formers [4, 9].

drates buoyancy, the hydrate will dissociate on the way to the water surface. Therefore, the Gas Hydrate Occurrence Zone (GHOZ) generally is below the seafloor. The Base of Gas Hydrate Stability (BGHS) is limited by the local geothermal gradient, which increases faster than the pressure relative to sediment depth. At a certain point, the temperature is too high for hydrate to form and the BGHS is reached.

Migrating free gas will accumulate beneath this BGHS if the sediment pore space above is filled with gas hydrate at the base. A hydrate layer with a Free Gas Zone (FGZ) beneath will leave a distinct reflection in the seismic record of the sediment. The drop in velocity from gas hydrate to free gas is termed the bottom simulating reflector (BSR), because the seismic reflector mimics the seabed topography [13–15]. The BSR is one of the most used evidences of gas hydrate occurrence, but gas hydrate may occur in sediments without BSR's as well [16–18], and there are also examples of drilling through

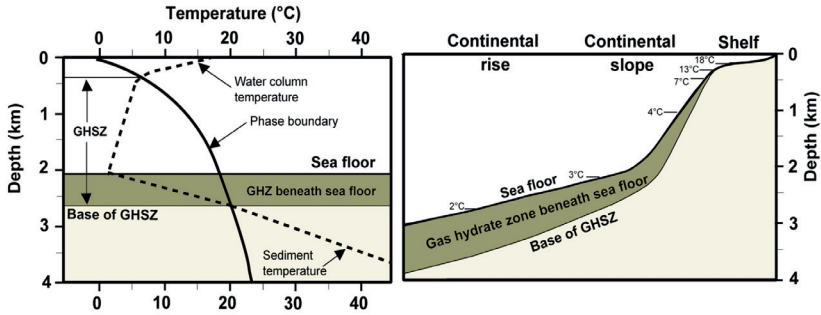


Figure 2.3: The left diagram show the Gas Hydrate Zone (GHZ) and the Base of the Gas Hydrate Stability (BGHS) zone, which are defined by pressure (depth) and temperature (dependent on sea water temperature and thermal gradient in the sediment). The solid line indicates the PT-dependent phase boundary at normal seawater salinity. The diagram to the right exemplifies the thickness of the Gas Hydrate Stability Zone (GHSZ) from Continental rise- to slope with typical bottom water temperatures marked [4, 19].

BSR's without detecting hydrates [11]. Hence, the true nature of the BSR is not yet fully understood.

### 2.2.3 Hydrate formation kinetics

When cooling down a water body with applied gas pressure in a compartment with pressure and temperature monitoring, the system is experiencing a meta-stability period that prevents hydrates from forming immediately after crossing the hydrate equilibrium boundary when entering the hydrate formation phase. Instead, as Fig. 2.4 shows, the pressure decreases (for hours) linearly with temperature until hydrate formation starts well inside the hydrate phase envelope and the pressure drops rapidly. The sudden drop in pressure is the result of abrupt hydrate formation i.e. water molecules encaging the gas molecules. The system's equilibrium point in the experiments in Fig. 2.4

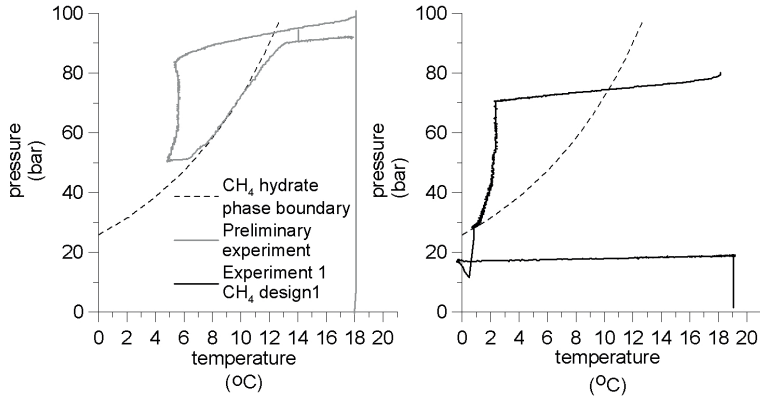


Figure 2.4: TP (temperature and pressure) diagram showing two hydrate formation experiments where a water body is cooled down to  $1^{\circ}\text{C}$  and  $4^{\circ}\text{C}$  with initial applied pressure of 80 bar and 100 bar respectively. The hydrate formation initiation is recognized by the substantial drop in pressure. In the preliminary experiment (left), the hydrate end point is at approximately 50 bar and  $4.3^{\circ}\text{C}$  before heat is applied. The hydrate body reaches the hydrate-gas/water phase boundary and follows the boundary until the hydrate decomposes fully. Experiment 1 from CH<sub>4</sub> design 1, end at approximately 29 bar and  $0.7^{\circ}\text{C}$  at the phase boundary line, then pressure is released and all hydrate decompose.

depends on the limiting factor (water or gas) and end temperature [20].

When the hydrate formation initiates, the water molecules create large cavities that collapse to ice if they are not occupied by a gas molecule [11]. If a gas molecule stabilises the hydrogen bonded water molecules they create structures built up by different cavities as described in Figure 2.1. The actual hydrate nucleation process is difficult to observe experimentally, but is a statistically probable (not deterministically certain) process [20].

In the sediment, hydrates have been identified to form by two mechanisms [11]. (i) Precipitation from pore waters oversaturated with gas, which results in formation of veins and massive hydrates in fractured and porous

sediments, respectively. (ii) Segregation: the gas that stabilizes the hydrate structures is migrating free gas and the water required is extracted from the sediment or the seawater [21]. Additionally, experiments have shown that in porous media, hydrates can form in absence of free gas and oversaturated pore water [22].

The sediments have an important influence on hydrate formation, either by altering the thermodynamic conditions for stability, or by providing nucleation sites [23, 24]. Conversely, the sediments are affected by the hydrate formation. E.g., salt is excluded from the pore water used for hydrate formation and thus makes the residual pore water saltier. Another example is segregating hydrates that dewater the sediment in the GHSZ [11], which in turn could affect the migration pathway of the fluids.

## 2.3 Carbon isotope fractionation

In general, the stable isotopic compositions of elements with low atomic numbers vary considerably in nature due to kinetic and thermodynamic mass constraints. When an element of two isotopic proportions is divided into two parties, the process is called isotopic fractionation. The stable carbon isotope has the standard notation of Pee Dee Belemnite (PDB) or Vienna Pee Dee Belemnite (VPDB) which is shown in equation 2.1 [25].

$$\delta^{13}C(\text{‰}) = \left( \frac{{}^{13}C/{}^{12}C \text{ sample}}{{}^{13}C/{}^{12}C \text{ standard}(PDB)} - 1 \right) \times 1000 \quad (2.1)$$

In the sediments, kinetic carbon isotopic fractionation is a consequence of more rapid reaction and diffusion of molecules with lower mass, and these are thus more frequently utilized than the heavier species [26]. A  ${}^{12}C - {}^{12}C$  bond is easier to break than a  ${}^{12}C - {}^{13}C$  bond [27]. This discrimination results in

isotopically light microbial derived methane compared to thermogenic and abiogenic methane.

## 2.4 Natural gas in hydrate bearing deposits

### 2.4.1 Source and migration of gases

Methane is almost always the dominant component of the natural gas mixtures. Sedimentary methane is formed by both biological and nonbiological decomposition of buried organic matter. Anaerobic microorganisms produce relatively pure methane enriched in the light isotope  $^{12}\text{C}$ . The breakdown of organic matter in anoxic environments involves a complex sequence of processes from organic tissues to acids, alcohols, aldehydes etc, with further breakdown depending on the inorganic electron acceptors available in the sediment [28].

We may consider three types of nonbiological methane generations. Decomposition at low temperatures ( $<75^\circ\text{C}$ ), high temperature degradation ( $>75^\circ\text{C}$ ) and outgassing of primordial methane from the mantle [28]. Regarding the first case, it should be added that the organic matter is required to be heated to temperatures around  $100^\circ\text{C}$  for the rates of production to become significant on the timescale of the development period of sedimentary basins (i.e. thermogenic gas). The temperature increases with sediment depth as a result of the geothermal gradient, thus the upper sediments are the location for microbial production of light hydrocarbon gas exclusively.

Migration of gases is the process of physical movement of gas from its source to a different location in the sediment column. The migration result in heterogeneous mixes of thermogenic and microbial gas and fluids<sup>1</sup>. Conse-

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<sup>1</sup>In geochemistry migrating gas are often termed as fluids. In the thesis migrating gas



quently the sampled gas is not necessarily obtained from the sediment where it was produced.

To deduce the origin of the natural gas, different geochemical monitoring approaches have been applied; (1) examining the composition of the gas [29], (2) investigation of isotopic composition and in particular carbon and hydrogen isotopes of methane [30, 31], (3) correlating the compositions (Bernard-plot [32]) and isotopes through classification plots (e.g. the Chung-plot, Whiticar-plot and Milkov-plot [26, 27, 32, 33]), and, (4) genetic characterisation of natural gases through large datasets of relevant properties [34, 35].

All classification schemes and diagrams assume that the isotopic composition of the hydrocarbons does not change appreciably during migration of gases in most situations [34], although exceptions are known [30]. This assumption, which includes the notion of negligible carbon isotope fractionation during hydrate formation, is the ultimate requirement for a genetic characterization of natural gases in the marine sediments, since the classification consider all variations in composition and isotopes to be a result of the natural gas formation [34].

### 2.4.2 Natural gas forming gas hydrates

There are several ways for gas to reach pore water saturation in the GHSZ. *In situ* microbial production of methane will, depending on the flux rate either achieve saturation of the pore water (a) in the GHSZ, (b) below the BGHS or (c) below the minimum of the methane saturation curve (Fig. 2.5).

While no hydrate formation would occur with a production gradient of scenario (c), both (a) and (b) would lead to gas hydrate formation. Only (a) would provide *in situ* produced gas hydrates (autochthonous) [33]. Microbial and fluid(s) will both be used

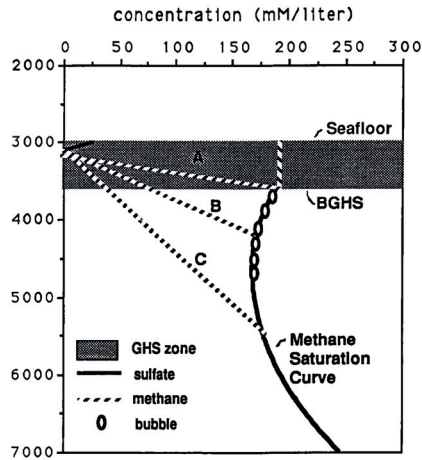


Figure 2.5: Examples of the relationship between possible microbial production rates, methane saturation levels and the methane hydrate stability field are shown. See 2.4.2 for further description. The diagram is a reprint from Paull et al. [36]

gas produced beneath the GHSZ (b), would migrate up to the BGHS and either enter it directly or accumulate as a FGZ at the BGHS.

Depending on sedimentation rates the BGHS could undergo gas recycling as the BGHS moves upwards in the sediment column with progressive burial and subsidence of the continental rise. Gas hydrates decompose beneath the BGHS and may rise buoyantly upward and re-enter the GHSZ to form hydrate [36].

# Chapter 3

## Geological Setting

### 3.1 Nyegga

Nyegga is located on the boundary between the Vøring and the Møre basins, to the north of the Storegga Slide (Fig. 3.1). The entire region is characterized by a broad distribution of polygonal fault systems and interconnects with the Norwegian Sea's second largest gas reservoir, called Ormen Lange [37, 38]. The Nyegga region is positioned at approximately 700-750 meters water depth and represents the 'shoulder' of the continental slope, which continues down westward onto about 3000 m depth [39]. There is a prominent BSR that spreads to the north, west and south of this area. Acoustic chimneys (fluid migration pipes) and fluid escape features are broadly distributed [40–43]. Pockmarks, which are types of fluid escape features described as seafloor depressions caused by fluid escaping the sediment, are also widespread as the seafloor endpoints of the chimneys [39].

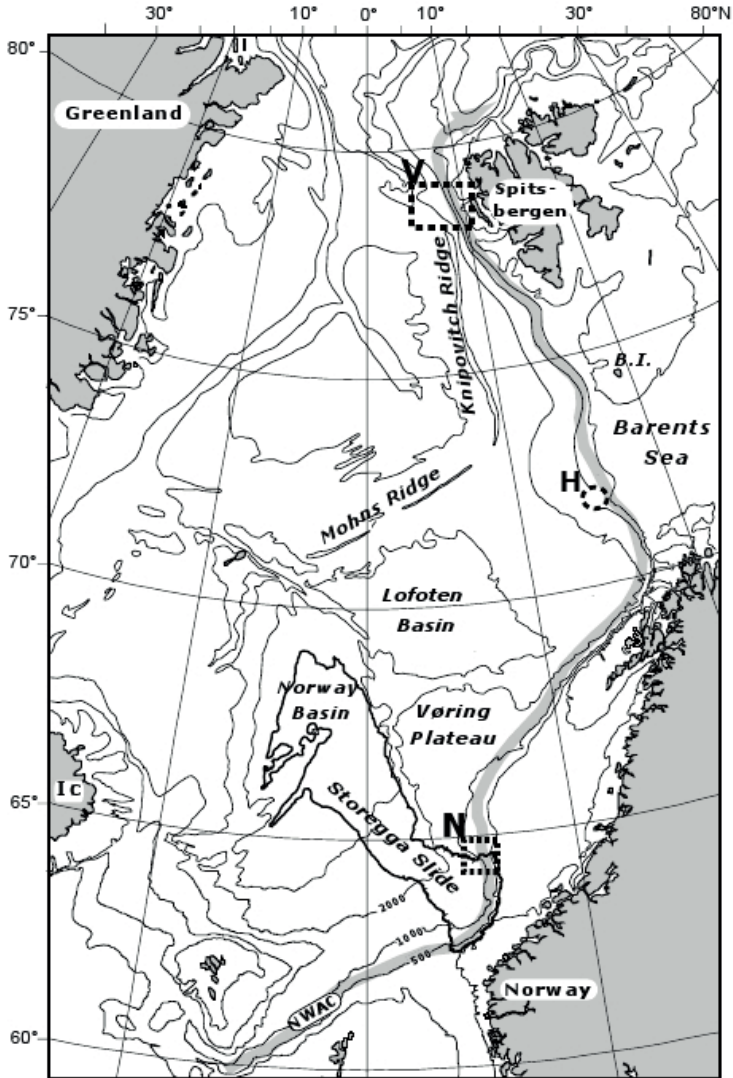


Figure 3.1: The Vestnesa Ridge noted with V and the Nyegga pockmark field noted with N are pointed out with dotted boxes in this overview map of the Norwegian - Svalbard margins. The abbreviation H is the location of Håkon Mosbye Mud Vulcano, while NWAC is an abbreviation for Norwegian Atlantic Current.

## 3.2 Vestnesa

The Vestnesa Ridge is located west of Svalbard at 80°N (Fig. 3.1). It is a sediment drift located on a hot and young oceanic crust at the eastern spreading segments of the Molly Rigde in the Fram Strait [44–46]. The heat flows is on average two to three times higher than in the mid-Norwegian margin [47]. Several seismic studies revealed the occurrence of a prominent BSR along the West-Svalbard margin [40, 48–50]. The crest of the ridge contains numerous pockmarks [51, 52], and gas flares in the middle of the ridge indicate ongoing focused fluid flux activity [46]. In [53] a 3D seismic data volume is presented which describes the pockmarked sediments at the north-western end of the Vestnesa ridge in detail. These pockmarks are located at 1300 meters water depth and this part of the ridge is termed western Vestnesa in the thesis.



## Chapter 4

# The GANS Project: Gas Hydrates on the Norway - Barents Sea - Svalbard margin

GANS is an initiative by six research institutions and the Norwegian Deep-water Programme, SEABED III. The project was lead by the Department of Earth Science, University of Bergen.

The overall objective was to make a coordinated effort on a national level to achieve the main objective by the following sub-goals:

- (a) Geophysical characterization of gas hydrates
- (b) Geological and geochemical setting of gas hydrate reservoirs and seeps
- (c) Gas hydrate dissociation and its effects on geomechanical properties
- (d) Theoretical and experimental evaluation of gas hydrate dynamics

Three contrasting target areas are of particular interest for field studies and experiments: (1) the mid-Norwegian margin at Nyegga, a national

laboratory for gas hydrate research, (2) the Svalbard margin frontier area; important for understanding the geological controls on gas hydrates and fluids, and (3) the Barents Sea, a prolific area with occurrence of gas hydrates and clear evidence for active cold seeps. The establishment of an acknowledged Norwegian academia-industry network on gas hydrates and the education of a new generation of interdisciplinary trained scientists have been central objectives [54].

## 4.1 Research tasks

The research tasks in the project was divided into 3, (A) Geophysical characterisation and quantification of natural gas hydrates, (B) Geological and geochemical characterisation and quantification of natural gas hydrate and (C) Laboratory testing and modelling of hydrate reservoir properties. This thesis focused on subtask B-2 and mainly B-3 defined as follows: (B-2) Detection and description of gas hydrate and seep-related features, their origin at the seabed and estimation of flux rates, (B-3) Identify the origin of gaseous hydrocarbons in hydrate and non-hydrate charged sediments [54].



# Chapter 5

## Methods and materials

### 5.1 Introduction

As the GANS initiative was somewhat of a pioneer within interdisciplinary gas hydrate research in the Norwegian academia, some methodology implementation was required. The PhD-project was the fortunate holder of two new analysis instruments, unfortunately lacking three implemented sampling techniques. Therefore, during the work of this thesis, these had to be defined and put into practice. Such work seldom proceeds without a rate of learning, and thus it is important to recapitulate on the procedures used to improve *future* work.

The prospect of geochemical characterization and quantification related to the subtask this PhD work had been given, depend strongly on the material obtained on the Cruises carried out (see Section 5.2) and the laboratory work performed on them. However, further down the PhD time line, a query enlightened by laboratory experiments was also to be encountered (see Section 5.3).



Figure 5.1: The left picture shows pore water extraction with a Rhizon syringe system. To the right, natural gas hydrate recovered during the GS08-155 Cruise, from the G11 pockmark at Nyegga, is dissociating on deck.

## 5.2 Sampling procedures on Cruises

All sediment and pore water samples were collected from Gravity Cores (GC) or Piston Cores (PC), which are hollow poly vinyl chloride tubes that penetrate the sediment (seafloor) and return to surface with a sediment column with depth equal to the length of the tube. These were immediately washed and split on deck, and one half was sampled as quickly as the routines would allow.

### 5.2.1 Pore water sampling

The pore water was sampled for two analyses; headspace analysis (light hydrocarbons) and isothacophoresis analysis (volatile organic acids). The pore water was extracted from the sediment with the Rhizon tube vacuum system (Fig. 5.1). The concept is based on the function of an artificial root. The thin tube consists of hydrophilic porous polymer, with a pore diameter of approximately  $0.1 \mu\text{m}$ . It has a special property; once vacuum is applied it becomes permeable to water, but not to air, after a short soaking in water.

The vacuum is applied by syringes which also retain the pore water. With the pores in the tube being under microbial scale [55], the extraction permits analysis without further treatment. It should be noted that the Rhizon tubes has been observed to adsorb VFA (volatile fatty acids) and DOC (dissolved organic carbon) as a result of the pore diameter of the tube material [56].

The pore water was transferred to vials (Fig. 5.2) for determination of headspace gas and VOA (volatile organic acids) and stored in fridge and in a  $-20^{\circ}\text{C}$  freezer respectively.

### 5.2.2 Sediment sampling

The sediment samples were obtained for two main purposes; headspace analysis (light hydrocarbons) and total organic carbon (TOC).

The split core sediments were penetrated with a cut 10 ml syringe, and filled with 3-5 ml sediment. Some sediments was pushed out to level the sediment an accurate ml level, the sediment was scraped off at the syringe top so that accurately 1 ml sediment could be transferred to the headspace vial. The vial was then corked or added 1 ml NaOH (for interstitial headspace treatment) and then corked. All headspace vials were stored in the fridge<sup>1</sup>.

### 5.2.3 Gas hydrate sampling

To sample the solid gas hydrate from the core, forceps and fingers (with gloves) were applied to transfer the hydrate into a steel autoclave designed for the elevated pressure of the dissolved gas and water (Fig. 5.2). The sediment surrounding the hydrate was removed manually or carefully with

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<sup>1</sup>In retrospect we have realized that these should have been stored in the freezer or contained in a different manner as fridge temperature is normal activity temperature for the microorganisms present in the sample.

distilled water.



Figure 5.2: To the right the autoclave used for hydrate sampling and containing is displayed. The left hand picture show a cut syringe used for sediment sampling and five sampling vials. From the left; pore water for VOA, pore water for headspace, sediment headspace samples, gas container for isotope analysis and a example of a interstitial sediment sample stirred with 1 ml NaOH.

## 5.3 Laboratory Experiments

During the thesis the hypothesis of isotopic fractionation by hydrate formation was taken up for validation. To test the hypothesis, laboratory experiments of gas hydrate incubation were performed.

### 5.3.1 The incubator

To perform hydrate formation experiments, an instrument setup with the capacity of holding high pressure and temperature variations is required. The instrument used is called the incubator due to the mission of incubating gas molecules in the water lattice. The incubator consists of a stainless steel cell (hydrate cell) with a torque stirring device incorporated, and a temperature controlled cabinet housing the hydrate cell (Fig. 5.3). Furthermore there



Figure 5.3: Left; the hydrate cell inside the heating cabinet and torque stirring system integrated through the top. Middle; the incubator shown in connection to gas supply and computer monitoring. Right; the hard shaft with the torque screw.

are three valves for sampling outtake and introduction of pressure. Thermo and pressure couplings are implemented on the inside of the cell wall so that temperature and pressure can be monitored using computer software.

Temperature regulations range from 0 to  $70^{\circ}\text{C}$  in the incubator oven. The diameter of the cell is 6.61cm, the height is 14.2cm, and the volume is  $468\text{cm}^3$ . The hard shaft provides stirring via the top cap of the cell and it is connected through a belt transmission to a 250 W electric motor, allowing the recording of the torque changes. The error in the readings of the calibrated pressure transducer is 0.1% and that in the temperature measurements equals  $0.6^{\circ}\text{K}$ .

### 5.3.2 Experimental design

Experimental design is a statistical tool used to systematically examine different types of problems that arise within research. Experiments that are performed randomly result in random results [57]. Therefore, it is a necessity to plan the experiments in such a way that the interesting information is obtained, or gain as much information as possible from limited experiments.

The experimental designs created for testing the theory of isotopic fractionation during hydrate formation, contained three variables. Temperature, mass (amount of water) and salinity varied while all other parameters were held constant in 8 experiments, gaining the factorial design  $2^3$  (see Table 5.1). The three variables are varied between high level (+) and low level (-).

experiment	$x_1$	$x_2$	$x_3$
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+

Table 5.1:  $x_1$  is temperature,  $x_2$  is amount of water and  $x_3$  is salinity.

### 5.3.3 Incubation procedure

Basically, the experiments consist of forming hydrate, taking a sample of the excess gas that is not incorporated in the hydrate structure, before all excess gas is evacuated and temperature is set to decompose the hydrate. When all the gas is free from the hydrate structure, a sample of the formerly incubated gas is obtained. For the specific procedure see Appendix III.

## 5.4 Analysis

### 5.4.1 Headspace analysis

The headspace is the gas volume in the sample vial above the sample (Fig. 5.4). Headspace analysis is therefore the analysis of the components present in that

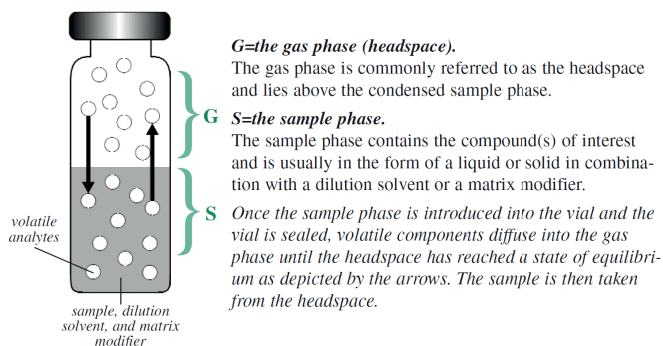


Figure 5.4: Basic principal of headspace analysis [61].

gas. The determination of the components is done by gas chromatography (GC) (see e.g. [58,59]). The total headspace gas is the gas that migrates out of the sediments more or less by itself. Interstitial (occluded) gas is released upon mechanical disintegration of the sediments in the headspace sample vial [60]. In this work 1 ml NaOH was added to the interstitial samples at the time of sampling. The gas chromatographs autosampler, a Teledyne Tekmar HT3, stirred the interstitial samples vigorously and heated them to  $60^{\circ}\text{C}$  for 5 minutes before they were injected onto the GC. The total gas samples were only heated, and the pore water headspace samples were only stirred. The compositional analysis onshore was carried out with an Agilent 7890A GC on a GS-Carbonplot 30 m, 0.32 mm, 3.0 column coupled to FID and TCD detectors with the temperature program;  $80^{\circ}\text{C}$  5 min,  $20^{\circ}\text{C}/\text{min}$  to  $140^{\circ}\text{C}$ ,  $15^{\circ}\text{C}/\text{min}$  to  $250^{\circ}\text{C}$ , hold 20 min.

To determine whether the headspace gas contained components originating from unwanted microbial activity in the sample container produced after sampling and before on shore analysis, off shore headspace analysis of the vials was conducted for comparison. A portable TOGA GC (Fig. 5.5) was

used.

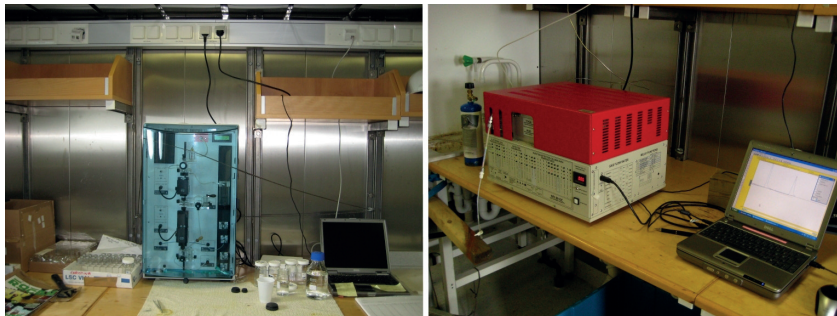


Figure 5.5: The left picture is the ITP-instrument and to the right the portable gas chromatograph. Both on board the RV G.O. Sars.

### 5.4.2 Isotachophoresis

Isotachophoresis is an electrophoretic analytical method. In this work it was applied to determine the VOA content in the pore water samples. Isotachophoresis is based on migration of ion species of the same sign in an electric field, all having a common counter-ion. A leading ion (electrolyte) migrates to the electrode placed on the same side of the sample as the electrolyte (Fig. 5.6). When the system is in equilibrium, all the ions move with the same speed, individually separated into a number of consecutive zones in immediate contact with each other, and arranged in order of mobility [62].

The apparatus is an ItaChrom II EA 202M, which includes a pre-separation column (FEP capillary tube 0.8 mm I.D., 1.0 mm O.D.) and an analytical column provided with 0.3 mm I.D. capillary tube of FEP with a length of 160 mm (Fig 5.5). Both columns are connected with contactless conductivity sensors and the analytical column has an on-column UV-detection cell. The ItaChrom is managed by the computer software called ACES 1.4., supplied



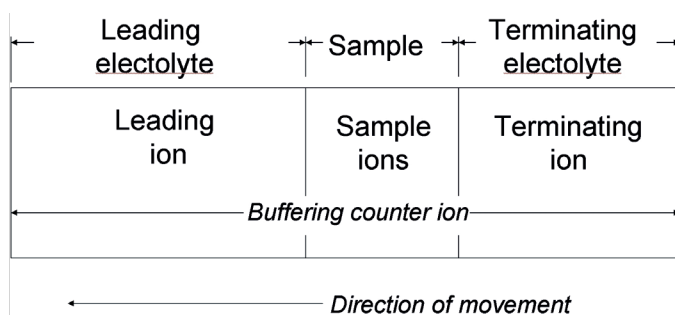


Figure 5.6: The scheme show an illustration of isotachopheresis electrolytes where the movement of sample ions never can pass the leading electrolyte ions because the effective mobility of the leading electrolyte is chosen so as to be higher. Similarly, the terminating anions can never pass the anionic species of the sample. In this way the sample zones of the sample is sandwiched between the leading and terminating electrolyte [62,63].

with the analyzer. For all the reagents super deionized water was used. Fixanal, Riedel-de Haen standard volumetric solutions were used for preparing 0,010 M HCl. The electrolyte solutions were the same as those described in Barth et al. [64].

The run parameters were different for each run due to salinity changes between the pore water samples. The primary step in the pre-separation column is driven with a current of 300 mA. The second step in the analytical column consists of a short period of 200 mA current followed by a step with 100 or 50 mA and ending up in a final level of 10 mA for zone registration. Identifications of the VOA and determination of concentrations were calculated with calibration curves of the standard solutions. In figure 5.7, a tachogram of a pore water sample is displayed.

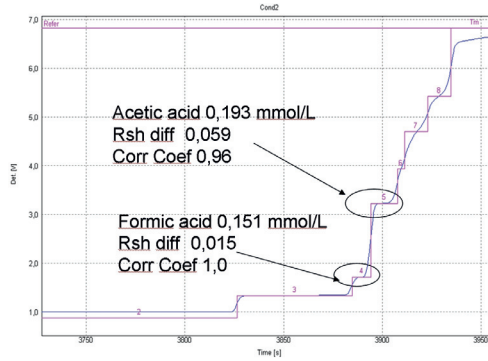


Figure 5.7: This tachogram is from the GS08-155-15GC at 56 cm below seafloor (cmbsf). The core was taken in the CN03 fluid escape feature. The length of the steps in the tachogram represents the concentration of the ions detected and the heights of the steps are the qualitative data reflecting the specific mobility of the species.

### 5.4.3 Isotope analysis

Statoil Research Centre Bergen (RD RCB LA Statoil ASA) performed the carbon isotope analysis of hydrocarbon species with their facilities.

The methane deuterium isotopes and the carbon isotopes of  $\text{CO}_2$  were determined at IFE (Institute for Energy Technology) on an isotope ratio mass spectrometer (GC-C-IRMS); GCpal and Trace GC2000 equipped with a Poraplot Q column, connected to a Delta plus XP IRMS. The deuterium values are reported in ‰ relative to the VSMOW standard. The reproducibility of  $\delta\text{D}$  values is better than 5‰VSMOW ( $2\sigma$ ). All the carbon isotope data has a precision better than  $\pm 0.5\text{‰}$ .

## Part II

# Synthesis



# Chapter 6

## Outline and background

### 6.1 Outline

In this Part of the thesis some background marine hydrate research is presented as an introduction to the main results. The background section provides insights in occurrence, light hydrocarbon formation and the isotope relations.

In Chapter 7, the results from the three papers included in Part III are discussed in four Sections. These include the topics of (i) isotopes and composition, (ii) fluid migration at Nyegga, (iii) additional isotope fractionation, and (iv) fluid escape features. This Part finishes off with chapters on concluding remarks and further work.

### 6.2 Background

The immediate perception of natural gas hydrate is that they are fascinating. It is a solid water substance that contains gas. It is an ice cube one could set on fire and watch the gas burn while the water molecules goes from solid to



Figure 6.1: Natural gas hydrate from the G11 pockmark at Nyegga just after recovery.

liquid state. It is *one* substance that at the same time contains three phases. To form this magic ice cube, only water, gas and the right temperature and pressure conditions are required.

To find these conditions occurring naturally, one has to wander the upper 2000 m of marine sediments at water depths deeper than 300-500 m (it is also found in the permafrost sediments in lesser magnitude). As these conditions occur globally, the potential amount of hydrocarbon (HC) trapped in gas hydrate is immense (about the double of all known HC reserves), but estimates vary greatly [8]. Within the hydrate stability zone (HSZ), the occurrence of meaningful accumulations of gas hydrate is sporadic and disperse (i.e. not of large massive blocks) [65], and the main occurrence of hydrates are in marine reservoirs with limited permeability. Therefore, the research focus has recently turned slightly from challenging and approximating estimation of amounts, to characterization of the deposits in terms of the hydrate resource pyramid potential (i.e. commercial potential) [66].

The gas hydrates are both a sink and a source of HC. The hydrate bound

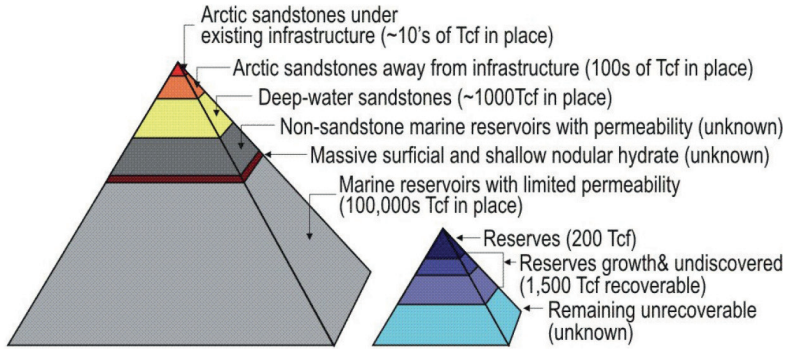


Figure 6.2: The gas hydrate resource pyramid (to the left) hold both quantitative and qualitative information on the global hydrate occurrence. Natural gas hydrate occurrence at Nyegga and Vestnesa is characterized by the three lower sediment structures. To the left an example of a gas resource pyramid for all non-gas-hydrate resources is displayed.

gas is a central component in the global organic carbon cycle that affects in different ways the lithosphere, biosphere, hydrosphere and atmosphere [67]. Hydrate bearing margins with dissociating gas hydrates and seep structures release gas into the ocean waters [68, 69], and minor parts directly to the atmosphere [70]. Kennett et al. (2003) proposed the debated ‘clathrate gun hypothesis’. This hypothesis has even given the gas hydrates the role of causing the climate change in the initial Eocene thermal maximum (IETM), but dissociating hydrate response on present century-timescale perspective, is proposed to be in order of a chronic methane release rather than an abrupt release [71]. Thus a catastrophic release of methane from hydrates to the atmosphere is considered to be improbable. Nevertheless, the impact of methane from the gas hydrates in the organic carbon cycle, and especially the release to the ocean with the resulting pH and bicarbonate alteration, is not well understood. Consequently, for the sake of a stable aquatic environment

and long term stable global climate, this area of interest should be well examined. It is therefore essential to understand the sediment in which gas hydrates occur, and characterise both hydrate bearing sediment and the hydrates themselves, as well as the migration paths of the gas and fluids, and the escape features in these margins.

An important factor in the pursuit of characterizing hydrate bearing sediments is identifying the source of the gas in the sediment, pore water and gas hydrate. HC gases, and the dominant component methane, originate from decomposition of organic matter by biochemical and chemical processes. Microbial methane is produced (biochemical decomposition) as an end product of the metabolism of a diverse group of obligate anaerobic archaea called methanogens. The most important substrates are  $H_2:CO_2$  (carbon reduction) and acetate (acetoclastic methanogenesis). Thermogenic HC is defined as gases (methane to butane) generated from thermal alteration of organic matter, deeper in the sediment ( $>1000$  mbsf) as part of the catagenesis [4].

Although the HC gases in general are associated with in situ processes in the first 1000 m of oceanic sediment, gases derived from thermal breakdown of organic matter may migrate along fractures and faults to the seafloor and appear as cold seeps [28]. Furthermore, in hydrate bearing deposits the fluid flow and the geometry of migration are highly complex [65]. Fortunately, microbial and thermogenic gases generally can be distinguished on the basis of compositional and isotopic composition. Biogenic gas<sup>1</sup>, i.e. microbial gas, is dominantly composed of methane, which is depleted in  $^{13}C$  relative to thermogenic methane [26]. Additionally, methane derived from carbon reduction is generally more isotopically depleted than gas derived from acetate, and

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<sup>1</sup>The term biogenic gas is sometimes presented as both thermal and microbial gas contrary to abiogenic gas (which has a much heavier isotopic signature). It is therefore preferred to use microbial gas rather than biogenic gas in this thesis, for all bacterial and archaeal produced gas.



the hydrogen isotope signatures also provide information on the metabolic pathways [72]. Isotopic discrimination should, nonetheless, be used with caution [4], like all research it is just a model of what we see as the reality.



# Chapter 7

## Main results

The Norway - Svalbard margins have the physical and geological conditions that support gas hydrate occurrence.

Through the GANS project, this sub-project was assigned to identify the origin of gaseous hydrocarbons in hydrate and non-hydrate sediments. On cruises to the Nyegga pockmark field and to the Vestnesa Ridge, traditional coring of the sediment (gravity core, piston core and multi core) was applied to obtain sediment samples of the hydrate bearing sediments.

In two fortunate core recoveries, gas hydrate from the complex pockmark G11 was successfully recovered. The hydrate filled both vertical and horizontal veins in the cores, which only penetrated 0.8 mbsf, probably due to extensive hydrate filling further down in the sediment pore space. The composition was used to calculate the structure of the recovered hydrate. Propane and *i*-butane force the hydrate structure to include sII cavities, but the major hydrate cavities are of structure I.

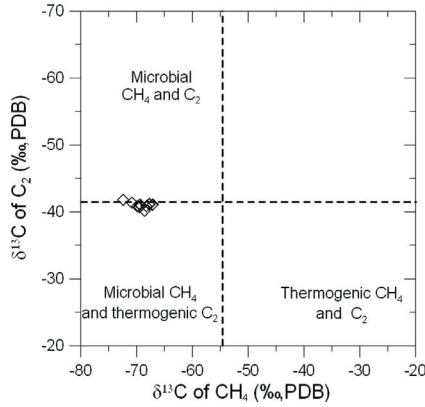


Figure 7.1: This diagram is a redrawn scheme from Milkov (2005) [33]. It displays the carbon isotopes of methane and ethane in the hydrate gas from the complex pockmark G11 (at the Nyegga pockmark field) plotted against each other, demonstrating their origins.

## 7.1 Isotopes and composition

The composition of the hydrate bound gas also indicate the complexity of the HC origin by comprising 99.66 mol% C<sub>1</sub>, 0.30 mol% C<sub>2</sub>, 0.03 mol% C<sub>3</sub> and 0.01 mol% i-C<sub>4</sub>. The methane content suggests microbial origin while propane and i-butane demonstrate thermogenic contributions. The methane was identified as microbial produced, with  $\delta^{13}C$  values ranging from -72.4 to -66.2‰ and with deuterium values ranging from -202 to -198‰. These are classic isotope values caused by CO<sub>2</sub>-reduction [72].

In the hydrate bound gas the ethane carbon isotopes are remarkably light, in fact about the lightest detected in natural gas hydrates [33]. In a Milkov plot, where  $\delta^{13}C$  of methane and ethane are plotted, there is a clear indication of microbial produced ethane (Fig. 7.1).

The isotope values reported (paper 1) together with later reports [37], give evidence of a more microbial dominated HC origin than suggested in

earlier work, regarding the Nyegga pockmark field and the southern Vøring Plateau [43, 73, 74].

## 7.2 Fluid migration at Nyegga

As mentioned in section 2.4.1, the HC produced within the upper 1000 m of the sediments is considered to be microbial gas due to the geothermal gradient. At Nyegga there is a free gas zone (FGZ) blocked for further upward migration by glaciogenic debris formation (GDF) and GH [75]. This is all within the upper 1000 mbsf. With the light methane and ethane carbon isotopes it is apparent that microbial activity is the root of the gas captured in the hydrate. Nonetheless, the thermogenic signature of the total gas composition leaves no alternative to a thermogenic contribution in the fluids of the Nyegga sediments. The schematic cartoon in Fig. 7.2 illustrate the basics of the proposed fluid flow. In addition to the FGZ at the BGHS, the gas fluids are proposed to contain large contributions of migrated fluids from the deep sediment due to the low *in situ* total organic content modelled [73]. From paper 1 we deduce that thermogenic carbon supplied by the polygonal faulting in the area [76, 77] reached the GDF and accumulated until pressure build up forced the fluid into the GHSZ [75]. In the build up of the FGZ, microbial carbon cycling of the fluid is proposed to contribute to the depleted carbon isotope values.

The above section describes a scenario that could be considered an allochthonous hydrate deposit, where the fluids are supplied from the deep sediment. However, the gas incubated in the hydrate is formed within the bounds of the GHSZ, which could be considered as autochthonous.

From the ROV-monitoring of the fluid escape features at Nyegga we con-

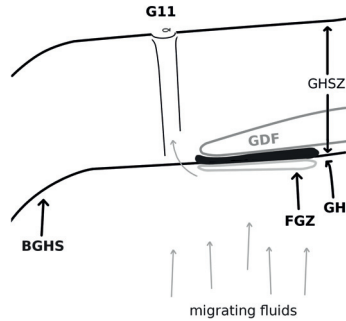


Figure 7.2: Schematic of the proposed carbon circulation and fluid flow beneath the G11 pockmark. A contribution from the deep sediments is proposed to reach the Base of the Gas Hydrate Stability (BGHS) and accumulate as Gas Hydrates (GH) and a Free Gas Zone (FGZ) underneath the Glacigenic Debris Formation (GDF). When reaching overpressure the fluids would spill around (or through) the GDF and migrate through the Gas Hydrate Stability Zone (GHSZ), probably as under-saturated pore water.

firmed the proposed ongoing micro seepage by documenting extensive micro and macro fauna in the pockmark depressions and in the nearby. There was no sign of macro seepage (actual bobbles) pointing at a low gas flux (LGF) system. However, there may have been a high gas flux (HGF) system in the fluid escape formation period [43, 75].

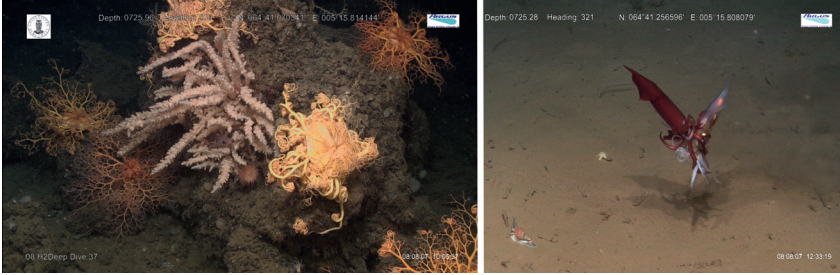


Figure 7.3: ROV pictures from the G11 pockmark. The micro seepage most probably fuels the entire ecosystem of the complex pockmark.

### 7.3 Additional isotope fractionation

In paper 3 we concluded that isotope fractionation during hydrate formation could not be a considerable contributor to the light carbon isotopes in the methane and ethane detected in the GH. The composition of the hydrate bound gas is relative close to a single forming hydrate, with methane as the hydrate former. In the laboratory experiments, the hydrate lattice had a preference of lighter gas molecules in the cavities when methane was a single hydrate former. This rule out the scenario of gradual fractionation of the gas fluid as it migrates through the GHSZ with the heavier molecules chosen first for hydrate incubation. In the case of a petroleum fingerprint in the hydrate bound gas, the laboratory experiments show a slight fractionation of heavier methane carbon isotopes incubated in the hydrate. Ethane and propane showed no significant fractionation trend or magnitude (Fig 7.4).

Although the laboratory experiments in paper 3 establish some carbon isotope fractionation, the magnitude does not inflict with the common classification schemes built on isotope discrimination. However, it should be emphasized that the laboratory conditions of hydrate formation do not fully mimic the formation in situ hydrate bearing sediments. The timescale of

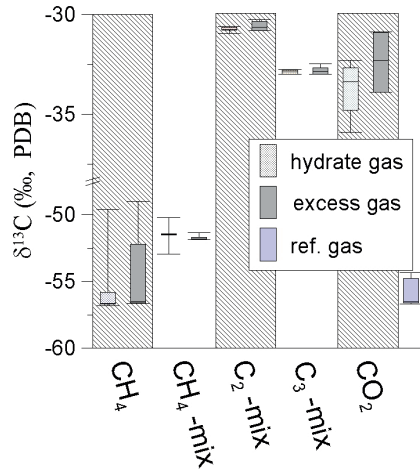


Figure 7.4: A Box-and-Whisker plot of the carbon isotope values from the three hydrate formers, hydrate gas and excess gas isotopes are presented with dotted and grey bars respectively. The reference gas is to the right.

the natural environments could provide conditions for slower kinetics and a formation process that enhances carbon isotope preference.

The kinetic isotope effect of transportation has been proposed to explain light carbon isotopes in methane derived autigenic carbonate (MDAC) at Nyegga [78, 79]. How the fluids pass through the GHSZ of a LGF system with chimneys of acoustic transparency is not fully understood. The chimney beneath the G11 is proposed to not be filled with free gas as the bounds of the columns of seismic transparency holds velocity pull-ups, which are associated with gas hydrate or carbonate. Furthermore, the shallow SMT (sulphate methane transition) zone indicate that the carbonate only exists near the surface [80]. The pore water, which is oversaturated with methane, would form hydrate and, furthermore, the hydrate at this location is estimated to require temperatures of 7-10 °C before dissociation [78, 81].

From this one could deduce that the fluid migration consist of pore water



with gas constituents not exceeding saturation. Taken into account the extensive microbial and macro-faunal activity in the surface sediment it could be speculated that the shallow hydrate interacts with the microbial community.

By ruling out hydrate formation as additional isotopic fractionation, we infer the isotopic signature of the hydrate bound gas in the G11 pockmark to be caused by carbon cycling in the FGZ or in the deep sediments. The most imminent substrate for such carbon cycling is  $\text{CO}_2$  [82]. The assumption of  $\text{CO}_2$  cycling has the prerequisite of  $\text{CO}_2$  reduction by hydrogen oxidation, which again requires that there is hydrogen present in the fluid. Alternatively, methane could come from the deep cycle through  $\text{CO}_2$ , and back to methane again on different migration stages through the sediment column. These are mere speculations and represent unexplained issues of the HC origin in the area of Nyegga, which only drilling could answer.

## 7.4 Fluid escape features

Within the Nyegga pockmark field the fluid escape features vary greatly. The most examined feature, G11, is a 50 m wide, 10 m depression that at the same time contains marine pingos, which range about 10 m above sea floor level. The CN03 seeping feature is characterized as a 300 m in diameter topographic high (2-3 m) [37]. These two features are the most sampled fluid escape features in the GANS project (Fig 7.5).

The three gravity cores from CN03 mentioned in paper 2 illustrate the uncertainty of sediment core sampling in respect to lateral changes. The diameter of the core used is about 10 cm while the penetration depth is several meters (up to 5m). The picture of the fluids in complex fluid escape forma-

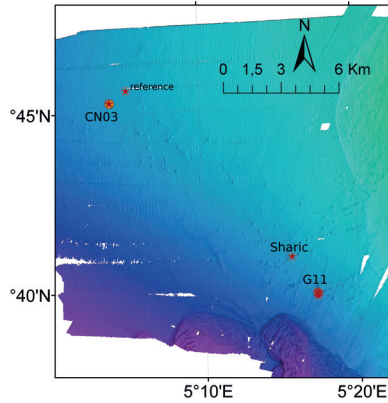


Figure 7.5: Topographical map over the Nyegga pockmark area. Three fluid escape features, CN03, Sharic and G11, are marked with stars. The Storegga slide scar is located south of the G11 and Sharic.

tions as G11 and CN03 is thus of limited resolution regarding lateral changes, although the two pockmarks were pierced with 9 and 3 cores, respectively. It has been proposed that the edges of a seeping feature would hold larger flux rates compared to the centre, due to MDAC and/or near-seafloor hydrate formations [43, 53, 83]. The cores from Nyegga do illustrate large differences in light HC content, both between fluid escape features and within one feature. Yet, the overall impression from the headspace analysis of the cores is that each core reflects the local sedimentation and migration history. This implies that some cores describe the overall picture of the pockmark/seep mound better than others, and some describe special cases.

The GS08-155-22GC (Geo Sars, 2008, cruise 155, station 22, Gravity Core), penetrated the centre of the G11 and reported very low headspace values compared to other cores obtained nearby. In paper 2 it is speculated that this is due to carbonated crusts creating migration conduits for the HC gas. It may also be near seafloor stable hydrates as proposed for a

corresponding pockmark at western Vestnesa Ridge (paper 2). Here, a large acoustic segment approximately 50 m below the pockmark feature is apparent on the 3D seismic imaging [53]. Paper 2 elaborates on how this segment is proposed to be the end of a periodic high flux venting episode that at present is inactive, and in this case the headspace content reports of minimal microbial activity.

However, isotacophoresis (ITP) analysis of the pore water reported anomaly high formate concentrations in two sediments samples at western Vestnesa. These formate appearances could not be explained by the sediment texture or other examinations. The sediment texture was on the whole homogenous olive gray to gray clayey sediments, and supports the headspace analysis in documenting a non present microbial community and low HC-flux rates. Paper 2 thus supports the proposal of episodic venting at the contourite deposits at Vestnesa [38].

Paper 2 describes the two distinct hydrate bearing deposits with similar seismic signature of the fluid migration features. The sampling of Vestnesa Ridge and Nyegga pockmark field illustrates the importance of ground truthing and sediment sampling for research of hydrate bearing sediments. Also, the light HC-comparison show how the water masses and heat flow are crucial for the seafloor living community.



# Chapter 8

## Concluding remarks

From the cruises organized by the GANS initiative and the samples obtained from these, this thesis has elaborated on the subtasks it was intended to explore.

Successful recovery of natural gas hydrate from the G11 pockmark allowed us to be the first to report isotopic values from hydrate bound gas at Nyegga, Norwegian Sea. Through the isotope values of the hydrate bound gas, the headspace gas of the sediment samples and the composition of these gases, the origin of the gaseous HC in hydrate and non-hydrate charged sediments was identified.

The HC is to a large extent produced microbially. Both methane and ethane show light isotope signatures. However, the geographical origin of the carbon is not identified, but hypothesized to be migrated HC or carbon dioxide from the deep. Near the GHSZ the migrated carbon accumulated and is proposed to have been converted into isotopically light HC by microbes before migrating into the GHSZ.

The samples from the Vestnesa Ridge showed that the pierced pockmark is an inactive site formed by former or periodically thermogenic venting.

Nature always seems to have unique site specifics. Through the Nyegga site this challenged us to examine the common discrimination schemes of carbon and deuterium isotopes. Similarly, this exploration showed that it is not easy to put nature into the laboratory. Although some questions were answered, the projection of the results into nature is not straight forward.

To some extent the scientific cliché is preserved: In the quest of solving a problem, tenfold new ones arise (see Chapter 9).

# Chapter 9

## Further work

**Isotope Fractionation** The most apparent way of gaining more knowledge on the topic is by performing more experiments. To improve the designs, it would be helpful to run control experiments regarding carbon isotope fractionation during methane dissolution in water.

New experimental designs would benefit from parameters describing the equilibrium between the hydrate and water/gas phases better. Monitoring the difference between excess and hydrate gas well inside the phase envelope and excess and hydrate gas at the phase boundary, especially at different time levels, would be useful in this respect. Also, an interesting aspect is the different kinetics and recognition pattern of reforming hydrates. To evaluate this on the subject of isotope fractionation would involve thawing the hydrate in the incubator and then re-crystallize the hydrate structure again, by only regulating the temperature.

For practical improvement and enhancing the monitoring capacity, a better incubation cell setup and sampling procedure is needed. There are of course numerous engineering challenges, but regarding the setup used in this thesis, the primary aspects would be shorter time from gas sampling to iso-

tope analysis and visual monitoring of the hydrate formation. The latter addresses the importance of reaching equilibrium between the phases so that the preference of isotopes is not overwhelmed by kinetics. With a sapphire cell [84] (which would impose pressure sensitivity issues) or a peep eye in a steel cell, one would make sure that hydrate is in ‘slush form’ and not a solid block when sampling excess gas.

**Hydrate gas origin** In the pursuit of characterizing the HC in the hydrate bearing deposits on the Norwegian margins, more samples are of the essence. Regarding new samples from the sites all ready sampled at Nyegga, isotope analysis of carbon dioxide would help improve the interpretation of the carbon regime in the shallow sediment and would give confirmations and new insights on the fluid origin and deeper HC character. If hydrate recovery were to happen, the sediment below (preferably) and around the hydrate should be analyzed for carbon and deuterium isotopes as for the hydrate bound gas, to get a broader data base on *in situ* isotope fractionation. Preserving hydrate samples for geo-microbial research is also of increasing interest.

At the Vestnesa Ridge longer cores and new locations/sites would be important parameters of getting detailed information on the hydrocarbon content and character in the contourite deposits. Especially the recently mapped venting area at the middle of the ridge would help progress in the HC characterization and source interpretation. General pore water analysis with SMT -and flux rate determination would be natural steps in geochemical detailing of these potent sediments.

The hydrate research on the Norwegian margins has of course challenges and assignments beyond the scope of this thesis, but regarding a more general note on the topic of this chapter, the further work should include an



evaluation on the geochemical sampling techniques employed at the research institutes in the GANS collaboration. Hereunder, pressure core sampling would be a shared appreciation.



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