Oil & Natural Gas Technology

DOE Award No.: DE-FE0013531

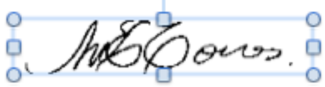
Quarterly Research Performance

Progress Report (Period ending 6/30/2014)

Assessing the response of methane hydrates to environmental change at the Svalbard continental margin

Project Period (11/1/2013 to 10/31/2015)

Submitted by:
Marta E. Torres



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United States Department of Energy
National Energy Technology Laboratory

Office of Fossil Energy

EXECUTIVE SUMMARY

In November 2013, Oregon State University initiated the project entitled: **Assessing the response of methane hydrates to environmental change at the Svalbard continental margin**. In this project, we will take advantage of a unique opportunity to collect samples from two settings on the Svalbard continental margin, by participating in two expeditions to the region organized and co-funded by Germany and Norway. These expeditions target sites where methane plumes have been observed to emanate from the seafloor at the upper edge of gas hydrate stability (area 1) and over acoustic chimneys and seafloor pockmark structures in the Vestnesa Ridge (area 2). Our objectives related to examining and modeling the biogeochemistry of these sediments nicely dovetail with our colleagues' objectives to conduct detailed mapping, hydroacoustic surveys of methane plumes, heat flow measurements and quantification and characterization of gas hydrates in areas of contrasting methane flux characteristics.

To date we continue preparations for the expedition. Details given in the cruise plan document attached

PROGRESS, RESULTS, AND DISCUSSION

1. We began testing and calibrating the green house analyser (results attached). We will conduct additional field testing on a one day expedition offshore Germany (Erkenforde Bay) on July 2nd. We developed a MatLab routine for ease of data reduction during the cruise. The second instrument (isotope measurements) is still under manufacturing, but we have been assured of delivery by the end of June. If delayed beyond the 4th July shipping date, we will ship directly to Iceland (port call).
2. We held a meeting in Kiel, Germany and established geochemical sampling plan with the Geomar team. We also coordinated efforts regarding supplies, reagents, bottle preparation etc. The equipment is all ready to go on the container that is leaving Bremen on July 4th.
3. We continued coordination with Michael Carroll (CAGE) and incoming CAGE postdoc fellow Friederike Gründger regarding microbiological sampling during the Svalbard expeditions. We have developed a sampling plan and identified areas for scientific collaboration between CAGE, Bremen and OSU. All supplies for the OSU microbiologic sampling efforts were shipped from Oregon on 19 June, 2014. Should arrive in time for shipping with the container
4. We have made significant progress with modeling of two-phase transport associated with gas hydrate systems known to occur near the seafloor over acoustic chimneys such as those to be sampled during the MSM 41 expedition. The model is being trained using data from the DOE-cofunded expedition to the Ulleung Basin, Korea. Results of this model will be presented at a shallow seep meeting in Taiwan this fall. Abstract attached

MILESTONE STATUS

We are well within our planned progress regarding Milestone 1:
Title: Complete preparations for expedition
Planned Date: July 1, 2014

PROBLEMS OR DELAYS

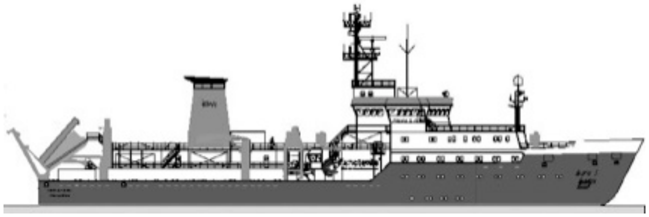
The second instrument from Los Gatos Research (MCIA-Range 3 (QC-EP-L enhanced performance configuration for Range 3 with LN2-cooled detector) is back ordered analyzer due to material supply shortages. According to the vendor, the instrument would be on track to deliver by the end of June as originally promised, and still within our schedule to test and use on the expedition

PRODUCTS

This progress report

Cruise plan document (attached)

Conference abstract: Wei-Li Hong, Malgorzata Peszynska, Marta Torres, and Ji-Hoon Kim, 2014. Methane hydrate stability and saturation in Ulleung Basin: A numerical model perspective. GIMS conference, September, Taiwan

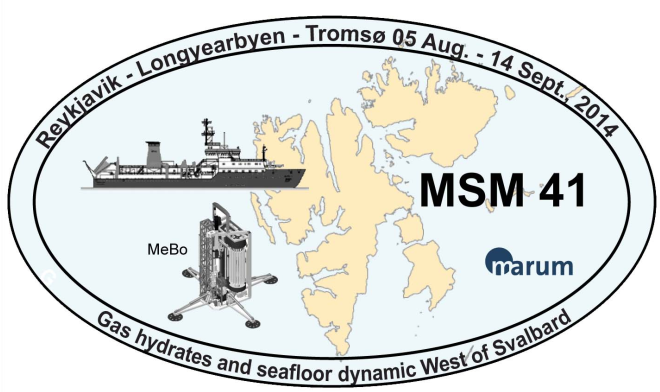


MARIA S. MERIAN

Cruise Nr. MSM 41

05. 08. 2014 – 15. 09. 2014

Methane venting and gas hydrates off west coast of Spitzbergen, Svalbard



CRUISE PLAN

30 JUNE, 2014

Scientific Rationale

The cruise primarily is aiming to collect field data in the area of the West-Spitsbergen continental margin (**Figure 1**) that will allow investigating the gas hydrate dynamics. There is evidence that an increase in bottom water temperature has already changed the gas hydrate stability zone at the upper continental margin. Many active gas emission sites (see **Fig. 2**) are caused by the gas liberation from methane hydrates (Westbrook et al. 2009).

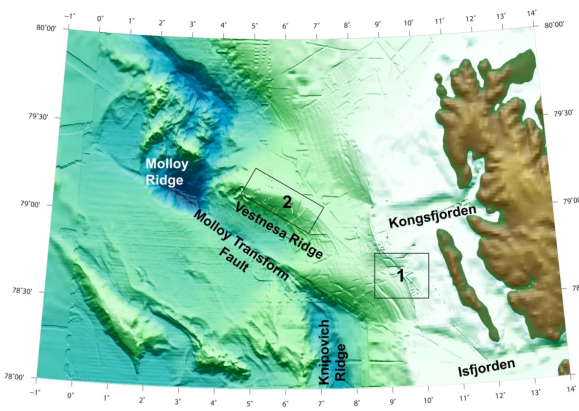


Figure 1 Areas of planned investigation at the upper continental slope (box 1) and at Vestnesa Ridge (box 2) west of Svalbard (bathymetry data are combined from AWI, NOC and GEOMAR).

In this setting, it is important to understand how the gas hydrate reservoirs will react to future increases in the bottom-water temperature, and if future bottom-water warming might trigger the sudden release of large amounts of me-thane leading to accelerated climate warming. In a first step hydrate dynamics has to be recorded from sediment drilling, and we therefore plan to drill down to 50-60 m sediment depth and cover the entire gas hydrate stability zone in such shallow water depths (see Fig. 3).
By drilling 5 sites defined by gas flare positions, the actual temperature field and seismic information we are addressing the following questions:

- How are hydrates distributed in the glacial and Holocene sediments of the slope, in relation to the gas hydrate stability outcrop zone?
- How is the fabric of the hydrate in relation to the lithology? More massive hydrates? Disseminated hydrates, layers of hydrate parallel to stratification, lenses or fracture fillings?
- What is the detailed chemical composition of the hydrates; which gases are bound in the hydrate structure? Is there a fractionation in the gas composition between the gas emanating at the seafloor and the gas in the hydrate structure?

The second part of the cruise is to obtain a

- To evaluate stability conditions of the gas hydrates based on the analysis of the geochemical compositions and temperature lance measurements.
- To obtain a better understanding of stratigraphic development and sedimentation rate on the Vestnesa Ridge.
- To obtain baseline information on fluid expulsion processes on the Vestnesa Ridge which allow an optimized design of a planned seafloor observatory to be deployed in this area.

Work program

High-resolution 3D-seismic data are the basis for determining at least two of the three proposed drilling locations. Many of the chimney structures are variable in the seismic characteristics. However, all of them show significant amplitude anomalies within the upper 50-100 m of the subsurface, i.e. well within reach of the MeBo drilling platform. Whether these anomalies are related to free gas, gas hydrates and/or carbonates is an important question in itself and will clearly help to better understand how gas-rich fluids migrate through the subsurface.

Major work is to drill cores using the drilling system MeBo (https://www.

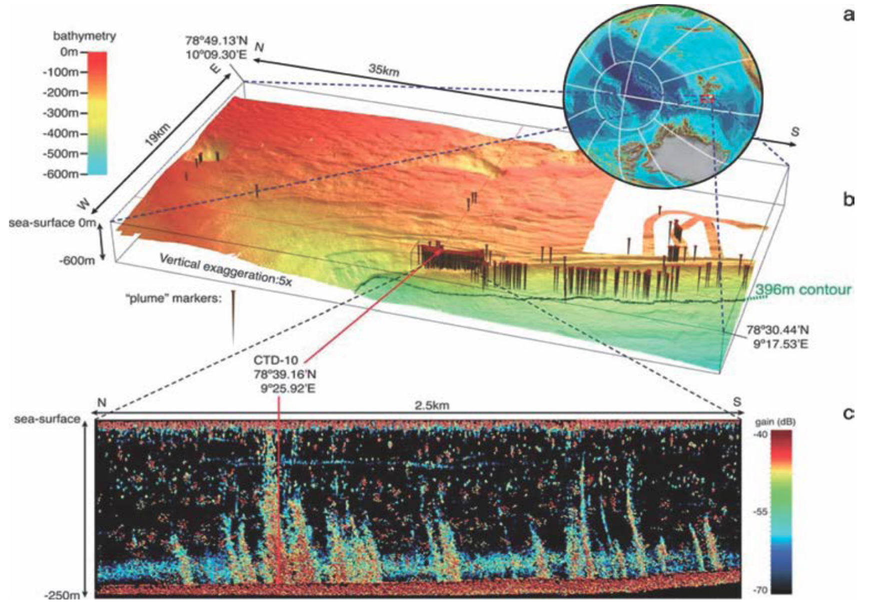


Figure 2. Location of survey area west of Svalbard and position of plumes (from West-brook et al. 2009). Location of survey area west of Svalbard and position of plumes (from West-brook et al. 2009).

marum.de/en/Sea_floor_drill_rig_MARUM-MeBo.html). Guided by detailed seismic information and the current temperature field measured during the cruise we are planning 5 double drill sites. MeBo cores will be handled by standard procedures on board of MARUM cruises. Before the liners will be split, a thermal scanning with an infrared camera will be performed in order to locate hydrate layers. Since decomposing hydrates are easy to detect as cold spots in IR images, we will document the complete sequence of all hydrate layers. Immediately after splitting the cores, hydrates will be stored in liquid nitrogen. Pore waters will be retrieved and microbiological sampling will be performed in the ship's cold room. Cores will be macroscopically described and photographed in detail and a color scanning will be performed. Physical measurement using a multi-sensor core logger will be performed before a de-tailed sampling for post-cruise sedimentological analyses of the core work halves will be done. Gas hydrate samples from the specific sediment sections will be obtained for-gas analysis. At selected pressure levels prevailing in the MDP (recorded with a digital pressure sensor), gas subsamples will be taken out of the stream of released gas, such that only volatiles liberated during core de-pressurization are collected.

During the cruise, pore water will be analysed for pH, ammonium, alkalinity, phosphate, and chloride. For on board measurements of molecular compositions, the gas samples will be analyzed with a cavity ring down spectrometer. A standard winch-operated heat flow probe will be used to obtain in situ- sediment temperature and thermal conductivity measurements.
A mapping program is planed that focuses on gas bubbles in the water column and de-tailed bathymetry of the seafloor. Multi-beam systems of RV MARIA S. MERIAN will be used to complement the already existing bathymetry but, if available, however the multi-beam system EM120 will be used for the detection of acoustic anomalies (flares) caused by gas bubbles in the water column. The system on the research vessel can dis-play and record the water column data for the entire swath and have been successfully employed for the detection of flares. In addition, the 18 kHz signal of Parasound echo-sounder is a powerful tool to detect flares. The hydro-acoustic systems will be used to find and localize gas bubble emissions but also to study how high and constantly gas bubbles will rise in the water column.

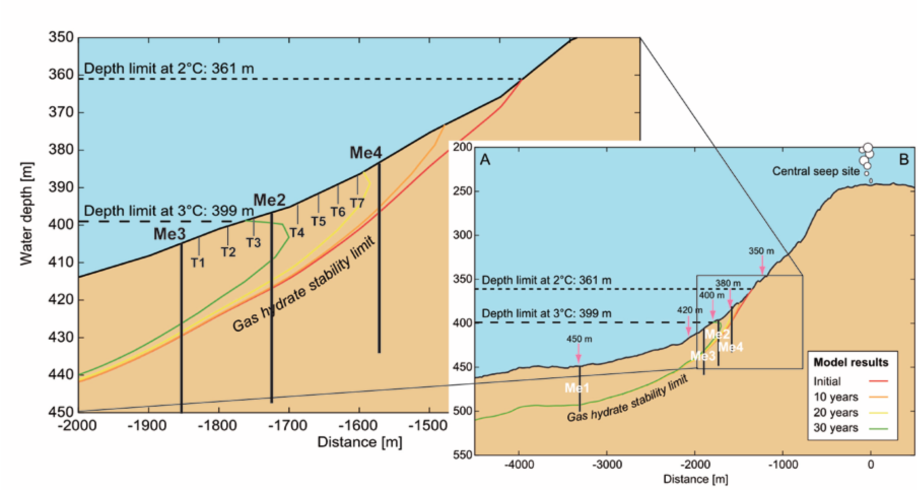


Figure 3 West to east transect, with detail insert at the upper limit of the gas hydrate stability zone at 2° and 3° C of the bottom water and locations for drilling.

Additional station work for CTD/rosette, gravity corer and TV-sled is planned in or-der to complement the investigations. CTD connected with hydro-casts are used to sample and measure background methane concentrations in the water column and me-thane concentrations specifically close to the plume sites, which are known form detected acoustic anomalies. Gravity corer and TV-sled deployments will help to under-stand backscatter patterns of EM 120 maps obtained during the cruise and to identify additional sites of recent hydrocarbon emissions**.**

Water column program

Goals:
To track and quantify methane released from seafloor vents. A sampling protocol is being design to best constrain the water column signals in the context of the regional hydrography. The oceanography of the region west of Spitsbergen comprising the working area of the planned expedition is dominated by two currents, both originating from S-SE and generally flowing to the North (Figure 4).

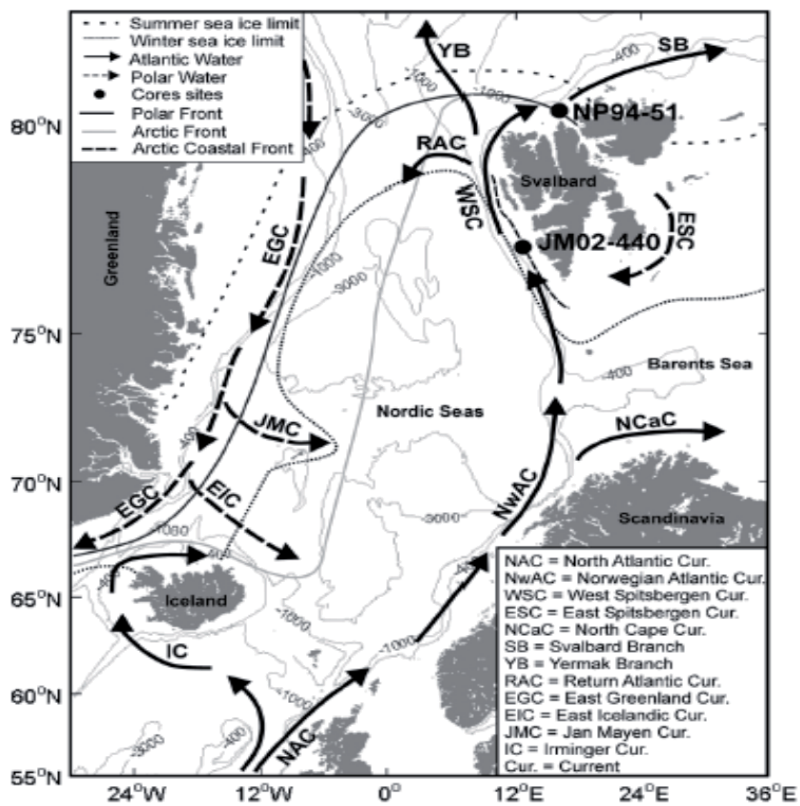


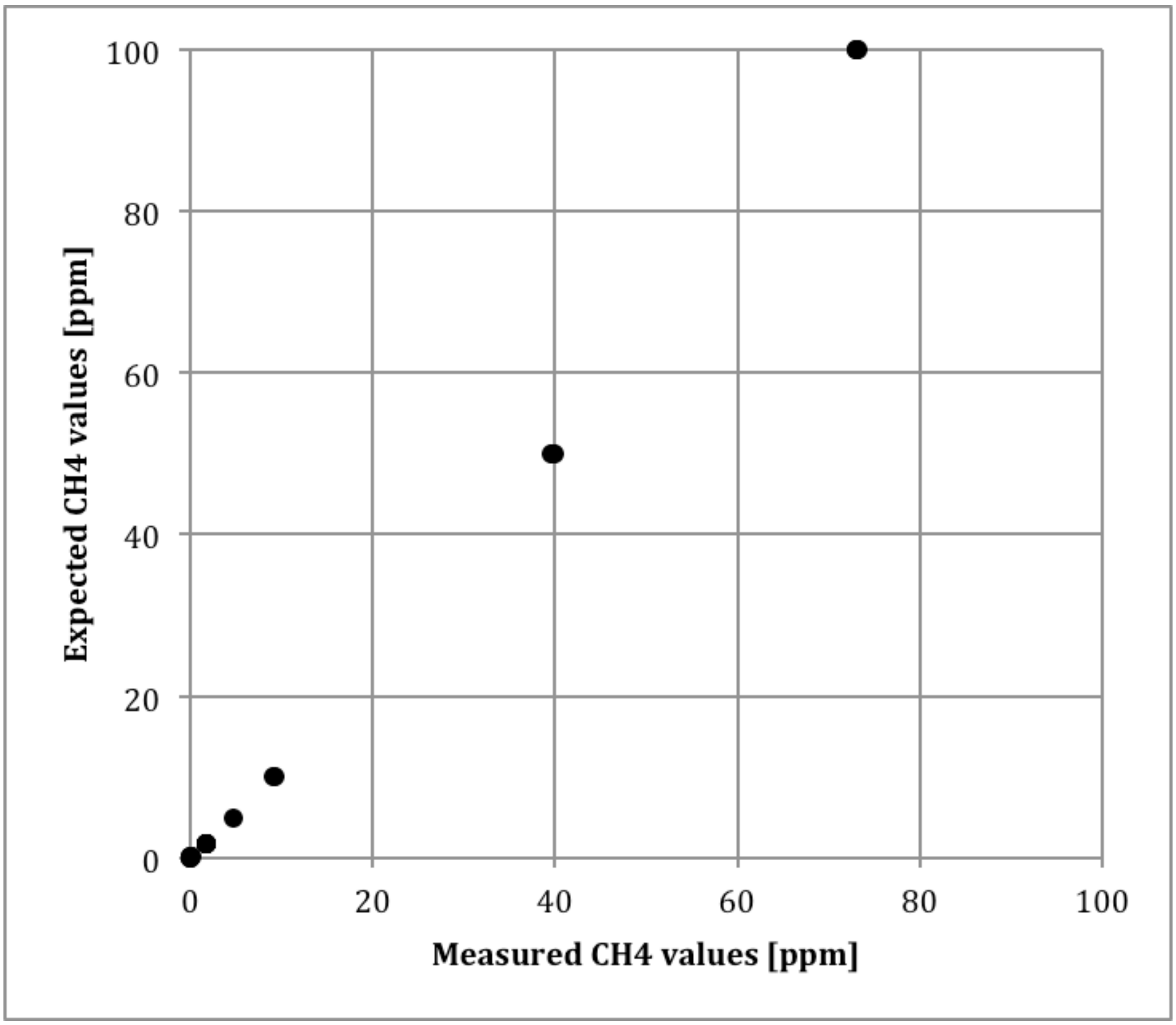
Figure 4. Major surface water currents affecting water masses on the shelf and slope off Svalbard (Slubowska-Wodengen et al., 2007)

The Coastal Current (CC) is sourced from the East Spitsbergen Current (ESC) and runs close to the western coast of Spitsbergen. The ESC originates from the area east of Spitsbergen, surrounds the southern tip of the peninsula and transports relatively cold and low saline water into the working area. Distant to the coastline, waters masses are being transported by the West Spitsbergen Current (WSC) along the Spitsbergen shelf break and slope. The WSC is an extension of the North Atlantic Current, which transports relatively warm and saline waters into the region.

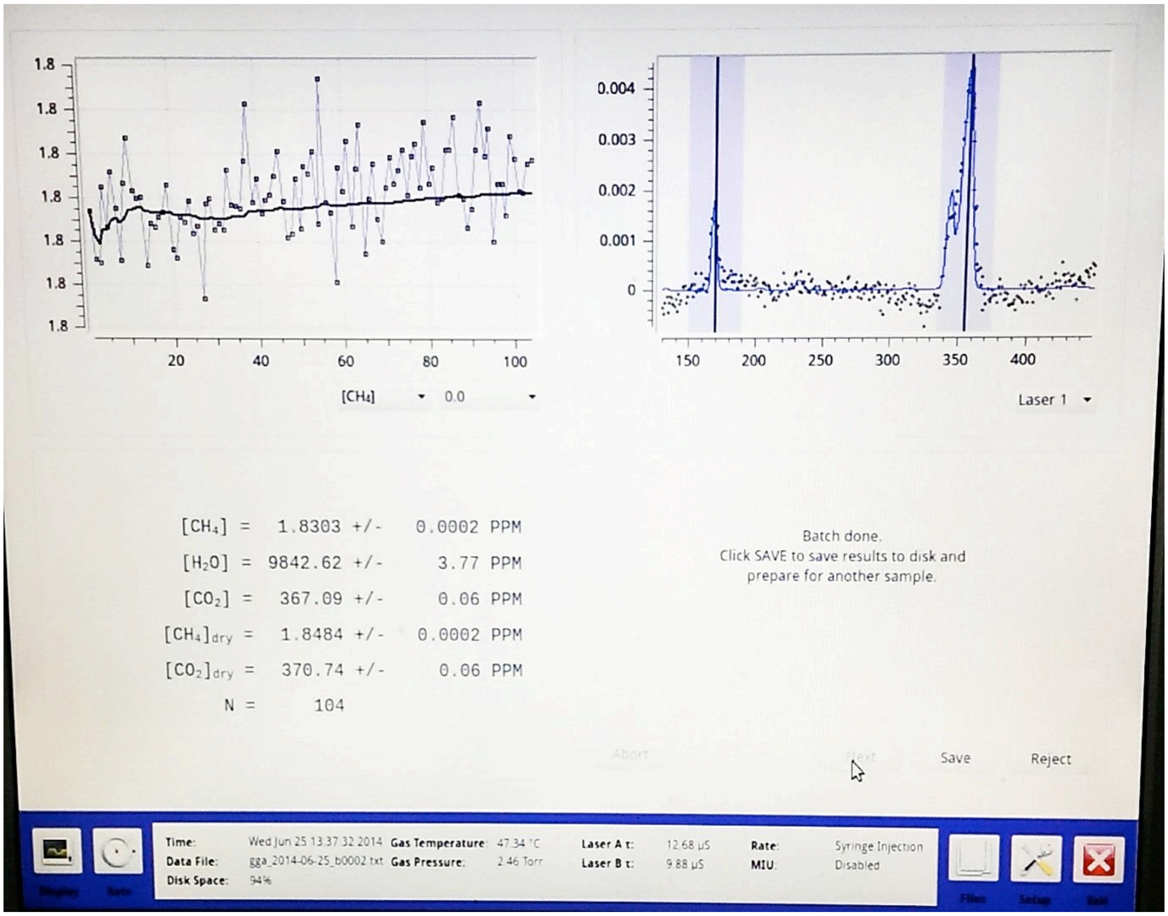
During the planned MSM expedition we will collect temperature, salinity, dissolved oxygen and oxygen isotopic data to best constrain the hydrographyc context of the methane data

Methods

We received the Cavity Ring Down Spectrometer (GGA) for methane concentration. The instrument has been tested and seemed to perform adequately. An additional field test will be conducted in July 2nd, during a one day cruise offshore Germany, to measure methane with this instrument over some known seep areas (Erkenforde Bay). The data will be cross calibrated with samples analyzed with other local laboratories.



Calibration curve using GGA and standard methane gas



Screen shots from the GGA instrument showing repeated measurement that are used to calculate methane concentrations.

Geochemistry plan

Goals:
Prepare for and collect water and sediment core samples from a high latitude setting (the Svalbard Margin) across gradients where methane hydrates show vulnerability to environmental change. Samples will be used for chemical and microbiological analyses to assess changes in chemistry and microbiology across vertical gradients (i.e., within a core) and horizontal gradients (i.e., across the putative upper edge of gas hydrate stability) that constrain the biogeochemical response at locations where methane hydrates are sensitive to environmental change. The geochemical shore-based program includes analyses of pore water, lattice water and water column samples for isotopic composition of the water and the dissolved inorganic carbon, which will be conducted at Oregon State University.

Subsampling sediment from core before splitting:

- Take samples from bottom end of each core section, starting with the bottom-most section
- **Methane Sampling**:
  - Sediment subsamples with cut-off syringes (these do not need to be acid-washed and can be re-used)
  - Extrude each sample into a 20-mL glass serum vial containing 5mL 1M NaOH
  - Stopper and crimp-top glass vials, and store upside-down at 4C
  - Analyzed onboard (Thomas and Patrizia)
- **Porosity Sampling Mathias- protocol**:

Rhizone Sampling:

Store cores in 4C lab
Rhyzones (2-3 cm) need to be pre-washed and dried

- Carry out the rhizone sampling within 4 hours of pulling up the cores (optimal)- in the case of 2 holes, we may want to sample the pore fluids AFTER all gas hydrate has dissociated-so cores will be left to dissociate and GH will be monitored with IR
  - Note how many hours post-coring the rhizone sampling is done
  - If there is a large amount of methane, the caps may pop off – in this case, holes for rhizons must be drilled immediately.
- Take 1 x ~10-mL sample at 20 cm intervals, below SMTZ (where methane bubbling I apparent), one sample every 50 cm 1 m is OK – record how much porewater is collected get
  - Must be done in cold room (at 4C)
  - Make sure that the rhizon is not inserted into a 'hole' in the sediments created by methane or microbio sampling
  - Use *acid-washed* 20-mL syringes for shallower sediments (more water) and *acid-washed* 10-mL syringes for deeper sediments
  - Make a note of depth from the top of each core section (and core/section numbers) for each rhizon sample
  - Subsampling from syringe (after ~10mL has been collected) may be done at room temperature.
  - All pore water must be filtered though accrudisks. 0.2 or 0.45 um?

Core squeezing- If possible-

To compare with rhyzone data
For REE
Maybe one sample per meter, when time permits

Subsampling

- 1.) **Shipboard analyses**:
  - Refractometer – Put a drop of porewater on the refractometer to determine salinity, and record results. Refractometer must be cleaned off between each sample using DI water and Kimwipes. May need to calibrate refractometer periodically against sample with IAPSO-
  - Alkalinity,
  - H2S
  - NH4
  - Cl,
  - SO4 desirable

2) Shipboard subsampling

- 2.1.) δ13C – 1-mL in an Agilent Vial containing 10uL $HgCl_2$
  - Need *at least* 0.75mL for analysis
  - If H_2S is present, a brown precipitate will form

2.2) d18O, D/H – 2 ml in glass agilent vial

- 2.3.) Chloride – Put 2-mL porewater in an empty glass vial (Wheaton vials)
  - Minimum 1-mL per sample
- 2.4.) Sulfate – Add 1.5 mL to a glass vial (Wheaton vials) containing 0.1 ml 10% ZnAc solution, note the sample volume if different from 1.5 mL
- 2.5.) Put 3 mL in a 15-mL Falcon tube and freeze for nutrients (PO4 NO3 Si)
- 2.6) DOC 2ml in dark glass vial- previously treated in a furnace
- 2.7.) Put remainder in acid-washed Nalgene bottles
  - Acidify with HNO_3 (optima grade)
  - Make sure bottles are tightly closed and put all Nalgene bottle samples from one core in a Ziploc freezer bag

Sediment samples

Phys props (density)
Solid- TOC/TIC
Anoxic samples (selected) for redox sensitive elements

Microbiology program

Goals:

Analyze the samples to assess changes in chemistry and microbiology across vertical gradients (i.e., within a core) and horizontal gradients (i.e., across the putative upper edge of gas hydrate stability) that constrain the biogeochemical response at locations where methane hydrates are sensitive to environmental change. In particular, examine how microbial communities influence carbon, iron, manganese and sulfur cycling.

Sample request:

Samples for microbiological analysis will be obtained from the cores in close physical proximity to samples obtained for geochemical and physical parameters of the sediments. Ideally we would like to obtain samples for DNA and RNA every 25cm within the SMTZ, at 1 and 2 meters above and below the SMTZ, and every 5 meters along the core from the seabed to the bottom of the core. Additional "samples of opportunity" will be taken if sediment features such as fractures indicate active fluid movement in the samples, or biofilms are observed in the cores.

Optimally we need 50 g sediment for each DNA and RNA (roughly 40 cc's sediment per falcon tube). The samples can be collected just by pushing a 50 ml falcon tube down into the core until the tube is ~40 ccs full.

DNA extraction samples should be put in liquid nitrogen as soon as possible. The RNA samples should also either be frozen in liquid nitrogen immediately or preserved with RNAlater to prevent RNA from breaking down. At the end of the expedition frozen samples will be shipped to OSU in dry shippers (MVE Biomedical Inc., Washington, PA) for analysis.

Analyses:

Molecular ecology analysis of the samples will be conducted with sample selection for intensive molecular characterization being guided by the results of the geochemical porewater analyses that occur shipboard or shortly thereafter.

We will extract DNA from cells using a method optimized for marine sediment communities (Luna et al. 2006) and with which we have had success (Colwell et al. 2011; Briggs et al. 2011; Briggs et al. 2012).

We will determine the presence and numbers of genes for methyl coM reductase subunit A (mcrA), dissimilatory bisulfite reductase (dsrAB), fermentation (hydA), and particulate methane monooxygenase (pmoA) which are indicative of methanogens/anaerobic methane oxidizers, sulfate reducers, fermenters, and aerobic methanotrophs, respectively, all involved in methane and organic carbon cycling in the sediments. To enumerate these genes we will use quantitative polymerase chain reaction (qPCR) as we have previously (Colwell et al. 2008; Nunoura et al. 2008) and with recent improvements of primers and methods to distinguish between ANME-I and methanogens, both of which possess mcrA (Lever, 2008; Joye et al. 2009; Lever 2013; M. Lever, personal communication).

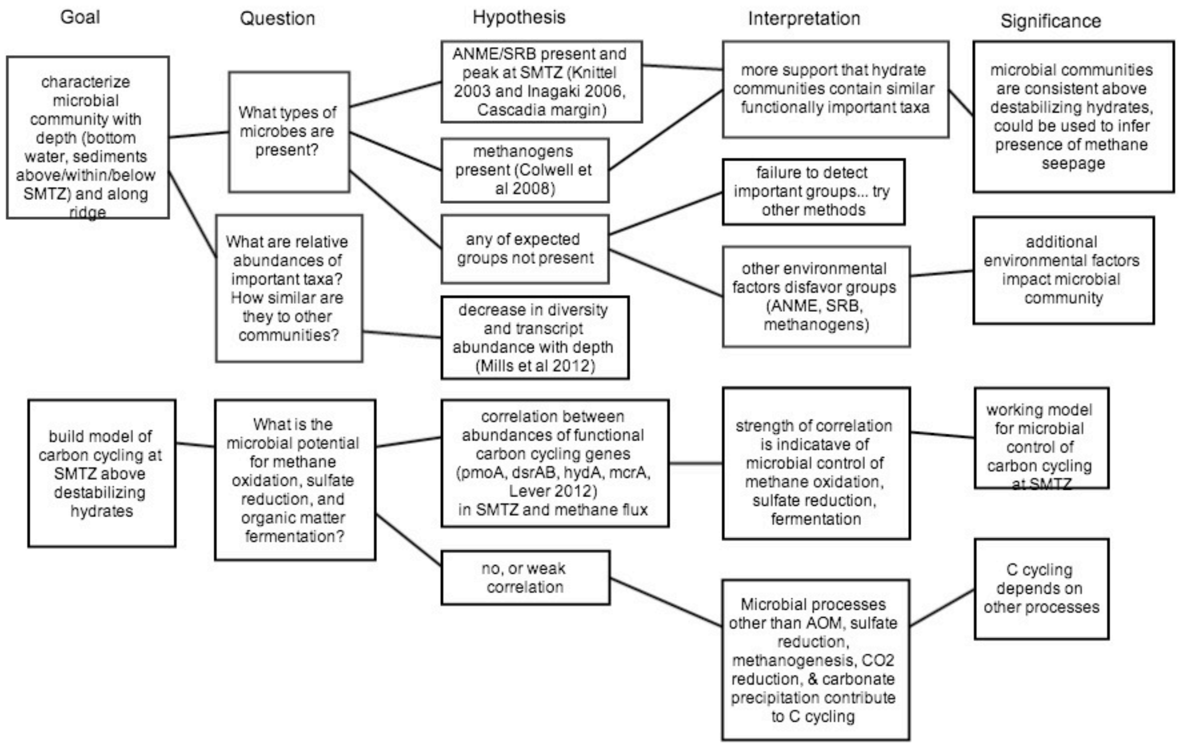
To complement the qPCR studies we will determine the diversity of Bacteria and Archaea in selected samples using high-throughput, nextgeneration Illumina sequencing.

On selected sediment cores we will examine the relative activity of microbes that play a key role in methane carbon cycling. This will be approached using either 16SrRNA:rDNA ratios for microbial communities (Muttray and Mohn 2000) or an approach that targets the mRNA (messenger RNA) characteristic of the ANME cells as identified in the aforementioned studies

(Chen et al. 2007; Freitag et al. 2010). These methods provide specific data on the activity of selected microbes based on the relative amounts of specific rRNAs or mRNAs.

Microbiological data obtained through qPCR to enumerate key functional genes will be compared using multivariate statistics (PC-ORD ver. 5.0; MjM Software, Inc.; McCune and Mefford, 2006) and QIIME (Caporaso et al. 2010) to determine the degree of similarity of the communities. Non-metric multidimensional scaling overprinted with biplots highlighting the values of abiotic parameters measured in the sediments will be used to evaluate how the microbial community patterns are aligned with key environmental parameters (Colwell et al. 2011; Huber et al. 2010; Briggs et al. 2012).

We will explore the possibility of using transcriptomics (RNA) to determine classes of genes microbes are transcribing, to hopefully gain insights into additional biogeochemical cycles that involve microbial activity.


Goal
Question
Hypothesis
Interpretation
Significance
characterize microbial community with depth (bottom water, sediments above/within/below SMTZ) and along ridge
What types of microbes are present?
What are relative abundances of important taxa? How similar are they to other communities?
ANME/SRB present and peak at SMTZ (Knittel 2003 and Inagaki 2006, Cascadia margin)
methanogens present (Colwell et al 2008)
any of expected groups not present
decrease in diversity and transcript abundance with depth (Mills et al 2012)
more support that hydrate communities contain similar functionally important taxa
failure to detect important groups... try other methods
other environmental factors disfavor groups (ANME, SRB, methanogens)
microbial communities are consistent above destabilizing hydrates, could be used to infer presence of methane seepage
additional environmental factors impact microbial community
build model of carbon cycling at SMTZ above destabilizing hydrates
What is the microbial potential for methane oxidation, sulfate reduction, and organic matter fermentation?
correlation between abundances of functional carbon cycling genes (pmoA, dsrAB, hydA, mcrA, Lever 2012) in SMTZ and methane flux
no, or weak correlation
strength of correlation is indicatave of microbial control of methane oxidation, sulfate reduction, fermentation
Microbial processes other than AOM, sulfate reduction, methanogenesis, CO2 reduction, & carbonate precipitation contribute to C cycling
working model for microbial control of carbon cycling at SMTZ
C cycling depends on other processes

CRUISE PARTICIPANTS

MSM 41; Leg 1: Reykjavik departure: August 5, 2014
Longyearbyen arrival: August 31, 2014

MeBo drillings (T-measurements; MeBo-CORKS?)
Temperature lance measurements (from GEOMAR)
Parasound + EM120/EM710
Magnetic Susceptibility Logging (Tromsø)
CTD/Hydrocasts/OA-ICOS
Gravity cores
TV-sled

	LEG 1		
1	Bohrmann, Gerhard	Co-chief scientist/sediments	MARUM
2	Dumke, Ines	Seismics	GEOMAR
3	Haeckel, Matthias	Pore water	GEOMAR
4	Thoenissen, Verena	Pore water	GEOMAR
5	Torres, Marta	Pore water	OSU
6	Hsu, Chieh Wei (Jeff)	IR imaging, sediments	MARUM
7	Gründger, Friederike	observer	CAGE-UiT, Norway
8	Riedel, Michael	MSCL, sediments	NRCan
9	Feseker, Tom	T-lance deployments/Corks	MARUM
10	Römer, Miriam	Data handling, Hydroacoustics	MARUM
11	Gepprägs, Patrizia	Autoclave sampling, OA-ICOS	MARUM
12	Pape, Thomas	Gas analyses, CTD	MARUM
13	Freudenthal, Tim	MeBo 1	MARUM
14	Düßmann, Ralf	MeBo 2	MARUM
15	Klein, Thorsten	MeBo 3	MARUM
16	Rehage, Ralf	MeBo 4	MARUM
17	Leymann, Tom	MeBo 5	MARUM
18	Stamp, Andreas	MeBo 6	MARUM
19	Fröhlich, Siefke	MeBo 7	MARUM
20	Kaszemeik, Kai	MeBo 8	MARUM
21	Mai, Hoang Anh	MeBo 9	MARUM
22	Schmidt, Werner	MeBo 10	MARUM

MSM 41; Leg 2: Longyearbyen depature: September 1, 2014
Tromsø arrival: September 12, 2014

MeBo drillings (MDPs; T-measurements)
Parasound + EM120/EM710
Magnetic Susceptibility Logging MSL (Tromsø)
CTD/Hydrocasts/AO-ICOS
Gravity cores

	LEG 2		
1	Bohrmann, Gerhard	Co-chief scientist/sediments	MARUM
2	Bünz, Stefan	Co-chief scientist/multi-beam	CAGE-UiT, Norway
3	Gründger, Friederike	Microbiology/Pore water	CAGE-UiT, Norway
4	Faust, Johan	Pore water/MSL/Hydroacoustic	CAGE-NGU, Norway
5	Panieri, Giuliana	Micropaleontology/Stratigraphy	CAGE-UiT, Norway
6	Wallmann, Klaus	Pore water	GEOMAR
7	Anke Bleyer	Pore water	GEOMAR
8	Torres, Marta	Pore water	OSU
9	Hsu, Chieh Wei (Jeff)	Sediments, IR imaging	MARUM
10	Römer, Miriam	Hydroacoustics	MARUM
11	Geprägs, Patrizia	Autoclave sampling	MARUM
12	Pape, Thomas	Gas analyses, CTD	MARUM
13	Freudenthal, Tim	MeBo 1	MARUM
14	Bergenthal, Markus	MeBo 2	MARUM
15	Spagnoli, Giovanni	MeBo 3	MARUM
16	Rehage, Ralf	MeBo 4	MARUM
17	Leymann, Tom	MeBo 5	MARUM
18	Noorlander, Kees	MeBo 6	MARUM
19	Rosiak, Uwe	MeBo 7	MARUM
20	Mai, Hoang Anh	MeBo 8	MARUM
21	Kausche, Arne	MeBo 9	MARUM
22	Hohnberg, Jürgen	MeBo 10	MARUM

Methane hydrate stability and saturation in Ulleung Basin: A numerical model perspective

Wei-Li Hong[1], Malgorzata Peszynska[2], Marta Torres[1], and Ji-Hoon Kim[3]

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[2]Department of mathematics, Oregon State University, USA
[3]Petroleum and Marine Research Division, Korea Institute of Geosciences and Mineral Resources, South Korea

The evolution of methane hydrate stability field in marine sediments, as well as the factors controlling gas transport and hydrate formation are the focus of active research. One particularly interesting issue is the formation of the near-seafloor massive hydrate deposits (MHD), which require migration of gaseous methane. The mechanisms that allow for gaseous methane migration to and through the gas hydrate stability zone remain unresolved. A recent drilling expedition to the Ulleung Basin, South Korea, provides a unique data set that specifically targets sites where acoustic data imaged chimneys characteristic of gas migration. MHDs here were observed as shallow as ~7 mbsf (meters below seafloor) at three sites. Positive Cl anomalies, as high as 1440 mM, suggest very rapid formation of MHD. To accurately simulate the evolution of such near-seafloor MHD, a well-behaved numerical model (Peszyǹska et al., 2009) and proper expressions of methane hydrate stability and saturation, especially under high salinity condition, are fundamentally important.

To obtain proper expressions of methane hydrate stability and saturation, we first reviewed the available laboratory data from the literature. We then compared those data with prediction from various popular predictive models. Whereas at seawater values these models and data are very consistent, at salinites higher than seawater we observed significant inconsistencies among the various theoretical predictions , which point to potential issues that may arise when these theoretical predictions are applied. The best fit to laboratory data was achieved with the Sloan and Koh (2008) model.
We then incorporated the hydrate stability and saturation prediction of Sloan and Koh (2008) into our numerical model to simulate the dilution-corrected pore water Cl profiles from Ulleung Basin and confirm the significance of advective migration of gaseous methane below the methane hydrate stability zone.

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