

# Geochemical characterization of concentrated gas hydrate deposits on the Hikurangi Margin, New Zealand

## Preliminary Geochemical Cruise Report

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#### **v. Acknowledgements**

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## **vi. OVERVIEW**

This report provides a preliminary summary of a geochemical data contribution to methane hydrate research and exploration on the Hikurangi Margin, off the northeastern coast of New Zealand from June 20, to July 3, 2006. Geochemical porewater profiles taken from shallow piston cores and vertical fluid migration measured with heatflow probing were compared with seismic summaries of potential deep sediment hydrate deposits. Recent geochemical and geophysical investigation of hydrates on the Cascadia Margin, mid-Chilean coast, and Texas-Louisiana Shelf demonstrated a need to combine these data for prediction of deep sediment hydrate deposits. In addition to methane hydrate exploration basic sediment and water column research topics were addressed during this cruise. General research goals for this expedition include:

- a).** Refine geophysical, geochemical and microbiological technologies for prospecting hydrate distribution and content.
- b).** Contribute to establishing high-priority geographical regions of prospective interest, in terms of methane volume estimates.
- c).** Prediction of environmental effects and geologic risks at the continental margin associated to the natural resource occurrence and resource exploitation.
- d).** Expand understanding of the biogeochemical parameters and associated microbial community diversity in shallow sediments that influence the porewater sulfate gradient observed through anaerobic oxidation of methane.

This expedition combines several ocean research topics. On a global perspective, methane hydrates are being surveyed by many nations as a new energy source. Exploration through different regions of the world ocean contributes to the estimate of this energy resource relative to the total fossil fuel reserve. Also with recognition of the potential coastal sediment hydrate loading through the world ocean a more thorough understanding of ocean carbon and climate cycles requires consideration of methane.

This project continues NRL and ONR-Global goals for international collaboration on methane hydrate

research. The data support development of the NRL program on methane hydrate influence on sediment geoaoustic and geotechnical properties in various coastal regions. In addition the program extends the current data base from recent work in coastal regions around western Canada (Cascadia Margin), the Texas-Louisiana Shelf, Blake Ridge, and mid Chilean coast which show diverse seismic profiles that result from differences in the sediment morphology and hydrate gas sources. Finally, this international collaboration shares the high cost of ship time and development of new field technologies.

## **I. INTRODUCTION**

Continental margins throughout the world are rich in sediment methane hydrates. The amount of methane gas trapped in hydrates is estimated to be significant relative to the energy of the total conventional fossil fuel reserves. The NRL methane hydrate research focus is to develop improved models for study of the creation and dissociation of natural gas hydrates and to quantify the impact of these processes on the geophysical and geotechnical properties of marine sediments. In addition, a large global volume of methane promotes interest in a new energy source, coastal stability, alteration of global economy and understandings of time scale and steps in climate change.

Alteration of hydrate stability in coastal sediments can impact drilling platform stability and contribute to environmental hazards. Submarine geo-hazards (such as sediment instabilities and slope failures on local and regional scales, leading to debris flows, slumps, slides, and possible tsunamis) caused by gas-hydrate dissociation are of immediate and increasing importance as humankind moves to exploit seabed resources in ever-deepening waters of coastal oceans.

On a natural global cycle the vulnerability of gas hydrate to temperature and sea level change varies the stability of deep-water oceanic sediments. Scientists studying the recent geological past theorize that gas-hydrate dissociation during the last glacial period (some 18,000 years ago) may have been responsible for

the rapid termination of the glacial episode. During the glacial period the sea level fell by more than 300 feet, which lowered the hydrostatic pressure, leading to massive slumping that may have liberated large volumes of methane. This may be related to series of mass removals and glacial to non-glacial transitions. Such changes could have allowed methane to escape into the atmosphere as a greenhouse gas, possibly triggering climate change. As the frequency of slumping and methane release increased, a threshold was eventually reached where ice melting began, leading to a rapid deglaciation.

Hydrate methane trapped in the sediment originates from deep thermogenic sources or is generated by microbes in cycling of deposited organic matter, fixed through time in deep sediment. A portion of the deep sediment methane is transported by diffusion and advection upward toward the overlying water column. Near the sediment-water column interface, a large fraction of methane is removed by microbial anaerobic oxidation during which sulfate is reduced. Since the concentration of porewater sulfate is observed to decline at or adjacent to the same level in the sediment where methane is consumed, it has been proposed that these two phenomena are linked through a symbiotic consortium of methanotrophic *archaea* and sulphate-reducing bacteria (SRB).

This shallow anaerobic oxidation of methane from deep sediment provides an approach to evaluate variation in the coastal methane vertical flux from deep deposits to the shallow sediment. Moreover, from an environmental and regulatory perspective, it is important to understand the fundamental mechanisms of methane production, oxidation, and transport in the sediment, and the interplay between these processes which regulates the methane flux into the hydrosphere.

Currently seismic profiling is the primary method to estimate the distribution of hydrate reservoirs in the seafloor sediment. No other approach provides rapid surveys of large regions. However, hydrates are not directly detected with seismic surveys, but the presence is inferred by the existence of a bottom simulating reflection (BSR) with the acoustic transition through the free gas phase. This survey does not consistently provide reliable identification of hydrate beds; hydrate deposits have been incorrectly identified or not observed. To support seismic exploration of hydrates, geochemical porewater profiles in shallow sediments are being interpreted to confirm deep methane deposits. Significant work is needed to understand the

mechanisms and interactions between transport and methane sources and sinks, and to develop models that could be applied to evaluate the methane distribution and assess environmental impacts of gas recovery.

## II. OBJECTIVES

Research voyage Gas Hydrates 2006 had 9 primary objectives that are part of the GNS programmes, *National Petroleum Resources, Offshore Frontiers, Gas Hydrates* (Foundation of Research, Science, and Technology, FRST, Energy Portfolio), “*How do gas hydrates weaken the seafloor, causing submarine slides and tsunamis?*” (Marsden Fund, in collaboration with NIWA and the University of Otago), and the “DOE gas hydrates” Non Specific Output Fund (now Capability Fund). These objectives were combined with NRL research focus on an Advanced Research Initiative (ARI), *Quantify the processes responsible for the distribution of gas hydrate (meters to hundreds of meters scale) associated with representative seafloor seeps* and an ONR sponsored program for the Marine Biogeochemistry Section, Naval Research Laboratory and Hawaii Natural Energy Institute, University of Hawaii for *International Collaboration on Methane Hydrate Research and Development* and the Department of Energy, National Energy Technology Laboratory *National Methane Hydrate R & D*. In this broad collaboration the expedition also supported research questions addressed by scientists from the University of Rochester (New York, USA), the GeoForschungsZentrum Potsdam (Germany), and the University of Auckland.

The voyage focuses on two study areas, offshore of the Wairarapa (Study area A or Ridge I) and Rock Garden/Ritchie Ridge offshore of Hawke’s Bay (Study area B). The following objectives were addressed during this research expedition.

Objective 1. Acquire high-resolution seismic data with coincident swath and 3.5 kHz mapping across a potential gas hydrate “sweet spot” (layer with highly concentrated gas hydrates).



Objective 2. Collect sediment cores (piston or gravity) in a transect across a potential gas hydrate “sweet spot” for pore water analysis.

Objective 3. Measure heatflow in a transect across a potential gas hydrate “sweet spot”.

Objective 4. Collect microbiological samples above the potential gas hydrate “sweet spot”.

Objective 5. Acquire 12 kHz data and measure methane in the water column using CTDs for detecting potential methane “plumes”.

Objective 6. Retrieve a temperature sensor deployed in 2/2005. Study area B, Marsden.

Objective 7. Collect sediment cores (piston or gravity) for reconstruction of paleoceanographic conditions.

Objective 8. Collect dredge samples and/or sediment cores (piston or gravity) for investigation of rocks on Rock Garden, Study area B, Marsden.

Objective 9. To acquire high-resolution seismic data with coincident swath and 3.5 kHz mapping across Rock Garden to study pockets of shallow gas beneath gas hydrates.

This report provides initial geochemical and heatflow data. A total project report is available through Dr. Ingo Pecher at [Ingo.Pecher@pet.hw.ac.uk](mailto:Ingo.Pecher@pet.hw.ac.uk).

### III. REGIONAL DESCRIPTION

Potential gas hydrate desposits, outlined by bottom simulating reflections in seismic data, appear to be ubiquitous on the Hikurangi Margin [Katz, 1981]. The primary goal of this voyage was to spatially locate gas hydrate deposits as a potential energy resource. For this program available seismic data were used to select locations to conduct piston coring for geochemistry and to measure heatflow over potential gas hydrate “sweet spots”, i.e., locations of high gas hydrate concentration [Crutchley et al., 2006; Pecher and Henrys, 2003] (Figure 1). In addition, the voyage was intended to contribute to data on how gas hydrates may weaken the seafloor linking gas hydrates with seafloor instability, submarine landslides, and possibly Tsunamis by a

freeze-thaw mechanism similar to frost heave [Pecher et al., 2005]. This was addressed with piston coring for paleoceanographic temperature studies, additional seismic data acquisition, and coring/dredging to survey sediment properties.

Another part of the expedition was to retrieve a temperature sensor on the seafloor that was deployed in March of 2005 in the study area. The combination of these data with previously collected data should significantly improve scientific knowledge of potential gas hydrate reservoirs and will allow a comprehensive analysis to test the hypothesis of “gas hydrate frost heave”.

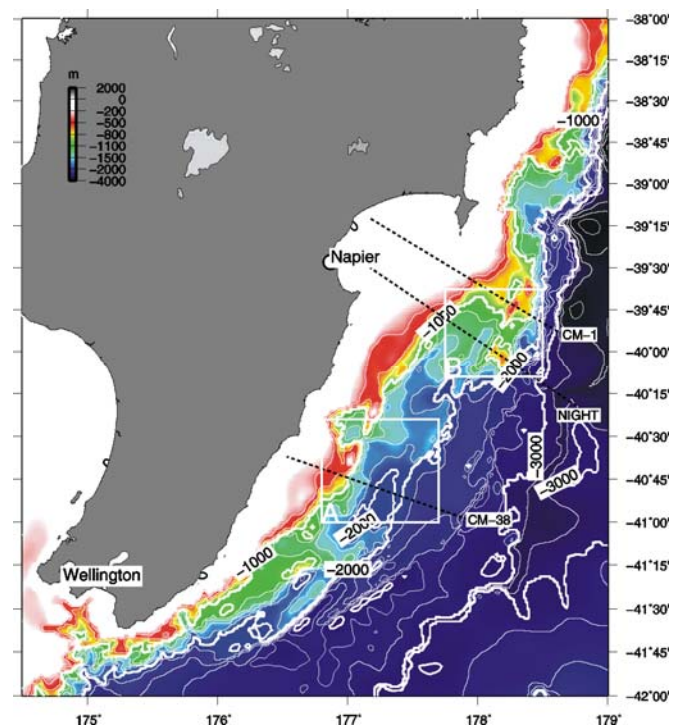


Figure 1: Regional map showing the two study areas. Dashed lines are crustal seismic data.



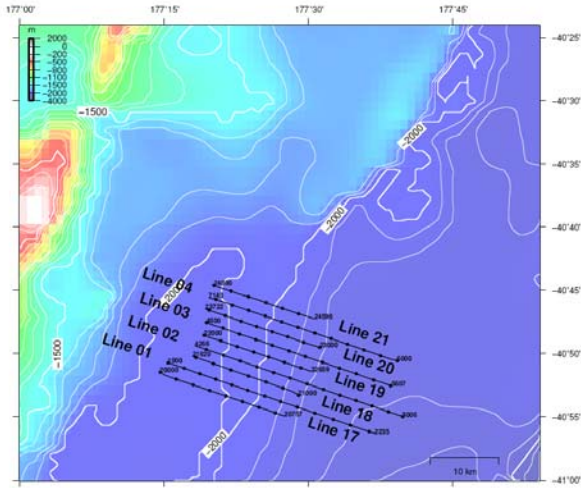


Figure 2: Study area on Ridge I with piston coring and heatflow conducted on seismic Line 1 and Line 3.

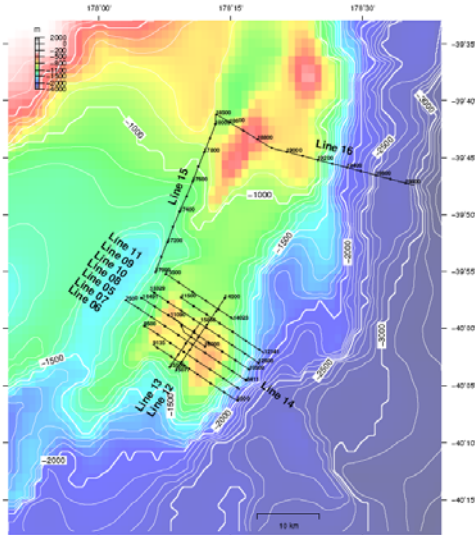


Figure 3: Study Area B, Rock Garden, dashed lines show most relevant existing seismic data, both crustal and high resolution.



Figure 4: Science team participating in the research cruise (see Table 1).

The broad plan of the voyage is to undertake multi-channel seismic surveys, EM300 multi-beam, 3.5 kHz, and 12 kHz mapping, sediment sampling by means of drop/piston coring and rock dredging, heatflow observations of the seabed, the analysis of water masses and water samples obtained by CTD-drops, and a retrieval of a temperature sensor.

We are focusing on two areas. Ridge I selected in the Study Area A is located offshore of the Wairarapa (Figure 2), where a suspected gas chimney has been observed in seismic data, potentially indicating a deposit of highly concentrated gas hydrates. Rock Garden in Study Area B offshore of Hawkes Bay is the location at which we suggest that gas-hydrate-related seafloor erosion occurs (Figure 3).

#### IV. CRUISE PARTICIPANTS AND LAND-BASED COLLABORATORS

Scientists from New Zealand, United States, Belgium, Canada and Germany, representing 11 University and Government research institutions contributed to this expedition (Table 1, Figure 4). Expertise of the science team resulted in the contribution geochemical, geophysical, geological, molecular ecology and biological data to address ocean water column, sediment, and porewater research questions. Research cruise and laboratory participants are recognized for the data contributions to the research questions outlined for this survey. This diversity in expertise, contributed through senior scientists, post doctoral researchers, graduate students, and technicians was necessary to successfully address the research goals.

Table 1: Cruise participants, affiliations and project goals..

Pecher	Dr. Ingo	GNS	Voyage leader, seismic, multibeam, 3.5 kHz
Coffin	Dr. Richard	NRL	Voyage co-leader, piston core/heat flow
Henrys	Dr. Stuart	GNS	Voyage co-leader, seismic, multibeam, 3.5 kHz
Faure	Dr. Kevin	GNS	Water column chemistry
Greinert	Dr. Jens	GNS/U. Ghent Belgium	GNS coordinator piston cores, water column chemistry, 18 kHz, carbonates
Orpin	Dr. Alan	NIWA	Paleoceanographic coring, multibeam, 3.5 kHz
Gerring	Pete	NIWA	Engineer/technician
McGill	Kevin	NIWA	Engineer/technician
Mitchell	John	NIWA	Engineer/technician
Wilcox	Steve	NIWA	Engineer/technician
Gorman	Dr. Andrew	U of Otago	Seismic, student advisor
Crutchley	Gareth	U of Otago	Student watchstander
Fohrmann	Miko	U of Otago	Student watchstander
Kilner	Jeremy	U of Otago	Student watchstander
Senger	Kim	U of Otago	Student watchstander
Wood	Dr. Warren	NRL	Heatflow
Hamdan	Dr. Leila	NRL	Piston core/microbiology
Pohlman	John	NRL	Piston core/biogeochemistry
Smith	Joe	U of Mass (NRL)	Piston core
Dale	Celeste	NRL	Piston core
MacDonald	Bob	Biologica Ltd (NRL)	Heatflow/piston core
Downer	Ross	Milbar Hydro-Test (NRL)	Piston core/heatflow, engineer
Bryant	Layton	Milbar Hydro-Test (NRL)	Piston core/heatflow, engineer
Kurasaki	Ryan	U of Hawaii	Microbiology
Yoza	Dr. Brandon	U of Hawaii	Microbiology
Tomaru	Dr. Hitoshi	U of Rochester	Iodine isotopes, halogens, oxygen, hydrogen
Kukowski	Dr. Nina	GFZ Potsdam, Germany	Tectonics, multibeam
Schinteie	Richard	U of Auckland	Student watchstander, pore water analysis, carbonates

## V. METHODS

### 1. Site Navigation

The *RV Tangaroa* (Figure 5) had a single propeller, no bow thruster (during these operations), and no computer aided dynamic positioning capability. The station-keeping accuracy was affected by the weather and current conditions and varied throughout the cruise. For accuracy of the sample station selection it was necessary to determine the positioning capability. This was accomplished by monitoring variation in positioning during heatflow data acquisition at 5 stations. For stations 1-3 this was approximately +/- 30m, for station 4 approximately +/- 10m and for Station 5 approximately +/- 50 m. The position of the probe on the seafloor was taken to be the position of the ship at the time of insertion. This variation in the positioning was acceptable relative to the coring and heatflow sample regions selected across the seismic surveys. Given the circumstances, the piloting of the ship was extraordinary.



Figure 5: *RV Tangaroa* moored in Wellington, New Zealand.

### 2. Piston Coring

Piston coring (PC) was conducted over the mid starboard side of the vessel. PC was conducted on a 24 hour basis through a NIWA contract for the ship costs (Figure 6). The core barrel length was 6.5 m and water column depths above the regions studied ranged from 670 to 2200 meter. The piston core trigger was

initially set at approximately 3 feet above sediment penetration. Cores retrieved with this drop depth were too shallow, ranging from 1 – 3 meters. An increase in five feet for the trigger drop depth increased the core length to 3 – 4 meters at most locations. When the sediment structure did not allow the core penetration a 2.5 meter core barrel was used and the core weight was set as a gravity core.



Figure 6: Piston coring system provided by NIWA.

### 3. Pore Water

a. Press Loading and Squeezing – Core sections were retrieved from the piston core barrel in two 3 m sleeves. 10 cm whole round core sections, collected at a vertical resolution of 25 cm, were taken to the ship wet laboratory for processing (Figure 7). Sediment from the interior of the core was placed inside the body of the press. The press bodies were filled with sediment to maximum capacity with a minimum air volume. A clean latex sheet was placed on the air inflow side of the press body to prevent free airflow through the press. The press bodies were capped, placed on the pore water press rack and pressurized with 60-80 psi air over the latex sheet. Pore water was collected in a 60 ml syringe on the outflow line. Sediment from the press was placed on a sheet of ashed Al foil and frozen.





Figure 7: Porewater press lab setup with 24 press ports.

**b. Pore Water Processing** – The average volume of pore water collected for each sample was 23.4 ml with a range of <1 to 38 mls. Using the side port on a three-port stopcock, 1 ml was removed from the 60 ml syringe with a 10 ml syringe for analysis of total sulfides and 2 mls were removed for ion analysis ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) and transferred into 2 ml screw top vials. A volume of 100  $\mu\text{l}$  of 0.8 M  $\text{CdNO}_3$  was added to the sample for ion analysis to precipitate dissolved sulfides which could oxidize to sulfate. A 0.2  $\mu\text{m}$  filter in a holder was placed on the 60 ml syringe and the remaining contents of the syringe were placed into a scintillation vial. Using a 1 ml fixed volume pipet, 2 mls (exactly) of the sample were transferred into a 5 ml serum vial for DIC concentration, 2 mls were added to a 3 ml serum vial for analysis of  $\delta^{13}\text{C}$ -DIC,  $\delta^{13}\text{C}$ -DOC and DOC concentration. The serum vials were sealed with Teflon lined septa. Samples for sulfide, ion and DIC concentration analysis were delivered to the on-board geochemical

laboratory and processed immediately. The vials for carbon isotope and DOC concentration analysis were frozen at  $-20^\circ\text{C}$ .

Additional samples for analyses included, 2 mls in 5 ml amber ampoules for DOC fluorescence, 2 mls for volatile fatty acids (VFAs) in 3 ml glass screw top vials with Teflon lined septa, 7 mls for nutrients ( $\text{NO}_3$ ,  $\text{NO}_2$ ,  $\text{NH}_4$  and  $\text{PO}_4$ ), alkalinity, major anions and major cations (by ICP) in 10 ml polyethylene vials and 2 mls for iodine. The remaining water was archived in 5 ml amber ampoules.

#### 4. Ship Board Laboratory Analysis

##### a. Sulfate and Chloride Concentrations –

Sulfate and chloride were measured with a Dionex DX-120 ion chromatograph equipped with an AS-9HC column (Figure 8). Samples were diluted 1:50 (vol/vol) prior to analysis and measured against a 1:50 diluted IAPSO standard seawater (28.9 mM  $\text{SO}_4^{2-}$ , 559 mM  $\text{Cl}^-$ ). Chloride concentrations lower than values measured in seawater is used to interpret the present of melted hydrates in the core. The depth of depleted sulfate concentrations measured in porewater (limits of detection  $\sim 0.1$  mM) was used to assist in the prediction of hydrate beds below (described below).

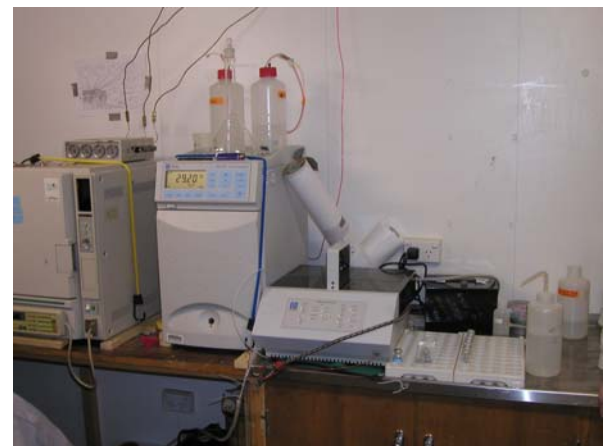


Figure 8: Dionex IC used for chloride and sulfate analysis.

##### b. Porewater Methane Concentrations -

Methane concentrations were determined from 3-ml sediment plugs using headspace techniques and were quantified against

certified gas standards (Scott Gas, Plumbsteadville PA). Headspace analysis was performed on board using a GC-FID Shimadzu GC-14A gas chromatograph equipped with a Hayesep 0.80/100 column (Figure 9). Methane concentrations are presented in millimolar units (mM).



Figure 9: Shimadzu GC 14A used for porewater methane analysis.

c. Sulfide concentrations - Pore water sulfide concentrations were measured with spectrophotometer (Figure 10), using the Cline method (Cline, 1969). Sulfide concentrations are presented in millimolar units (mM).



Figure 10: ThermoSpectronic Genesis 20 spectrophotometer used for porewater sulfide analysis.

d. Pore Water DIC Concentrations - Pore water dissolved inorganic carbon (DIC) concentrations were measured using a UIC coulometer (Figure 11) and standardized against a certified reference material (CRM, Batch 58). DIC concentrations are presented in millimolar units (mM).



Figure 11: UIC Inc. Coulometric system 030 used for DIC analysis.

## 5. Porewater Data Interpretation

Parameters for the porewater data include methane, sulfate, chloride, sulfide, and dissolved inorganic carbon concentration and stable carbon isotope ratio. Porewater geochemical data are plotted for comparison of methane and sulfate concentrations to assess the varying degrees of vertical methane fluxes and resulting methane oxidation (Borowski et al., 1999). Anaerobic oxidation of methane occurs as:



in sediment depths where vertical flow of deep sediment methane and sediment surface sulfate converge. This analysis is used to estimate the presence of methane deep in the sediments that could be concentrated in hydrate beds. DIC is added in these plots to support the interpretation of methane oxidation and sulfide is incorporated for comparison with sulfate reduction. Stable carbon isotope analysis of the DIC provides additional interpretation of methane oxidation and contribution to the DIC.

## 6. Heat Flow

Thermal data collected in the upper few meters of the seafloor using a heatflow instrument have proven to be reliable for a proxy for fluid flow and help define the limits of active flows around methane seeps and mud volcanoes associated with methane seeps and hydrates. The heatflow instrument used was a 3.5-meter-long “violin bow” or “Lister-type” instrument (Figure 12). Eleven thermistors were arranged 30 centimeters apart in a 1-cm-diameter tube held in tension parallel to a solid steel strength member. There was also a temperature sensor mounted on the top of the weight stand which recorded the water temperature near the sediment-water interface. The system measured both temperature gradient and thermal conductivity in-situ. Sediment temperatures were calculated from the decay of the frictional heat caused by penetration of the instrument into the sediment.



Figure 12: Sediment heatflow “Lister-type” system deployment.

Thermal conductivity was determined from the decay of a calibrated thermal pulse applied after a preset period of time. Heat flow values were determined at each station by computing thermal resistance values at each thermistor,

$$R = \int (1/\lambda) dz,$$

where  $\lambda$  is the thermal conductivity. In a situation of steady-state conductivity the heat flow is equal to the slope of the line on a Bullard Plot, a plot of temperature vs. thermal resistance. For each station, any non-linear data that might be attributed to bottom water warming or cooling, were removed so as not to bias the statistics. A heatflow value is determined from the slope of the best-fitting linear least-squares line through the remaining data. All heatflow values were corrected for instrument tilt.

High resolution transects were done over the seeps and mounds get an accurate summary of elevated thermal signatures. Stations were typically set no more than 100 meters apart to avoid oversight on fluid flow associated with distinct lateral distribution of seafloor seeps. Data typically show clear anomalies in sediment temperature and heatflow associated with the mounds and seeps.

## 7. Laboratory Analysis

a. DIC  $\delta^{13}\text{C}$  Analysis -  $\delta^{13}\text{C}$  is measured on pore water DIC. DIC in porewater was released as  $\text{CO}_2$  into the headspace by adding 100  $\mu\text{l}$  of 10% HCl into sample serum vials. Gases are analyzed with a Finnigan Delta S Isotope Ratio Mass Spectrometer with a sample injection through a Varian GC. For  $\delta^{13}\text{C}$  analysis the standard is PeeDee Belmenite.

b. Sediment porosity is calculated through the core profiles with subcore sediment samples. Samples are placed in pre-weighed 47 mm Petri dishes and frozen until returned to the laboratory. Back in the laboratory samples are thawed, the outer Petri dish is dried at room temperature overnight. Samples are then placed in a drying oven at  $50^\circ\text{C}$  overnight. Thoroughly dried sediment is weighed again and the change is used for the water content in the calculation of sediment porosity that is incorporated in the calculations of vertical sulfate diffusion.



## 8. Molecular Biology

a. DNA extraction and conditions for Length Heterogeneity-Polymerase Chain Reaction (LH-PCR). Genomic DNA was extracted from 500 mg (wet weight) of sediment using Bio 101 FastDNA ® SPIN kit for soil (Q·BIOgene, Inc.), and stored at -20°C. Approximately 10 ng of DNA was used as template for LH-PCR in triplicate reactions. PCR amplification of the first two variable regions of the small subunit (SSU) rRNA was performed using a fluorescently labeled (6-FAM-27F) forward primer (5'-6-FAM-AGAGTTTGATCM TGGCTCAG-3') and a non-fluorescent reverse primer, 355R (5'-GCTGCCTCCCGTAGG AGT-3') (PE Biosystems). Positive (*E. coli* laboratory culture) and negative controls accompanied each reaction. PCR mixtures and conditions are according to Hamdan et al. (in prep). Briefly, a final concentration of 1X PCR buffer, 2.5 mM MgSO<sub>4</sub>, 0.20 mM of dNTPs, 0.5U Taq Gold DNA Polymerase (Applied Biosystems, Inc.), 0.5 µM of primers and DEPC water up to a final volume of 20 µL per reaction. A GeneAmp System 9700 (Applied Biosystems, Inc.) was programmed for an initial denaturation step at 95°C for 15 min. followed by 35 cycles of 95°C for 30 sec, 48°C for 30 sec. and 72°C for 2 min plus 5sec per cycle with a final extension at 72 °C for 30-45 min. LH-PCR product was run on a 1% agarose gel to visualize and quantitate product. The PCR Product was diluted based upon the strength of the product, mixed with internal size standard (ILS-600, Promega), and HiDi formamide (Applied Biosystems, Inc.) and loaded on an SCE 9610 capillary sequencer (Spectrumedix, LLC). After analysis of LH-PCR fingerprints with GenoSpectrum software (SpectruMedix, LLC) a custom PERL script was used to extract the LH-PCR data, normalize profiles with respect to the total peak area in profiles and interleave profiles being analyzed. Reproducibility was tested by comparing triplicate PCRs for each sample.

b. Cloning and sequencing. New PCR products with non-fluorescent primers will be cloned using a TOPO TA cloning kit (Invitrogen). Transformed cells were plated on

imMedia-AmpBlue (Invitrogen) agar and incubated at 37°C for 20±4 h. For each clone library, at least 96 individual white colonies were obtained, and extracted DNA from colonies was used as template for PCR using M13 forward (5' – GTAAAACGACGGCCAG - 3') and reverse (5'- CAGGAAACAGCTAT GAC - 3') primers (Invitrogen). After visualizing on a 1% agarose gel, PCR products were purified with AMPure magnetic beads (Agencourt BioScience Corp.). After quantitating purified products on an agarose gel, sequencing reactions were performed with Big Dye Terminator Cycle Sequencing Kit v3.1 (Applied Biosystems) and purified using Sephadex G-50 (Sigma-Aldrich). Reactions were reconstituted in HiDi formamide (Applied Biosystems) and run on a SEC9610 capillary sequencer (SpectruMedix LLC). After analyzing raw data with BaseSpectrum software (SpectruMedix LLC), sequences were imported in Sequencher (Gene Code Corp.) for manual base calling.

Clone sequence data were used in MEGABLAST searches against GenBank, and the Ribosomal Database Project (RDP) v8.1. Clone libraries were analyzed using classic rarefaction analysis to determine the estimated diversity of the phylotypes in the community. Clone sequences were aligned with matching sequences from GenBank or RDP v8.1 using Clustal X and phylogenetic trees were constructed using PAUP.

c. Nucleotide sequence accession numbers. Partial environmental 16S rDNA sequences were deposited in the GenBank database and be made available to the public.

## VI. PRELIMINARY GEOCHEMICAL RESULTS

The following presentation of geochemical and heat flow data will be finished with laboratory sample and data analyses. These data are presented for overview of the preliminary results and to provide focus for the key issues in data interpretation. These data will be compared to recent and current field activity that this research team is involved with on the mid Chilean coast, Cascadia Margin off



the western coast of Canada, and Texas-Louisiana Shelf in the Gulf of Mexico.

A core log summary is presented in Table 2. These cores were obtained at a nearshore region to the northeast of Wellington, NZ, across Ridge I and over the Rock Garden, on the Hikurangi Margin. Data presented in this

report are the first geochemical field analysis to survey methane hydrate deposits along the coast of New Zealand. These data will be available for future methane hydrate exploration in this region.

Table 2: Piston coring log for samples taken at the nearshore control site, Ridge I and Rock Garden.

Cruise log ID	NRL log ID	Seismic line	WC depth (m)	Core depth (cm)	Lat-long (40 meters up) (Core in)	Pull out (lbs)	Comment	Lab
<b>Nearshore</b>								
TAN0607-2	NZ Core 1				S40°93.687 E176°72.492			NIWA
TAN0607-3	NZ Core 2		687	350	S40°93.687 E176°72.492		shallow test and control core	NRL
<b>Ridge I</b>								
TAN0607-17	NZ Core 3	4610	1998	332	S40°50.143 E177°22.242	9.4	sleeve cracked the full length	NRL
TAN0607-18	NZ Core 4	4510		480	S40°50.498 E177°22.518	9.2		NRL
TAN0607-19	NZ Core 5	4098	2128	----	S40°51.408 E177°25.993	8.0	core did not trigger	NRL
TAN0607-20	NZ Core 5	4098	2124	285	S40°51.406 E177°24.990	10.3		NRL
TAN0607-22	NZ Core 6	4279	1912	----	S40°51.009 E177°24.471	10	bent pipe no core retrieved	NRL
TAN0607-23	NZ Core 7	4230	2020	275	S40°51.053 E177°24.669	10.2	sulfide odor	NRL
TAN0607-24	NZ Core 8	4255	1993	250	S40°51.116 E177°24.872	9		NRL
TAN0607-25	NZ Core 9	4400	1993		S40°50.751 E177°23.449	9.2	Light sulfide	NIWA
TAN0607-26	NZ Core 10	4175	2068	98	S40°51.135 E177°25.336	10.2	no pipe bend, stiff sediment	NRL
TAN0607-27	NZ Core 11	4400	1981	250	S40°50.735	9.2	lost trigger	NRL

					E177°23.445		core	
					S40°50.737 E177°23.466			
TAN0607-28	NZ Core 12	4371	1945	128	S40°50.804 E177°22.688	9.6	trigger cable extended	NRL
					S40°50.799 E177°23.705		Bent core	
TAN0607-45	NZ Core 13 (20)	4175	2089	240	S40°51.2352 E177°25.3319	10.0	core logging changed by I. Pecher in the NZ notation. Core #'s in their log are NRL numbers + 7.	NRL
					S40°51.2346 E177°25.3321			
TAN0607-46	NZ Core 14 (21)	4200	2031	450	S40°51.1700 E177°25.1399	9.8	statement from first mate navigation resolution is 50 m	NRL
					S40°51.1718 E177°25.1459			
TAN0607-47	NZ Core 15 (22)	4135	2134	424	S40°51.3217 E177°25.6815	9.6		NRL
					S40°51.3225 E177°25.6837			
TAN0607-48	NZ Core 16 (23)	4400	1979	----	S40°50.7377 E177°23.4594	8.9	core cap was lost – no core	NIWA
					S40°50.7396 E177°23.4554			
TAN0607-49	NZ Core 17 (24)	4385	1968	220	S40°50.7605 E177°23.5724	10.3	Bent core pipe	NRL
					S40°50.7710 E177°23.5772			
TAN0607-50	NZ Core 18 (25)	4330	1912	200	S40°50.8910 E177°24.0255	8.3	gravity core used on top of the mound	NRL
					S40°50.8970 E177°24.0267			
TAN0607-51	NZ Core 19 (26)	4330	1911	NIWA	S40°50.8777 E177°24.0300	12.0	Short ~5M piston core used	NIWA
					S40°50.8889 E177°24.0218		Bent core pipe	
TAN0607-73	NZ Core 28N	4155	2119	310	S40°51.2817 E177°25.5062	9.8	Last core on this line	NRL
					S40°51.2799 E177°25.5119		Trigger was set back to previous length	
TAN0607-74	NZ Core 29N	1319	1962	350	S40°48.847 E177°24.351	9.2	First core 2 km north	NRL
					S40°48.8461 E177°24.3447			
TAN0607-75	NZ Core 30N	1405	1952	381	S40°48.930 E177°24.7130	9.5		NRL
					S40°48.9400 E177°24.7161			

TAN0607-76	NZ Core 31N	1536	1987		S40°49.0742 E177°25.2670	9.6		NRL
					S40°49.0704 E177°25.2765			
TAN0607-77	NZ Core 32N	1777	2086	400	S40°49.3512 E177°26.2712	8.8		NRL
					S40°49.3561 E177°26.2804			
<b>Rock Garden</b>								
TAN0607-62	NZ Core 22		891	350	S40°03.66 E178°08.47			NRL
TAN0607-63	NZ Core 23		892	60	S40°043.51 E178°87.03		Very thick clay	NRL
TAN0607-64	NZ Core 24		2523	350	S40°06.6466 E178°21.2087	10.7		NRL
					S40°06.6457 E178°21.2079			
TAN0607-65	NZ Core 25		2693	NIWA	S40°05.5965 E178°18.8682	9.3	Short core redo	NIWA
					S40°05.6966 E178°18.8679		The trigger chain was shortened	
TAN0607-66	NZ Core 26		2693	NIWA	S40°05.5736 E178°18.8488		No core bent barrel	NIWA
					S40°05.5736 E178°18.8436			

## A. Core Testing Region

Preliminary instrument and equipment testing was conducted at a shallow region (670 m) outside Wellington S40°48.02, W176°54.5 (Figure 13). Porewater sulfate, methane sulfide and DIC concentrations from a core in this region provided a control data base away from methane hydrate deposits (Figure 14). Seismic surveys indicated no bottom simulating reflector and hydrates were not present in the sediment. The water column depth in this region was 687 m. The piston core retrieved was 350 cm long. Sulfate profiles showed a shallow slope through the core that corresponded with near zero methane concentrations. The sulfide and DIC concentrations show conservative, slight increases through the core concentrations. These control site data will be compared with SMIs and related geochemical data over Ridge I and Rock Garden.

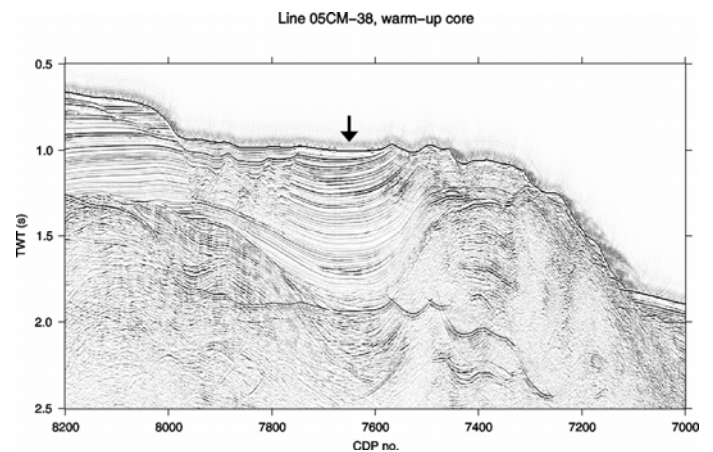


Figure 13: Seismic line for the control piston coring (indicated by the arrow) and heatflow analysis. CDP spacing was set at 12.5 m.

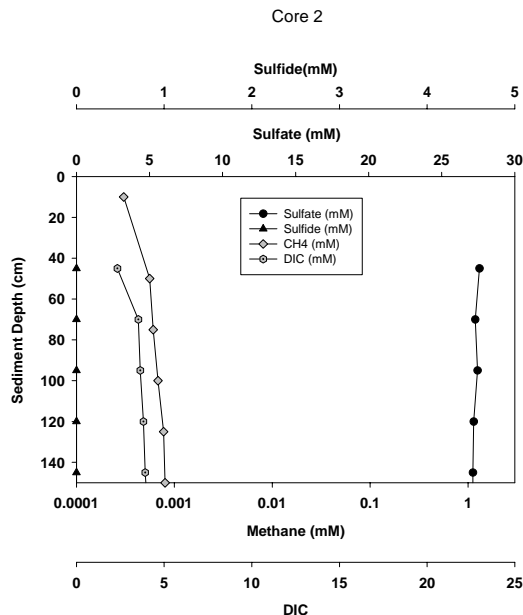


Figure 14: Porewater sulfate, DIC, sulfide and methane concentrations from a piston core taken at a non active control region.

## B. Ridge I

### 1. Geochemistry/Piston Coring

Piston coring was conducted along the seismic profile 2 on Ridge I (Figure 15). Seismic, geochemical analysis of porewaters and heatflow are combined for a survey of potential deep hydrate deposits in this study. Coring sites selected were planned to assess interpretation of the seismic profiles for strong BSR and vertical fluid migration to the sediment surface and high gas wipe out regions. Thorough seismic interpretation is being prepared by I. Pecher (GNS).

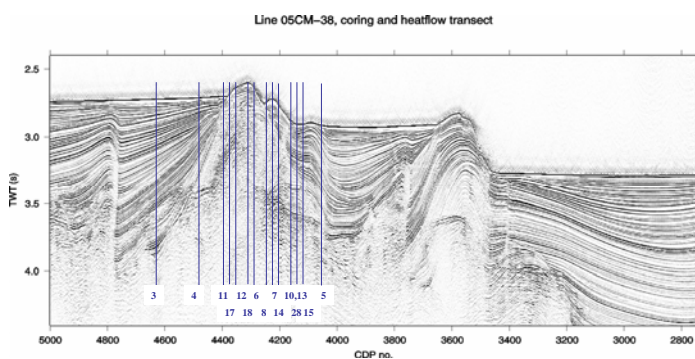


Figure 15: Ridge I piston core sites presented along the seismic CDP number. CDP spacing was set at 12.5 m.

Figures presented here are intended for a preliminary overview of the data acquired during this expedition. The total data set is

presented in Appendix 1. Plots are included in Figure 16 for an outline the vertical methane diffusion in the sediment, in terms of methane and sulfate profiles, on the landward side, seaward side and top of the mound. Overall the sulfate profiles from these piston cores were non-conservative. Non-conservative sulfate profiles in porewaters can result from several different factors; including variation in vertical diffusion caused by recent deposits of modern sediments, variation in vertical sediment properties, horizontal porewater advection, and bioturbation. Observation of these cores found worm channels in the surface sediment that suggests bioturbation causes vertical methane profiles in the shallow core regions. Vertical sulfate diffusion was calculated on the linear points of the sulfate profile below segments where bioturbation appeared to mix seawater sulfate through the core.

A comparison of the vertical variation in methane and sulfate (Figure 16) results in inverse concentration gradients, with declines in sulfate from reduction to sulfide coinciding with increases in the DIC upon anaerobic oxidation of methane. Core 3 was taken on the landward side, well off the mound, in a region with a level BSR observed in the seismic profile (Figure 16). The porewater sulfate profile in this core was similar to the data from the control site with a shallow slope. Methane concentrations in the porewater from this location were at the limits of detection. Similar sulfate and methane profiles were measured in Core 18 on top of the mound located in the Ridge I survey area. These data indicate low vertical porewater and methane diffusion, perhaps impeded by carbonate formation on the mound. Rapid vertical methane diffusion was observed in the sulfate and methane profiles at the coring locations on the landward and seaward edges of the mound. Cores obtained near the mound were consistently shallower and methane concentrations through the SMI were depleted to the limits of detection. The sulfate and DIC concentrations indicate that this was a region in which anaerobic oxidation of methane was active.

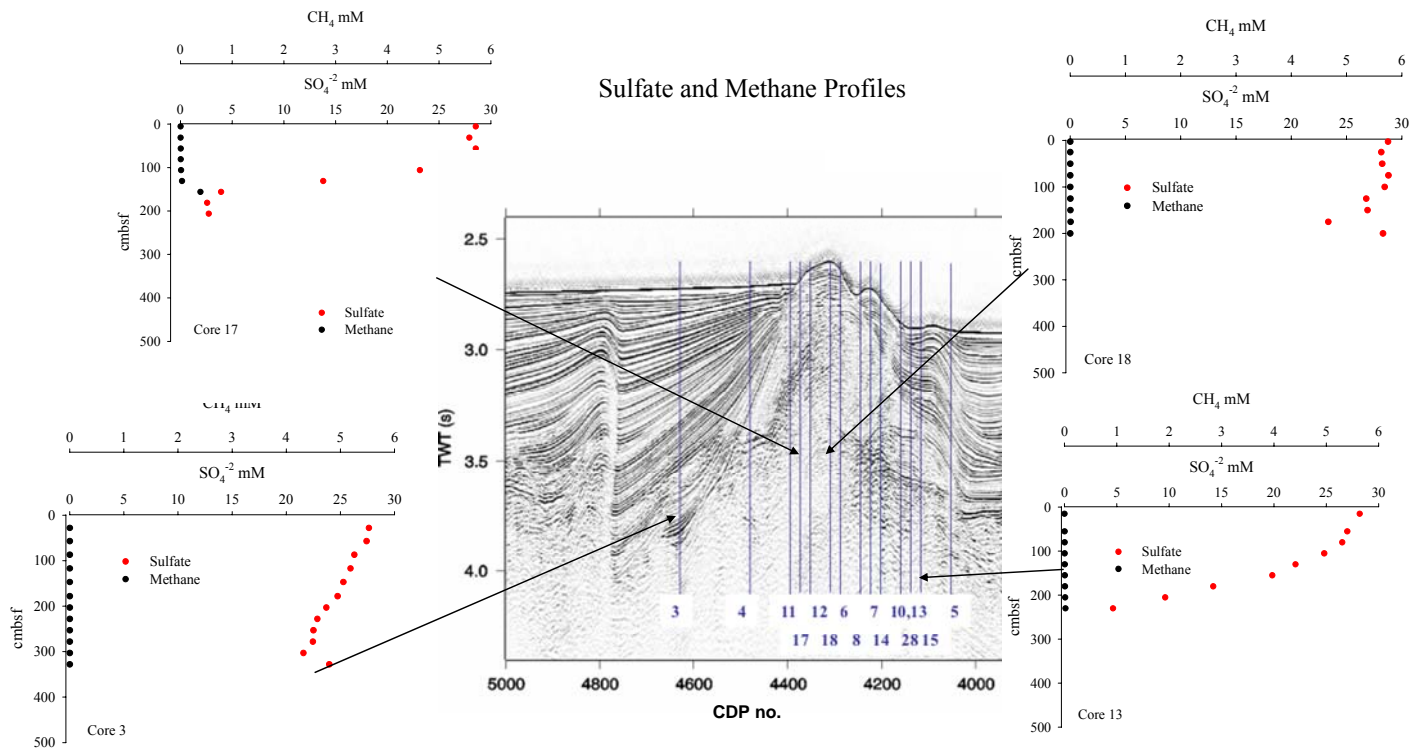


Figure 16: Ridge I piston core sulfate and methane porewater data presented along the seismic CDP number. CDP spacing was set at 12.5 m.

A summary of DIC profiles in sediment porewaters are presented in Figure 17. The concentration of DIC follows the sulfate profiles with the variation in the vertical methane diffusion across the seismic line. Shallow DIC concentration gradients were measured on top of the mound and at the landward site off the mound. Gradients on the landward and seaside slopes of the mound were significantly steeper.

Sulfide concentrations in porewaters follow the variations in DIC resulting from methane oxidation during sulfate reduction (Figure 18). Sulfide concentrations were below the limits of

detection on the mound and at the landward site. An interesting comparison of the sulfide profiles is the large difference in the concentration gradients between the landward and seaward slopes (Figure 18). While there was not a large difference in sulfate profiles between these core sites, the higher sulfide end product in the sulfate reduction suggests a greater anaerobic oxidation of methane at the landward coring locations. This observation supports the heatflow data presented below with active fluid advection on the landward side of the mound and diffusion on the seaward point (presented below).

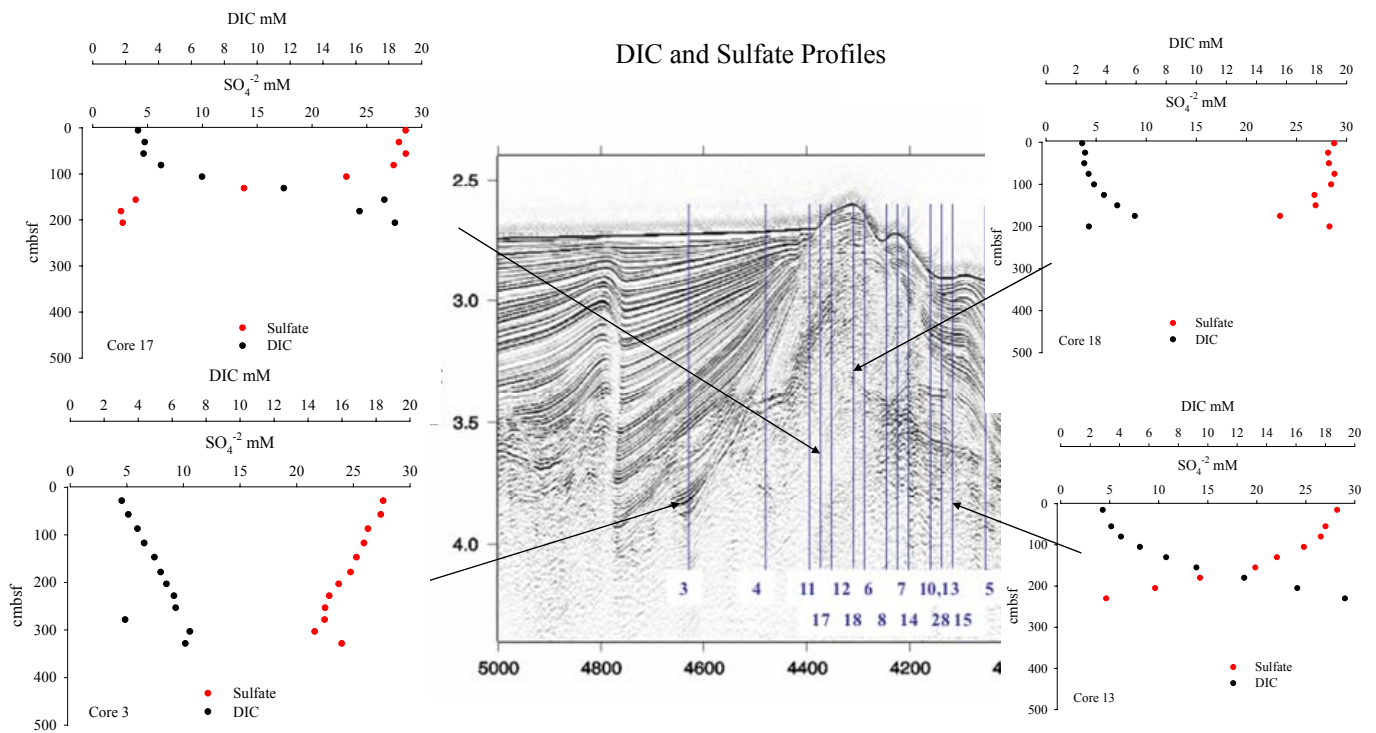


Figure 17: Porewater DIC and sulfate concentrations for samples representative of variations during coring on Ridge I. CDP spacing 12.5 m.

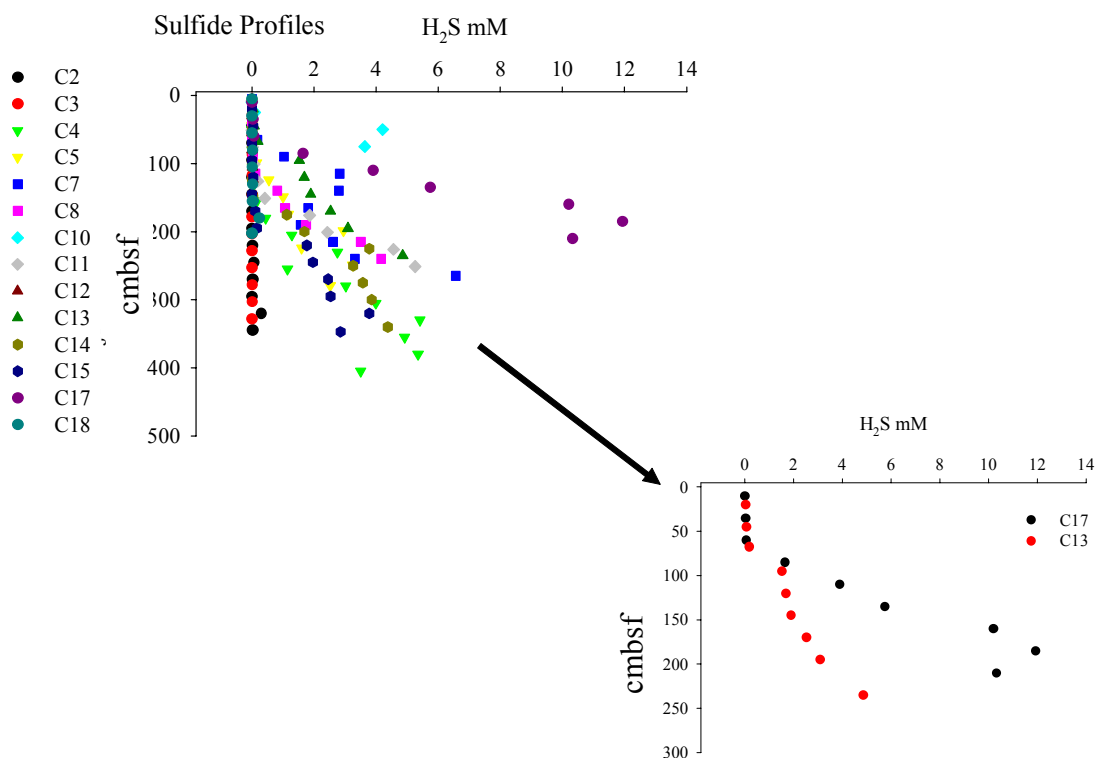


Figure 18: Porewater sulfide concentrations at piston core sites through Ridge I. Total data are presented and a comparison of cores 13 and 17 is included for additional data interpretation.

Porewater Sulfate Methane Interface

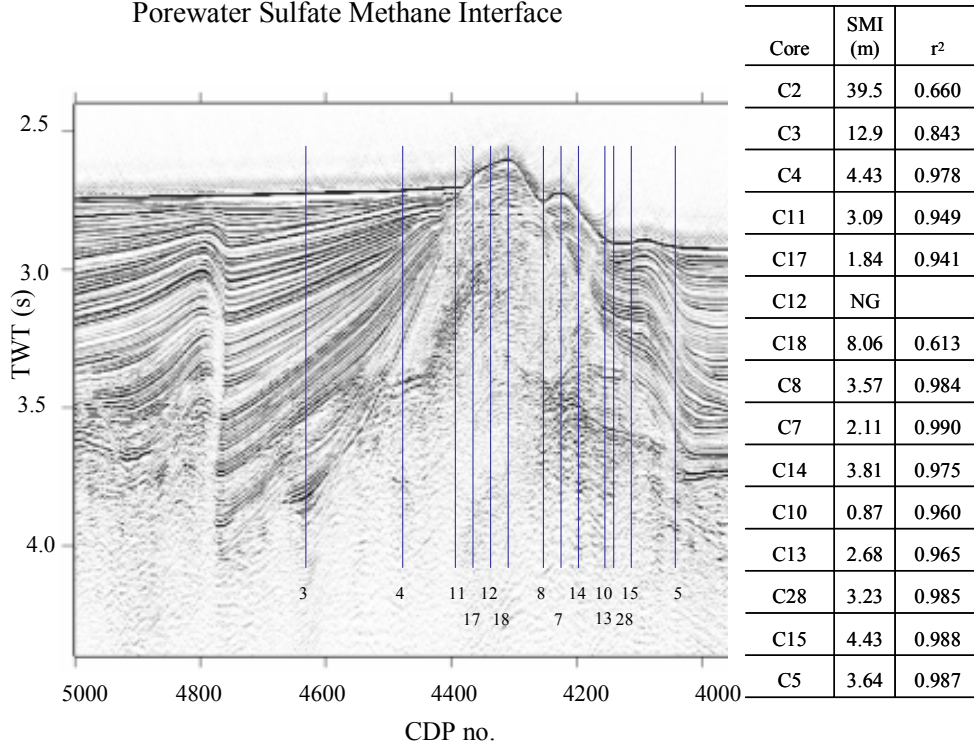


Figure 19: SMI calculated for porewaters from piston cores at sites across Ridge I. CDP was spacing at 12.5 m.

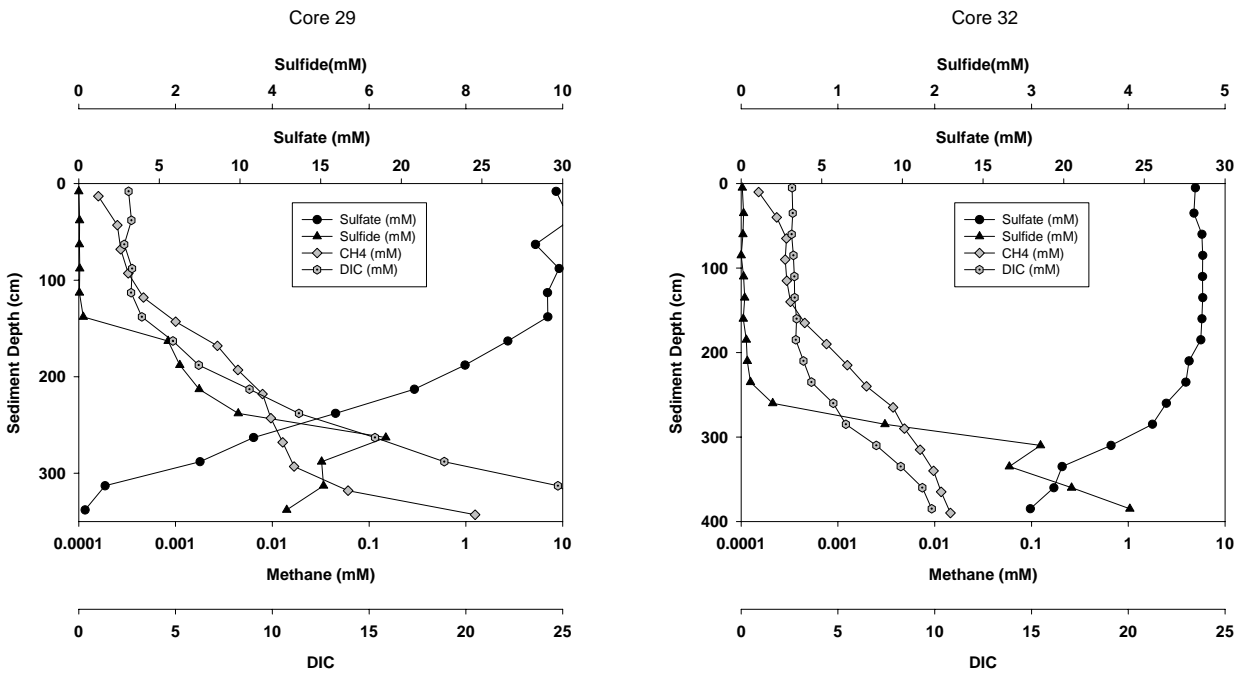


Figure 20: Porewater geochemical profiles selected from locations on the seaward (Core 32) and landward (Core 29) side of the Ridge I mound.

SMI measured across the Ridge I seismic profile is presented in Figure 19. The deepest measured SMI was at the nearshore control region at 39.5 m (Figure 13). On the landward side of the Ridge I transect the deepest SMI was 12.9 m. Moving toward the slope of the mound the SMI, resulting from a steep sulfate gradient,

was 1.84 m in Core 17. A similar SMI, 2.11 m, was measured on the seaward side of the mound at Core 7. Geochemical porewater profiles did not provide a sulfate gradient on top of the mound (C12).

Another transect was taken on a parallel seismic survey along Ridge I (Figure 2). Time allowed for 4 cores to be taken in this region.



The slopes of the sulfate, H<sub>2</sub>S, CH<sub>4</sub> and DIC profiles were considerably steeper on the landward side of this coring transect (Figure 20). These data were similar in the spatial variation in comparison to the primary Ridge I data base. The SMI measured through this location ranged from 3.34 to 9.45 m below the seafloor (Figure 21). Similar to the previous coring line the SMI was shallow on the landward side and deeper SMIs were measured on the seaward side of the mound. The porewater H<sub>2</sub>S concentrations were also greater on the landward side, as observed along the primary geochemistry transect.

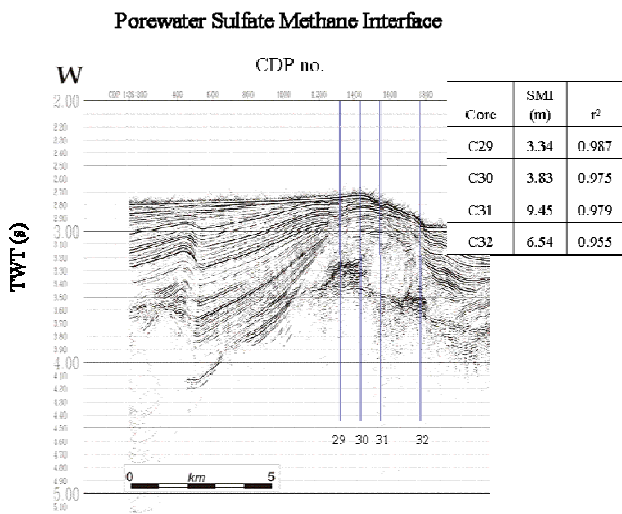


Figure 21: Overview of coring locations and SMI measured close and parallel to the primary coring on the Ridge I seismic profile.

### C. Rock Garden

Preliminary coring was conducted on the landward and seaward edges of a mound located in Rock Garden (Figure 22). Porewater sulfate, methane, DIC and sulfide concentration profiles were similar to values measured along the Ridge (Appendix I). The SMI estimated for Cores 22 and 24 was 341 cm and 398 cm, respectively (Figure 23). Future fieldwork will provide time for further investigation of this area.

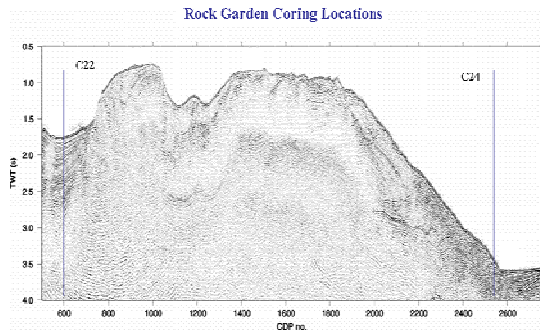


Figure 22: Seismic profiles and piston core locations on Rock Garden

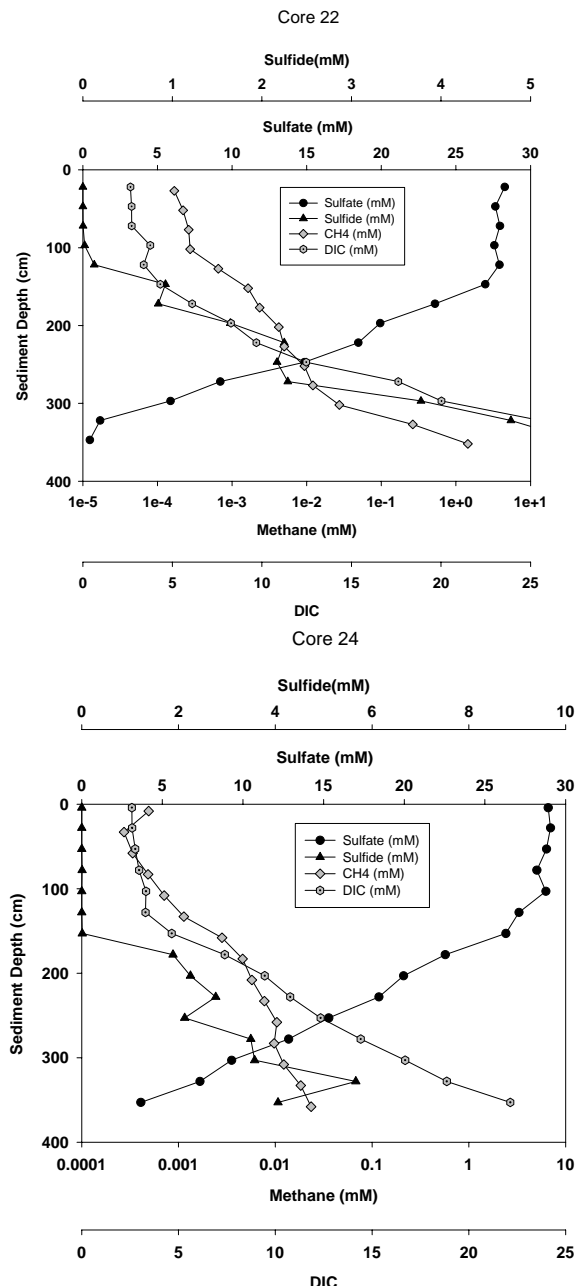


Figure 23: Porewater geochemical profiles for cores taken on the seismic line across Rock Garden.

## VII. PRELIMINARY HEATFLOW RESULTS

### A. Background

The thermometry program on NZ06 was designed to transect a fold of accreted sediments on the Hikurangi Margin (Figures 1 & 2). Reflection seismic profiles of this particular fold exhibit a bottom simulating reflector (BSR) indicative of methane hydrate, and show relatively undeformed slope fill sediments on both the landward and seaward side of the NE-SW trending fold, which is largely opaque seismically. Numerous faults and gas wipeouts exhibited in the seismic profiles, together with the BSR, suggest significant fluid flux at this location on the Margin, and it is this presumed flux (and the resulting thermal anomaly) that was the target of investigation along the two, parallel thermometry dip transects across the fold.

### B. Operations

The thermometry data were acquired with a violin-bow type instrument rented from the Canadian Geological Survey (PGC) and operated under contract by Robert MacDonald. The probe contains eleven independent seafloor thermistors, and one water thermistor at the top of the case yielding twelve independent temperature measurements from 0 to 3.3 meters below the seafloor.

The data were acquired in five deployments (stations) varying from two to eleven penetrations per station. A total of forty penetrations were acquired, of which two (HF38, and HF39) were discarded due to excessive tilt. For each penetration the thermal probe was inserted into the sediments for 7 minutes after which a heat pulse was triggered. Extraction occurred five to seven minutes after the heat pulse to allow sufficient decay to calculate thermal conductivity and subsequently the total heat flux. The final calculations for thermal conductivity and heat flow will be done on shore, but preliminary calculations of the steady-state temperature were performed via a method described below. It is these preliminary temperatures that are displayed in the figures in this report (Figures 24 & 25). Each penetration is named uniquely, with the designation HF

followed by a sequential number, such that the penetrations are labeled HF01-HF40.

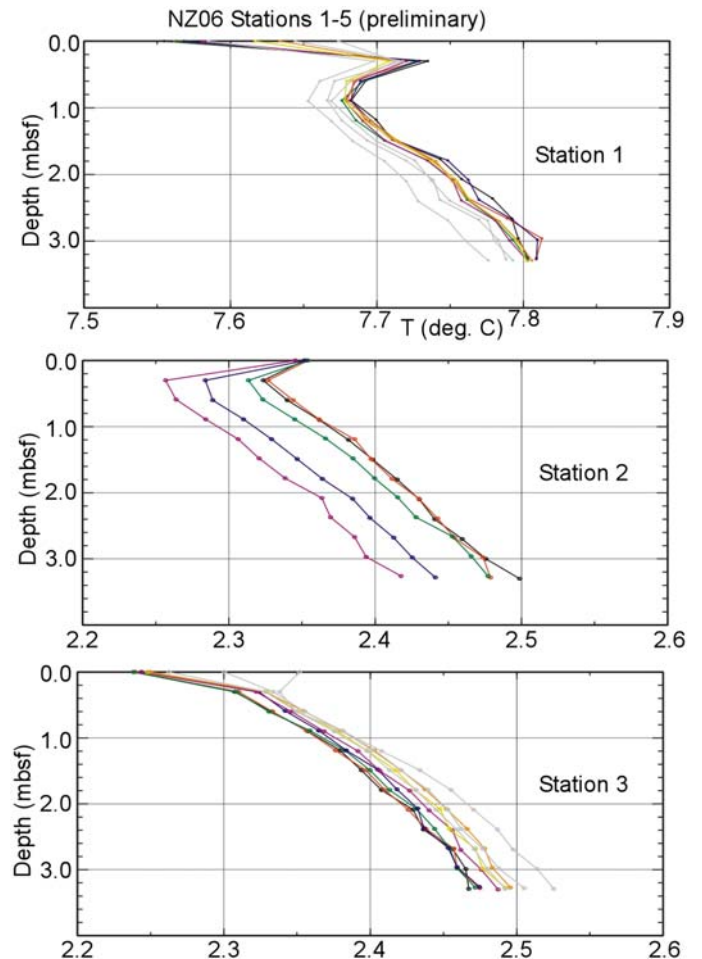


Figure 24: Heatflow profiles measured at the control site, seaward and landward of the mound.

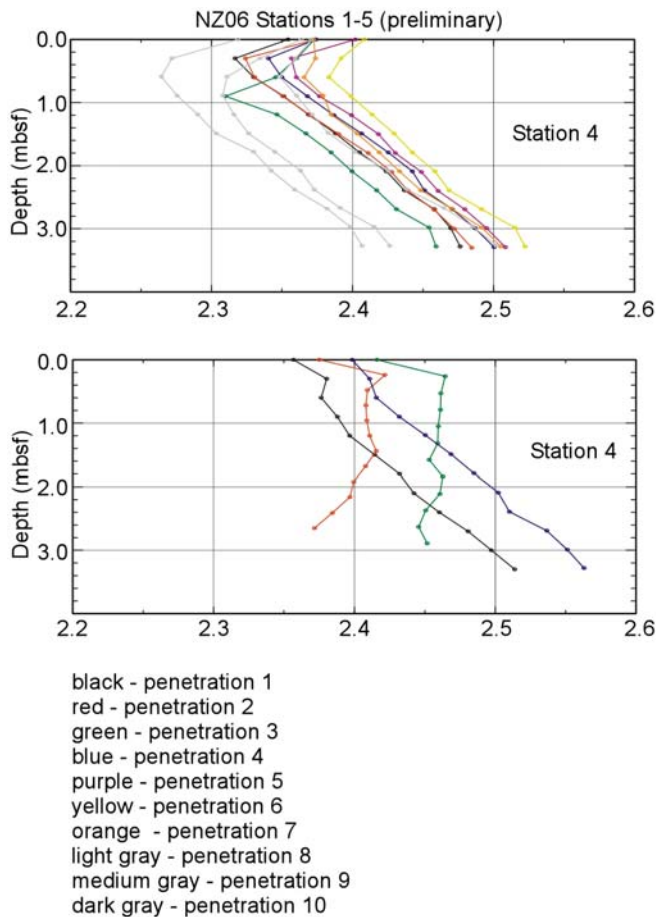


Figure 25: Heatflow profiles measured across the seismic profile located 2 km north of the primary seismic line.

### C. Acquisition

Station 1 was used to test ship board deployment, and instrument operation, as well as to serve as a background site to determine the no-flux thermal gradient in this region. Temperatures are rather high in this region (about 7 Deg. C) due to the shallow location (721 meters).

Station 2 (penetrations 1-5, HF11-HF15), Station 3 (penetrations 1-10, HF16-HF25), and Station 5 (penetrations 1-4, HF37-HF40) were all acquired along TAN0607 Seismic Line 2 (See Figure 26).

Station 4 (penetrations 1-11, HF26-HF36) was acquired along TAN0607 Seismic Line 3 (See Figure 27). Aside from the two discarded profiles the thermal data are remarkably consistent between neighboring sites, suggesting that; 1) the profiles are adequately spatially sampled, i.e. the major character of the thermal regime is likely to have been captured in our

measurements, and 2) the data were properly acquired, with small random errors.

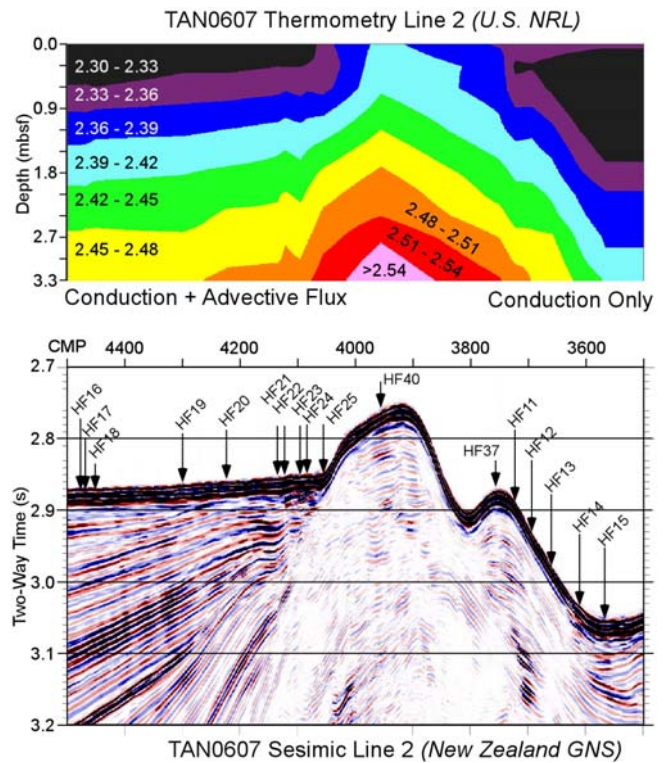


Figure 26: Heatflow data interpretation across TAN0607 seismic line 2.

### D. Preliminary Processing

The initial processing was performed using the software supplied with the thermal probe, such that data were reduced into \*.pen files. The software used to analyze the \*.pen files for steady state temperature and thermal conductivity was not provided so preliminary estimates were based on fitting the decay curves in each of the \*.pen files with curves of the form;

$$(T-T_o)/(T_h - T_o) = \frac{1}{2} \{ \text{erf}[(r+w)/(2\sqrt{kt})] - \text{erf}[(r-w)/(2\sqrt{kt})] \} \{ \text{erf}[w/(2\sqrt{kt})] \}$$

where T is the temperature at any given time (t) and radius (r) from a cylindrical rod of diameter (w) in a homogeneous medium with a thermal conductivity (k). T<sub>h</sub> and T<sub>o</sub> are the high and final, steady state temperature respectively. A fit of this equation to the observed curve was made by minimizing the difference between the observed thermal decay and the curve above computed for various selections of k, T<sub>h</sub> and T<sub>o</sub> (assuming w=1.0 cm, and r=0). The selections were guided



by a simulated annealing process in which many tens of thousands of parameters could be tried and only the best selected as the best fit, (Figure 28). The resulting steady state temperature  $T_0$  was used in the temperature plots in this report. All the data files, as well as the programs used to process them are included on the disk with this report. Shore based processing with standard thermal processing software is anticipated.

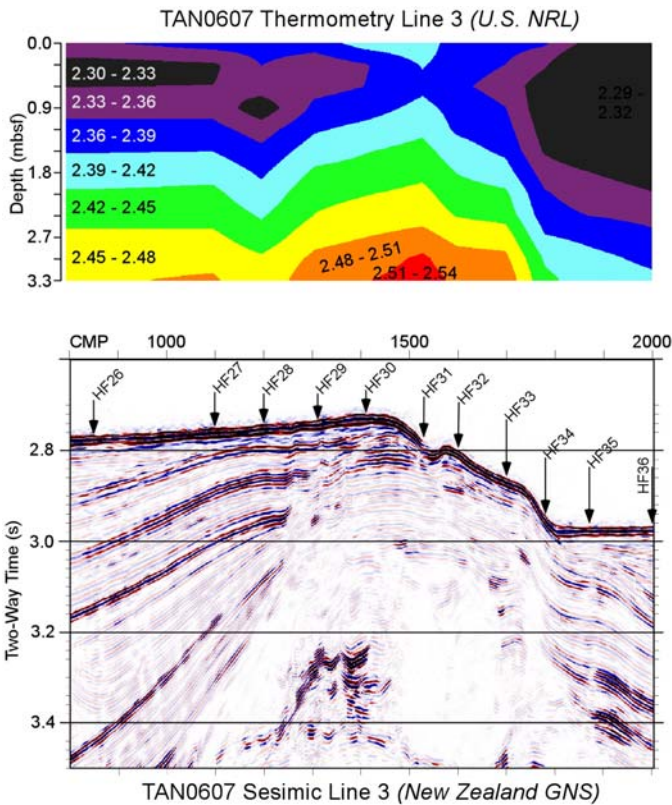


Figure 27: Heatflow data interpretation across TAN0607 seismic line 3

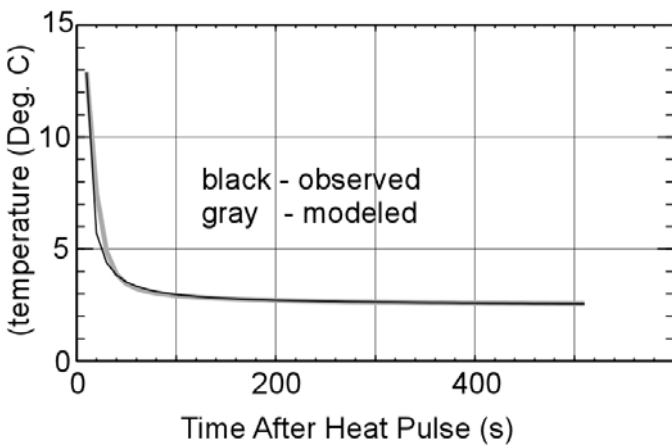


Figure 28: Modeling and data collection comparison of heatflow temperature pulses

## E. Preliminary Interpretation

Figures 26 and 27 clearly show a major thermal perturbation associated with the accretionary margin fold. However, unlike a single seafloor seep, there does not appear to be significant flux associated with the fold itself. Most of the thermal profiles exhibit linear character (Figures 24 & 25) suggesting minimal if any fluid advection. The exception is the profiles on the landward side of the ridge on Line 2, (Figure 24) whose concave downward character is indicative of fluid advection.

The second obvious feature of the thermal profiles is the presence of a laterally extensive cool zone in the regions dominated by conduction (all of Line 3 and the seaward portion of Line 2). The cause for this is unknown, but it is unlikely an artifact of processing, as it is not present in all the data. Quantitative estimates of fluid flux await final processing of the data to obtain values of thermal conductivity and heat flux.

## VIII. PRELIMINARY MOLECULAR BIOLOGICAL RESULTS

NRL cores 4, 7, 28 and 32 from Ridge I and core 22 from Rock Garden were selected for molecular biological analysis based upon the sediment and porewater geochemical characteristics. The SMI depth was specifically targeted for molecular biological analysis. This limited core selection to locations where the SMI was shallow enough such that the core barrel was able to penetrate the SMI. SMI depths for Ridge I cores are provided in Figure 19. The SMI depth for core 22 was 3.41m which was nearly at the bottom of the core. With respect to methane concentrations, cores 4, 7 and 28 were active flux cores whereas cores 22 and 32 represented control cores where methane flux was significantly reduced.

DNA was purified and extracted from 68 samples upon return to the NRL laboratory. Extracted DNA was sufficiently low in concentration such that it could not be visualized on an agarose gel prior to amplification. Initial attempts to amplify genomic DNA failed to yield



During a previous study, we identified a single amplicon length, 358.0 which dominated SMI community profiles in several cores over a methane seep and one over a hydrate mound. This amplicon was seldom detected in the data set for this study. However a large peak corresponding to this amplicon was detected in sample 30 from the SMI in NRL core 4.

Likewise, this amplicon was the largest peak detected in sample 59 which corresponds to the SMI sample from NRL core 7 (Figure 30). This peak accounts for approximately 47% of peak area for this core indicating that the phylotype corresponding to this single amplicon nearly accounts for the majority of bacterial diversity. Based upon our previous investigation it is likely that the phylotype associated with this amplicon corresponds to a relative of the *Desulfosaccinia variabilis* subgroup of sulfate reducing bacteria which have been documented to be key players in the anaerobic oxidation of methane at the SMI in numerous locations around the world (Hamdan et al. in prep and references therein). These data indicate that the LH-PCR analysis is a highly reliable tool for pinpointing the exact location of the SMI and potentially the location where anaerobic oxidation of methane is primarily occurring.

The phylogenetic analysis will proceed with the cloning and sequencing of SMI samples as

well as selected samples from above and below the SMI in cores with elevated methane flux and control cores which do not contain significant methane concentrations and will be reported later.

## IX. SUMMARY

This project is intended as a preliminary survey that will be expanded for future fieldwork. Data from this cruise will be combined for peer reviewed publications on seismic data application and interpretation. The seismic data will be combined with vertical fluid migration and geochemical analyses of porewater. Other manuscripts will address geochemical parameters that influence variations in the microbial community diversity and the flux and cycling of sediment methane into the water column. This review of the total data set will assist in planning future international research expeditions at this study site and nearby sites in the Hikurangi Margin. Future exploration will be open to expand international collaborations. For additional information on status and progress of this project contact Richard Coffin ([richard.coffin@nrl.navy.mil](mailto:richard.coffin@nrl.navy.mil)) or Ingo Pecher ([Ingo.Pecher@pet.hw.ac.uk](mailto:Ingo.Pecher@pet.hw.ac.uk)).

## X. REFERENCES

- Borowski, W. S., C. K. Paull, and W. Ussler III. 1999. Global and local variations of interstitial sulfate gradients in the deep-water, continental margin sediments: Sensitivity to underlying methane and gas hydrates. *Mar. Geol.* 159:131-154.
- Cline, J. D. 1969. Spectrophotometric Determination of Hydrogen Sulfide in Natural Waters. Pp. 454-458, *Limnology and Oceanography*.
- Crutchley, G.J., I.A. Pecher, S.A. Henrys, and A.R. Gorman, Gas hydrate "sweet spots" on the Hikurangi margin, from recently acquired multi-channel seismic data, in *Proc. New Zealand Petrol. Conf.*, pp. 7, Auckland, 2006.
- Katz, H.R., Probable gas hydrate in continental slope east of the North Island, New Zealand, *J. Petrol. Geol.*, 3, 315-324, 1981.
- Lewis, K.B., and B.A. Marshall, Seep faunas and other indicators of methane-rich dewatering on New Zealand convergent margins, *N. Z. J. Geol. Geophys.*, 39, 181-200, 1996.
- Pecher, I.A., and S.A. Henrys, Potential gas reserves in gas hydrate sweet spots on the Hikurangi Margin, New Zealand, pp. 32, Institute of Geological and Nuclear Sciences, Lower Hutt, 2003.
- Pecher, I.A., S.A. Henrys, S. Ellis, S.M. Chiswell, and N. Kukowski, Erosion of the seafloor at the top of the gas hydrate stability zone on the Hikurangi Margin, New Zealand, *Geophys. Res. Lett.*, 32, L24603, 2005.

APPENDIX I: Porewater data log.

Hikurangi Margin, TAN0706/NZ0606, June-July 2006  
Pore Water and Gas Data

Core	Pore Water Sed Depth (cm)	Chloride (mM)	Sulfate (mM)	Sulfide (mM)	DIC (mM)	Gas Sample Sediment Depth (cm)	CH <sub>4</sub> (mM)	C <sub>2</sub> H <sub>6</sub> (nM)	C <sub>1</sub> /C <sub>2</sub> (vol)	SMI (cm)
2	5					10	0.0003	bd		4987
2	45	543.2	27.59	0.00	2.20	50	0.0006	bd		
2	70	541.0	27.29	0.00	3.41	75	0.0006	bd		
2	95	540.8	27.45	0.00	3.52	100	0.0007	bd		
2	120	541.2	27.19	0.00	3.70	125	0.0008	bd		
2	145	538.4	27.13	0.00	3.80	150	0.0008	bd		
2	170	543.9	27.12	0.00	3.97	175	0.0009	bd		
2	195	545.2	27.08	0.00	3.99	200	0.0009	bd		
2	220	542.7	27.04	0.01	4.10	225	0.0011	bd		
2	245	560.8	27.67	0.05	4.14	250	0.0012	bd		
2	270	540.2	26.58	0.06	4.18	275	0.0010	bd		
2	295	541.4	26.11	0.00	4.28	300	0.0012	bd		
2	320	541.2	26.15	0.30	4.40	325	0.0014	bd		
2	345	548.3	25.98	0.06	4.56	350	0.0014	bd		
3	28	544.3	27.62	0.01	2.95	33	0.0001	bd		1287
3	57	544.7	27.41	0.01	3.34	63	0.0001	bd		
3	87	540.2	26.28	0.00	3.88	93	0.0002	bd		
3	117	537.8	25.93	0.01	4.27	123	0.0002	bd		
3	147	546.0	25.27	0.01	4.87	153	0.0002	bd		
3	178	540.8	24.74	0.00	5.24	183	0.0002	bd		
3	203	530.9	23.70	0.00	5.59	208	0.0003	bd		
3	228	532.6	22.87	0.00	6.02	233	0.0003	bd		
3	253	533.8	22.50	0.00	6.13	258	0.0003	bd		
3	278	548.7	22.45	0.00		283	0.0003	bd		
3	303	543.9	21.58	0.00	6.96	308	0.0003	bd		
3	328	558.1	23.97	0.00	6.69	333	0.0004	bd		
4	10	564.2	29.27	0.00	3.07	15	0.0002	bd		443
4	50	552.7	27.98	0.00	2.85	55	0.0006	bd		
4	80	544.8	27.35	0.00	3.12	85	0.0009	bd		
4	105	542.3	27.32	0.02	3.32	110	0.0012	bd		
4	130	539.7	27.15	0.07	3.43	135	0.0016	bd		
4	155	537.8	26.20	0.17	3.68	160	0.0021	bd		
4	180	560.7	26.18	0.43	4.24	185	0.0028	bd		
4	205	542.6	23.85	1.27	5.29	210	0.0043	bd		
4	230	548.8	22.09	2.74	6.53	235	0.0054	22.3	241	
4	255	549.2	19.44	1.14	7.94	260	0.0060	28.8	206	
4	280	549.6	17.05	3.01	9.29	285	0.0088	27.8	315	
4	305	543.7	14.18	3.97	10.83	310	0.0116	55.2	211	
4	330	544.2	11.06	5.39	12.76	335	0.0183	60.2	303	
4	355	558.2	9.21	4.90	13.64	360	0.0208	71.9	289	
4	380	542.6	4.54	5.33	16.83	385	0.0362	110.8	326	
4	405	538.0	1.59	3.49	19.68	410	0.1100	122.5	899	



Core	Pore Water Sed Depth (cm)	Chloride (mM)	Sulfate (mM)	Sulfide (mM)	DIC (mM)	Gas Sample Sediment Depth (cm)	CH <sub>4</sub> (mM)	C <sub>2</sub> H <sub>6</sub> (nM)	C <sub>1</sub> /C <sub>2</sub> (vol)	SMI (cm)
4	430	543.5	0.76	6.41	20.05	435	1.1409	134.1	8508	
4	455	546.1	0.38	4.17	19.61	460	2.4843	173.1	14354	
4	480	545.3	2.50	0.89	18.06	485	3.0913	130.1	23769	
5	9	546.8	28.68	0.00	2.73	14	0.0001	bd		364
5	44	544.4	27.65	0.00	3.21	49	0.0006	bd		
5	74	544.6	27.21	0.04	3.80	79	0.0011	bd		
5	99	537.4	25.66	0.15	5.21	104	0.0017	bd		
5	124	546.6	23.20	0.54	7.37	129	0.0028	bd		
5	149	540.6	20.93	1.00	8.89	154	0.0042	bd		
5	174	546.0	18.32	1.17	11.46	179	0.0052	bd		
5	199	538.0	15.11	2.93	13.07	204	0.0059	bd		
5	224	546.2	13.09	1.60	15.53	229	0.0069	bd		
5	249	532.9	9.87	3.23	17.99	254	0.0075	bd		
5	279	542.2	9.57	2.51	19.10	284	0.0094	bd		
7	5	551.0	28.75	0.00	2.52	10	0.0006	bd		211
7	40	546.5	28.33	0.00	2.86	45	0.0005	bd		
7	65	541.4	27.14	0.17	3.39	70	0.0017	bd		
7	90	540.2	22.34	1.03	5.85	95	0.0030	bd		
7	115	539.9	17.53	2.81	8.57	120	0.0051	83.5	60	
7	140	539.1	12.03	2.79	5.84	145	0.0076	115.9	66	
7	165	546.0	7.74	1.81	13.43	170	0.0128	142.7	90	
7	190	548.7	2.94	1.56	14.23	195	0.0283	189.3	150	
7	215	514.1	0.09	2.60	16.02	220	0.3245	184.2	1762	
7	240	540.5	0.06	3.31	17.43	245	1.3488	253.5	5320	
7	265	540.7	0.28	6.54	18.53	270	2.5198	299.6	8411	
8	10	537.9	27.24	0.00	2.53	20	0.0000	bd		357
8	40	541.7	27.65	0.00	2.64	45	0.0001	bd		
8	65	541.0	27.61	0.00	2.76	70	0.0002	bd		
8	90	539.8	27.48	0.02	3.04	95	0.0006	bd		
8	115	540.5	26.66	0.11	3.99	120	0.0015	bd		
8	140	521.9	22.98	0.81	6.06	145	0.0027	bd		
8	165	547.0	20.46	1.07	8.32	170	0.0045	bd		
8	190	547.5	17.57	1.74	10.50	195	0.0054	bd		
8	215	549.2	14.20	3.50	13.38	220	0.0081	bd		
8	240	540.8	13.23	4.16	16.80	245	0.0096	bd		
10	5	543.3	27.60	0.00	2.88	10	0.0005	bd		86.6
10	20	542.7	26.97	0.09	3.49	25	0.0020	bd		
10	45	555.4	14.20	4.21	12.01	50	0.0110	bd		
10	70	533.7	6.63	3.64	18.58	75	0.0329	bd		
10	95	547.1	8.21	4.65	18.54	100	0.2349	bd		
11	8	542.0	28.28	0.00	2.68	16	0.0001	bd		309
11	51	542.1	27.79	0.00	2.74	56	0.0003	bd		
11	76	548.7	28.22	0.02	3.07	81	0.0006	bd		
11	101	539.4	26.97	0.07	3.34	106	0.0010	bd		
11	126	539.8	25.81	0.19	4.32	131	0.0019	bd		
11	151	540.5	24.18	0.42	5.66	156	0.0032	bd		
11	176	540.4	20.19	1.86	8.39	181	0.0051	bd		
11	201	540.9	17.12	2.43	10.09	206	0.0067	bd		
11	226	537.2	12.48	4.56	13.58	231	0.0069	bd		

Core	Pore Water Sed Depth (cm)	Chloride (mM)	Sulfate (mM)	Sulfide (mM)	DIC (mM)	Gas Sample Sediment Depth (cm)	CH <sub>4</sub> (mM)	C <sub>2</sub> H <sub>6</sub> (nM)	C <sub>1</sub> /C <sub>2</sub> (vol)	SMI (cm)
11	251	539.7	6.47	5.26	18.10	256	0.0150	bd		
12	4	541.0	28.04	0.00	2.53	8	0.0011	bd		
12	23	538.6	27.65	0.00	2.67	28	0.0003	bd		
12	48	540.6	28.05	0.00	2.80	53	0.0002	bd		
12	73	541.8	28.34	0.00	2.80	78	0.0004	bd		
12	98	539.3	27.47	0.01	3.02	103	0.0005	bd		
12	123	544.7	28.47	0.03		128	0.0008	bd		
13	15	548.0	28.19	0.03	2.77	20	0.0006	bd		288
13	55	540.4	27.00	0.07	3.35	60	0.0017	bd		
13	80	543.6	26.52	0.18	4.02	85	0.0025	bd		
13	105	549.1	24.80	1.53	5.30	110	0.0038	bd		
13	130	548.4	22.05	1.69	7.08	135	0.0053	bd		
13	155	543.7	19.84	1.89	9.14	160	0.0068	bd		
13	180	542.5	14.20	2.53	12.39	185	0.0090	bd		
13	205	541.2	9.62	3.09	16.00	210	0.0135	bd		
13	230	543.9	4.63	4.86	19.16	235	0.0204	56.2	363	
14	6	547.3	28.68	0.01	2.59	12	0.0002	bd		381
14	47	546.2	28.34	0.01	2.66	52	0.0002	bd		
14	72	542.2	28.25	0.00	2.73	77	0.0002	bd		
14	97	550.7	28.44	0.00	2.82	102	0.0004	bd		
14	122	523.6	26.51	0.00	3.34	127	0.0011	bd		
14	147	552.3	26.94	0.04	4.33	152	0.0020	bd		
14	172	559.3	23.35	1.12	6.81	177	0.0029	bd		
14	197	549.1	21.25	1.69	10.35	202	0.0075	bd		
14	222	555.3	17.93	3.78	10.67	227	0.0124	bd		
14	247	547.8	14.97	3.25	12.92	252	0.0247	bd		
14	272	546.4	12.33	3.58	15.45	277	0.0319	bd		
14	297	542.3	8.29	3.86	18.09	302	0.0438	bd		
14	322	547.1	5.47	4.38	21.49	327	0.0735	bd		
15	7	544.4	28.84	0.00	2.40	14	0.0002	bd		443
15	34	529.8	27.06	0.04	2.64	39	0.0003	bd		
15	59	547.0	28.45	0.00	2.93	64	0.0005	bd		
15	84	546.0	27.93	0.00	3.09	89	0.0007	bd		
15	109	550.6	28.26	0.04		114	0.0010	bd		
15	134	548.5	27.89	0.01	3.65	139	0.0016	bd		
15	159	557.6	26.89	0.10	4.55	164	0.0027	bd		
15	184	549.8	24.69	0.16	5.86	189	0.0033	bd		
15	209	545.8	22.83	1.77	7.41	214	0.0045	bd		
15	234	553.2	20.98	1.97	9.35	239	0.0066	bd		
15	259	532.1	17.39	2.45	11.37	259	0.0094	bd		
15	284	541.3	14.89	2.53	13.91	284	0.0116	bd		
15	309	543.9	12.53	3.78	16.30	314	0.0139	bd		
15	334	559.1	9.83	2.85	18.30	339	0.0175	bd		
17	5.5	553.7	28.54	0.00	2.67	11	0.0003	bd		183
17	31	545.5	27.92	0.03	3.08	36	0.0009	bd		
17	56	548.9	28.55	0.06	3.02	61	0.0039	bd		
17	81	547.4	27.45	1.65	4.07	86	0.0046	bd		
17	106	543.8	23.14	3.90	6.49	111	0.0100	bd		
17	131	546.5	13.79	5.74	11.46	136	0.0281	339.3	83	

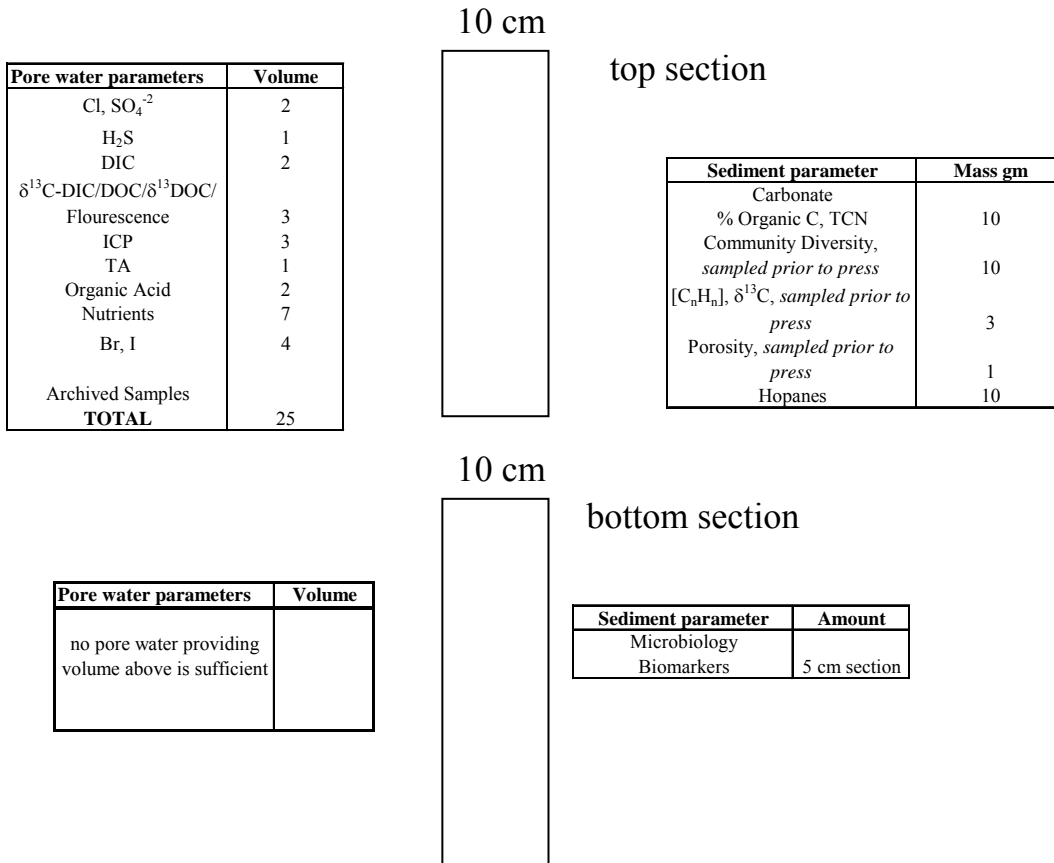
Core	Pore Water Sed Depth (cm)	Chloride (mM)	Sulfate (mM)	Sulfide (mM)	DIC (mM)	Gas Sample Sediment Depth (cm)	CH <sub>4</sub> (mM)	C <sub>2</sub> H <sub>6</sub> (nM)	C <sub>1</sub> /C <sub>2</sub> (vol)	SMI (cm)
17	156	543.8	3.92	10.20	17.65	161	0.3854	1640.9	235	
17	181	543.1	2.57	11.93	16.14	186	5.3071	4143.3	1281	
17	206	543.3	2.73	10.32	18.30	211	8.0925	5908.6	1370	
18	2.5	539.4	28.75	0.00	2.33	5	0.0003	bd		806
18	25	539.7	28.14	0.00	2.52	30	0.0002	bd		
18	50	543.8	28.22	0.00	2.47	55	0.0005	bd		
18	75	545.7	28.79	0.02	2.75	80	0.0005	bd		
18	100	541.6	28.45	0.01	3.12	105	0.0014	bd		
18	125	547.2	26.78	0.28	3.78	130	0.0028	bd		
18	150	549.9	26.90	0.24	4.66	155	0.0048	bd		
18	175	545.9	23.35	1.04	5.83	180	0.0073	bd		
18	200	cont w/sw								
22	22	541.2	28.27	0.00	2.66	27	0.0002	bd		341
22	47	538.7	27.64	0.00	2.73	52	0.0002	bd		
22	72	535.3	27.95	0.00	2.73	77	0.0003	bd		
22	97	535.6	27.58	0.02	3.77	102	0.0003	bd		
22	122	539.1	27.92	0.13	3.40	127	0.0007	bd		
22	147	539.2	26.97	0.92	4.33	152	0.0016	bd		
22	172	534.5	23.60	0.84	6.11	177	0.0023	bd		
22	197	522.4	19.93	1.65	8.28	202	0.0042	bd		
22	222	528.1	18.47	2.25	9.69	227	0.0050	bd		
22	247	535.8	14.85	2.17	12.48	252	0.0093	bd		
22	272	531.8	9.21	2.29	17.62	277	0.0122	bd		
22	297	539.0	5.88	3.78	20.03	302	0.0273	bd		
22	322	537.3	1.16	4.78	25.55	327	0.2642	37.2	7111	
22	347	518.8	0.47	5.50	26.53	352	1.4445	74.7	19346	
23	3	549.4	28.97	0.00	2.19	8	0.0003	bd		
23	13	539.9	28.29	0.00	2.27	18	0.0002	bd		
23	23	538.5	28.88	0.00	2.30	28	0.0002	bd		
23	43	544.5	28.16	0.00		48	0.0002	bd		
24	4	546.2	28.92	0.00	2.59	8	0.000	bd		398
24	28	547.6	29.07	0.00	2.60	33	0.000	bd		
24	53	550.9	28.82	0.00	2.77	58	0.000	bd		
24	78	551.8	28.21	0.01	2.97	83	0.000	bd		
24	103	556.4	28.78	0.00	3.32	108	0.001	bd		
24	128	551.9	27.11	0.00	3.30	133	0.001	bd		
24	153	562.8	26.29	0.01	4.65	158	0.003	bd		
24	178	555.2	22.54	1.89	7.39	183	0.005	bd		
24	203	554.4	19.95	2.25	9.46	208	0.006	bd		
24	228	562.2	18.43	2.77	10.77	233	0.008	bd		
24	253	552.9	15.32	2.13	12.34	258	0.010	bd		
24	278	554.7	12.83	3.50	14.42	283	0.0097	46.3	210	
24	303	559.6	9.30	3.58	16.71	308	0.0123	bd		
24	328	554.0	7.33	5.66	18.86	333	0.0184	69.2	265	
24	353	551.3	3.66	4.06	22.13	358	0.0235	bd		
28	7	547.0	29.23	0.00	2.87	12	0.000	bd		323
28	32	547.0	27.81	0.02	3.50	37	0.001	bd		
28	57	546.4	27.09	0.07	4.44	62	0.003	bd		

Core	Pore Water Sed Depth (cm)	Chloride (mM)	Sulfate (mM)	Sulfide (mM)	DIC (mM)	Gas Sample Sediment Depth (cm)	CH <sub>4</sub> (mM)	C <sub>2</sub> H <sub>6</sub> (nM)	C <sub>1</sub> /C <sub>2</sub> (vol)	SMI (cm)
28	82	547.3	25.92	0.16	6.47	87	0.003	bd		
28	107	553.5	24.95	0.14	7.28	112	0.005	bd		
28	132	540.7	23.88	0.80	7.22	137	0.006	bd		
28	157	548.1	19.48	1.45	11.56	162	0.007	bd		
28	182	545.5	17.03	0.84	13.29	187	0.011	bd		
28	207	545.8	14.18	1.41	15.30	212	0.013	bd		
28	232	545.4	10.77	1.29	19.18	237	0.022	bd		
28	257	546.5	8.67	2.81	21.00	262	0.034	bd		
28	282	530.6	4.21	4.30	24.93	287	0.084	bd		
28	307	552.2	1.00	3.01	29.67	312	0.208	bd		
29	8	546.6	29.59	0.00	2.58	13	0.0	bd		335
29	38	551.9	30.44	0.02	2.72	43	0.0	bd		
29	63	546.3	28.32	0.01	2.35	68	0.0	bd		
29	88	547.3	29.78	0.02	2.76	93	0.000	bd		
29	113	539.3	29.06	0.01	2.71	118	0.000	bd		
29	138	544.0	29.08	0.09	3.26	143	0.001	bd		
29	163	546.9	26.60	1.85	4.87	168	0.003	bd		
29	188	524.2	23.95	2.09	6.20	193	0.004	bd		
29	213	538.9	20.81	2.49	8.82	218	0.008	bd		
29	238	539.3	15.92	3.29	11.38	243	0.010	bd		
29	263	547.4	10.84	6.35	15.31	268	0.013	bd		
29	288	547.1	7.52	5.02	18.89	293	0.017	75.5	223	
29	313	520.6	1.63	5.06	24.76	318	0.061	110.9	548	
29	338	557.5	0.40	4.30	26.65	343	1.247	99.4	12547	
30	12	550.2	29.36	0.06	2.66	17	0.0	bd		383
30	42	545.3	29.28	0.05	2.73	47	0.0	bd		
30	72			0.05	2.71	77	0.0	bd		
30	97	542.3	28.81	0.04	2.82	102	0.0	bd		
30	122	546.6	28.82	0.04	2.93	127	0.0	bd		
30	147	545.4	28.59	0.11	3.26	152	0.0	bd		
30	172	544.8	27.15	0.23	4.07	177	0.0	bd		
30	197	541.8	25.22	0.25	5.16	202	0.0	bd		
30	222	544.2	22.87	0.46	6.59	227	0.0	bd		
30	247	547.6	19.65	3.13	9.19	252.00	0.01	bd		
30	272	537.4	16.39	3.29	11.41	277.00	0.01	bd		
30	297	543.6	11.90	4.94	15.08	302	0.0	95.5	115	
30	322	545.9	8.75	3.25	17.47	327	0.0	134.1	112	
30	347	547.3	2.27	2.89	23.41	352	0.1	179.4	453	
30	372	554.5	1.68	4.30	25.16	377	1.19355	210.652	5666	
31	10	541.5	28.35	0.01	2.68	15	0.0	bd		945
31	40	541.3	28.60	0.00	2.75	45	0.0	bd		
31	65	551.3	28.93	0.01	2.82	70	0.0	bd		
31	90	547.9	28.39	0.03	3.25	95	0.0	bd		
31	115	544.4	27.95	0.10	3.53	120	0.0	bd		
31	140	540.4	26.81	0.14	4.04	145	0.0	bd		
31	165	540.7	25.98	0.16	4.53	170	0.0	bd		
31	190	534.2	26.02	0.17	5.08	195.00	0.00	bd		
31	215	545.3	24.16	0.57	5.52	220.00	0.00	bd		
31	240			0.45	5.87	245	0.00471	bd		

Core	Pore Water Sed Depth (cm)	Chloride (mM)	Sulfate (mM)	Sulfide (mM)	DIC (mM)	Gas Sample Sediment Depth (cm)	CH <sub>4</sub> (mM)	C <sub>2</sub> H <sub>6</sub> (nM)	C <sub>1</sub> /C <sub>2</sub> (vol)	SMI (cm)
31	265	560.3	22.85	2.14	6.59	270	0.00627	bd		
31	290	544.3	21.57	2.59	8.14	295	0.0	bd		
32	5	544.7	28.16	0.01	2.63	10	0.0	bd		654
32	35	536.0	28.07	0.03	2.67	40	0.0	bd		
32	60	541.1	28.57	0.02	2.61	65	0.0	bd		
32	85	541.0	28.62	0.00	2.70	90	0.0	bd		
32	110	542.5	28.60	0.03	2.75	115	0.0	bd		
32	135	541.9	28.62	0.04	2.77	140	0.0	bd		
32	160	539.7	28.57	0.02	2.87	165	0.0	bd		
32	185	540.6	28.50	0.05	2.83	190	0.0	bd		
32	210	540.6	27.77	0.06	3.22	215	0.0	bd		
32	235	545.2	27.57	0.10	3.63	240	0.0	bd		
32	260	545.6	26.36	0.33	4.76	265	0.0	bd		
32	285	538.8	25.51	1.49	5.41	290.00	0.00	bd		
32	310	545.7	22.94	3.09	6.99	315.00	0.01	bd		
32	335	540.7	19.90	2.77	8.25	340	0.0	bd		
32	360	549.4	19.39	3.41	9.36	365	0.0	bd		
32	385	537.0	17.93	4.02	9.85	390	0.0	bd		

## Appendix II. Coring Notes

Core sample distributions were outlined for preliminary discussions on the sample processing.



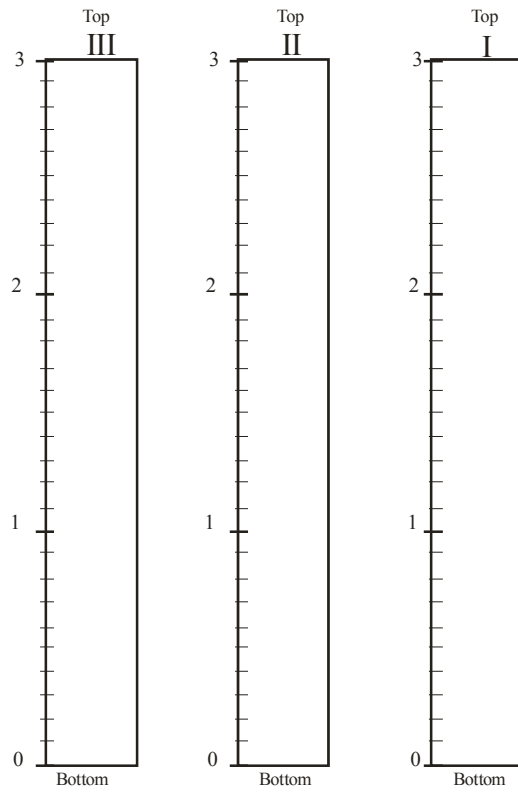
This figure represents one section of a core for the sample distribution

The preliminary core log sheet changes through the cruise according to core lengths.

Cruise \_\_\_\_\_  
Core ID \_\_\_\_\_  
Lat \_\_\_\_\_  
Long \_\_\_\_\_  
Date \_\_\_\_\_  
Time \_\_\_\_\_

Comments

Observer \_\_\_\_\_





### APPENDIX III CRUISE SCHEDULE

Times in hours, total maximum time available 12.5 days at sea = 300 hrs.

	Time	Total
<u>1. Transit Wellington/Study Area A:</u>		
To Waypoint cw-1		
~130 nm, + 1 h in port, 10 knots	14	14.0
<u>2. "Warm-up" core and CTD deployment</u>		
Study Area A, Objectives 2, 5, 7, Priority 1		
Approx. 600-800 m water depth		
3.5 kHz, 12 kHz, and multibeam Waypoints cw-1 – cw-2		
8.1 nm at 10 knots	0.8	
Back to cw-3	0.4	
CTD at Waypoint cw-3	1.5	
Change to coring	0.5	
Gravity/piston core Waypoint cw-3 or based on 3.5 kHz data	1.5	
Seismic survey starts close to cw-3		
(sub-total)	4.7	18.7
<u>3. Seismic survey A1</u>		
Study Area A, Objective 1, Priority 1		
45/105 cu-in GI gun, c. 25 m shot spacing, 0.5 msec sampling		
Source/streamer depth 5 m		
Also run 3.5 kHz, 12 kHz, and multibeam		
Deploy gear	4	
Survey Waypoints sa1-1 – sa1-8		
89 nm at 4.5 knots	19.8	
6 turns at 10 additional minutes	1	
Retrieve gear	1	
(sub-total)	25.8)	44.5
<u>4. Coring, heatflow, and CTD transect A1</u>		
Study Area A, Objectives 2-5 Priority 1		
Transect(s) between Waypoints ca1-1 and ca1-2		
~2000-2500 m water depth		
<i>Note: coring includes "failed" cores; heatflow and CTD numbers are essentially placeholders; coring will probably be broken up into at least 2-3 segments</i>		
Coring 11 Stations (3 hrs. each), 10 transits (0.5 hrs.)	38	
Heatflow 6 Stations (3 hrs. each), 5 transits (0.5 hrs.)	20.5	
CTD	8	
(sub-total)	66.5)	111.0
<u>5. Transit Study Area A / Temperature sensor</u>		
To Waypoint t_probe		
80 nm at 10 knots	8	119.0

6. Recover temperature sensor

Study Area B, Objective 6, Priority 1

Waypoint t\_probe, ~600 m water depth 2 121.0

7. Transit Paleo-core 1 stations

*Note: Location can change significantly*

To Waypoint cp1-1

7.9 nm at 10 knots 0.8 121.8

8. Paleo-core 1

*Note: Location can change significantly*

Study Area B, Objective 7, Priority 1

~800 m water depth

3.5 kHz, 12 kHz, and multibeam Waypoints cp1-1 – cp1-2

13.5 nm at 10 knots 1.4

Coring at Waypoint cp1-3 and/or additional based on 3.5 kHz

Coring 3 Stations (2 hrs. each) 2 transit (0.5 hrs) 7

(sub-total 8.4) 130.2

9. Transit to BOL of Seismic Survey B2

To Waypoint sb2-1

17.6 nm at 10 knots 1.8 132.0

10. Seismic survey B2

*Note: only if sufficient time to complete remaining*

*Priority 1 experiments (dredging+coring below)*

Study Area B, Objective 9, Priority 2

GNS' Mini-GI gun (chamber configuration tbd)

~25 m shot spacing, 0.5 msec sampling

Source/streamer depth ideally 2.5 m, but may need to be deeper unless seas are unusually calm...

Deploy gear 4

Survey Waypoints sb2-1 – sb2-19

84.0 nm at 4.5 knots 18.7

18 turns at 10 additional minutes 3

Retrieve gear 1

Dredging close to EOL

(sub-total 26.7) 158.7

11. Dredging and coring, Priority 1

*Note: Conducted before seismic survey above if time is tight*

Study Area B, Objective 8, Priority 1

Dredge at Waypoint db1 ~600 m water depth 3

Transit to core location cb1, 7.8 nm at 10 knots 0.8

Coring cb1 ~2700 m water depth 3

(sub-total 6.8) 165.5

(End of Priority 1—note: w/o Seismic Survey B2  
 Transit back to Wellington 21 138.8  
 -> 140.2 hours contingency -> 47% downtime) 159.8

12. Dredging and Coring Priority 2  
 Study Area B, Objective 8, Priority 2

Transit from Waypoint cb1 to db2, 11.32 nm at 10 knots 1.1  
 Dredge at Waypoint db2 ~600 m water depth 3  
 Transit to Waypoint cb2, 2.3 nm at 10 knots 0.2  
 Coring cb2 ~1400 m water depth 2  
 (sub-total 6.3) 171.8

13. Transit Study Area B

To Waypoint ca1-2  
 60 nm at 10 knots 6 177.8

14. Coring, heatflow, and CTD transect A2

Study Area A, Objectives 2-5 Priority 2  
 Locations tbd, likely transect(s) between Waypoints cw1 and ca1-2  
 ~500-2500 m water depth

*Note: 1. coring includes “failed” cores; heatflow and CTD numbers  
 are essentially placeholders; coring will probably be  
 broken up into at least 2-3 segments  
 2. Can be shortened to allow further Priority 2 work  
 3. Paleo-core 2 may be done this transect*

Coring 11 Stations (3 hrs. each), 10 transits (0.5 hrs.) 38  
 Heatflow 6 Stations (3 hrs. each), 5 transits (0.5 hrs.) 20.5  
 CTD 8  
 (sub-total 66.5) 244.3

15. Paleo-core 2

*Note: Location tbd  
 May be cored before Pore-water coring/heatflow transect*

Study Area A?, Objective 7, Priority 1  
 ~800 m water depth?  
 Transit to site (placeholder) 2  
 3.5 kHz, 12 kHz, and multibeam 1.5  
 Coring 3 Stations (2 hrs. each) 2 transit (0.5 hrs) 7  
 (sub-total 10.5) 254.6  
 (End of Priority 2 — use of any remaining time tbd,  
 likely in Study Area A)

1. Transit Study Area A/Wellington

(see 1) 14 268.6

-> 31.4 hrs for 300 contingency (10.5%)

## **Appendix IV. On Board Instrumentation.**

### NIWA/Vessel:

- SIMRAD EM 300 multibeam echosounder
- SIMRAD EA 500 echosounder (12 kHz, 38, 120 kHz), logging software by GNS, see below)
- SIMRAD EA 60 echosounder (on bridge)
- Knudsen 3.5 kHz subbottom profiler
- Standard piston/drop corer
- Multi-channel seismic system, GI gun (total 210 cu-in, preferred configuration 45/105 cu-in in GI mode), Hydrosience oil-filled streamer (500m, 6.25 m hydrophone spacing, 12.5 m group spacing), Geometrics recoder (preferred 0.5 msec sampling rate)
- CTD system
- Laboratory containers (2) 20-ft

### GNS

- GNS dredge (stored at NIWA)
- GNS mini-GI gun with spares (chamber configuration tbd)
- Gas chromatography for CH<sub>4</sub> analyses (including H-generator and laptop for data recording)
- Wet geochemical equipment for nutrients (including photometer, titrator unite, lab ware)
- Linux PC's for data logging and processing including Claritas seismic software (GNS private network)
- Plotter (GNS network)
- Windows PC for logging EK500 data with Echoview (ship's network)

### NRL/U Hawaii/U of Rochester

- Heatflow probe
- GC for CH<sub>4</sub> to C<sub>3</sub>H<sub>8</sub>
- Pore water press
- Ion chromatography for pore water analyses (including lab ware)
- Equipment for microbiological sampling
- Fluorometer for sulfide
- Coulometer for dissolved inorganic carbon
- Deck and lab tools

### Otago

- Linux laptops for data logging and processing (to hook into GNS network)

## APPENDIX V ON BOARD RESEARCH TEAM BREAKOUT

### *NRL coring/heatflow team:*

PI: Coffin

Scientists: Wood, Hamdan, Pohlman, Smith, Dale, MacDonald, Downer,  
Bryant, Kurasaki, Yoza

### *GNS coring:*

PI: Greinert

Scientists: Schinteie, Tomaru, (+Faure, Kurazaki, Yoza, Kukowski,  
if available)

### *Seismic and 3.5 kHz:*

(in addition to operation conducted by NIWA personnel)

PI: Gorman

Scientists Crutchley, Senger, Kilner, Fohrmann, (+Wood, Pecher, Henrys,  
if available)

*(beyond here, very flexible)*

### *GNS water-column chemistry (CTD):*

PI: Faure

Scientists: (Greinert, if available)

### *Paleo-coring:*

PI: Orpin

Scientists: tbd (+Schinteie, Kurazaki, Yoza, Tomaru, Kukowski, if available)

### *12 kHz:*

(in addition to operation conducted by NIWA personnel)

PI: Greinert

Scientists: tbd, if needed

### *Multibeam:*

(in addition to operation conducted by NIWA personnel)

PI: Kukowski

Scientists: tbd, if needed (+Orpin, if available)

# Appendix VI. NIWA Data Log Sheet

## STATION RECORD (2003 EDITION)



Trip code  
 Vessel Year No Station Number  
 TAN 06 07 0101

RECORDER: \_\_\_\_\_

**S T A T**

User categories	Area	Station code	Stratum/ Transect code	Course

Day	Month	Year	Time (NZST)	Method of fix	Time since fix	Latitude	N/S	Longitude	EW	Depth of gear	Bottom at gear	Depth at vessel
							S					
							S					

Minimum depth of gear	Maximum depth of gear	Gear method	Gear code	No of units	Performance	Speed	Distance	Headline Ht	Code	Distance between wings	Code	Distance Between doors	Code	Length of warp	Fish at net mouth

Wind direction	Wind force	Air temperature	Air pressure	Cloud cover	Sea cond	Swell Ht	Swell dir	Bottom type	Surface temp	Bottom temp	Wind speed	Secchi	Other

**ENVIRONMENT**

Station Number  
**S C O M**

**STATION COMMENTS**  
 continue to separate sheet if necessary

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_