

## Methane seepage along the Hikurangi Margin of New Zealand: Geochemical and physical data from the water column, sea surface and atmosphere

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### ABSTRACT

The concentration and carbon isotope values of dissolved methane were measured in the water column at Rock Garden, Omakere Ridge and Wairarapa areas in the first dedicated cold seep investigation along the Hikurangi Margin of New Zealand. These measurements provide a high resolution impression of the methane distribution in the water column and show that these seep sites are actively venting methane with varying intensity. The highest concentrations (up to 3500 nM) measured in water samples obtained from Conductivity–Temperature–Depth (CTD) operations were at Faure Site of Rock Garden. Here, seafloor bubble release was observed by ROV. The Omakere Ridge area is actively venting over almost its entire length (~25 km), in particular at Bear's Paw, a newly discovered seep site. In the Wairarapa area another new seep site called Tui was discovered, where methane measurements often exceeded 500 nM. No evidence was obtained from water column or sea surface measurements along the Hikurangi Margin to indicate that methane from seeps is reaching the sea surface. In fact, a consistent upper boundary was observed at a density of 26.85 kg/m<sup>3</sup>, which occurs at about 500 m below sea surface, above which methane decreased to background concentrations. No obvious oceanographic feature is associated with this 500 m CH<sub>4</sub> boundary. Bubble dissolution calculations show that about 500 m was also the model-derived maximum bubble rise height. A wide range of  $\delta^{13}\text{C}_{\text{CH}_4}$  values from –71 to –19‰ (VPDB) were measured, with the highest CH<sub>4</sub> concentrations having the lowest  $\delta^{13}\text{C}_{\text{CH}_4}$  values of about –71 to –68‰. Simple mixing and isotope fractionation calculations show that changes of  $\delta^{13}\text{C}_{\text{CH}_4}$  values are predominantly caused by the dilution of seep fluids with the seawater, with some anaerobic oxidation also occurring.

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### 1. Introduction

There is general consensus that methane hydrates represent a significant methane reservoir (Milkov, 2004; Kvenvolden, 1988). Methane hydrates and hydrocarbon seepages (cold seeps) found at the world's continental margins (Judd and Hovland, 2007) have therefore drawn considerable attention because of their potential contribution to atmospheric methane levels (Judd, 2004; Kvenvolden and Rogers, 2005). However, quantitative seepage estimates are rare because submarine sources are difficult to find. Ongoing research at

the continental slope off New Zealand enables us to better estimate the impact and distribution of CH<sub>4</sub> from seeps on oceanic and atmospheric CH<sub>4</sub> budgets.

Marine geophysical studies along the Hikurangi Margin have been ongoing since the 1970's, but have mainly focussed on regional tectonic features associated with the Pacific–Australian subduction plate boundary (Barnes et al., 2010–this issue and references therein). These studies have shown that wide-spread, bottom simulating reflectors (BSR), as indicators of free gas below gas hydrate cemented sediment horizons, are widespread along the Hikurangi Margin and that they are a potential target for gas hydrate exploration (Katz, 1982; Townend 1997; Henrys et al., 2003). The first indication of active fluid seepage of CH<sub>4</sub> and H<sub>2</sub>S-rich fluids from an area called Rock Garden was made in 1994 by fishermen who obtained live specimens of mussels of the genus *Bathymodiolus* that are associated worldwide with CH<sub>4</sub> vents and seeps at depths from 400 to 3600 m (Lewis and Marshall, 1996; Von Cosel, 2002). Fishermen were also the first to observe hydroacoustic evidence for gas bubbles in the water

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column (Lewis and Marshall, 1996), which has been confirmed by subsequent studies (Greinert et al., 2010–this issue; Naudts et al., 2010–this issue; Klaucke et al., 2010–this issue; Linke et al., 2010–this issue). Subsequent dredge sampling of the LM-3 site at Rock Garden confirmed seep fauna and flares rising 250 m above the seabed (Lewis and Marshall, 1996). Lewis and Marshall (1996) reported a total of four seep-related sites (LM-1, LM-3, LM-9, LM-10; Fig. 1) along the Hikurangi Margin.

With respect to seepage, methane distribution and related water column studies, Faure et al. (2006), published results of a 24 hour survey of Rock Garden area in 2004 that included the Lewis and Marshall LM-3 site (Fig. 1). At Rock Garden, elevated concentrations of methane (up to 10 nM, ~6 times background) were detected by onboard GC-based analyses and methane sensor (METS) measurements. The location of these higher concentrations is close to an area where a bottom simulating reflector (BSR) pinches out at the seafloor (~630 meters below sea level – mbsl).

Here, results of two surveys are presented (RV TANGAROA in 2006 and RV SONNE in 2007) that were dedicated to exploring the seep sites along the Hikurangi Margin. The water column studies described here concentrated on three different seep areas (Rock Garden, Omakere Ridge, Wairarapa; Fig. 1). The regional geological setting of

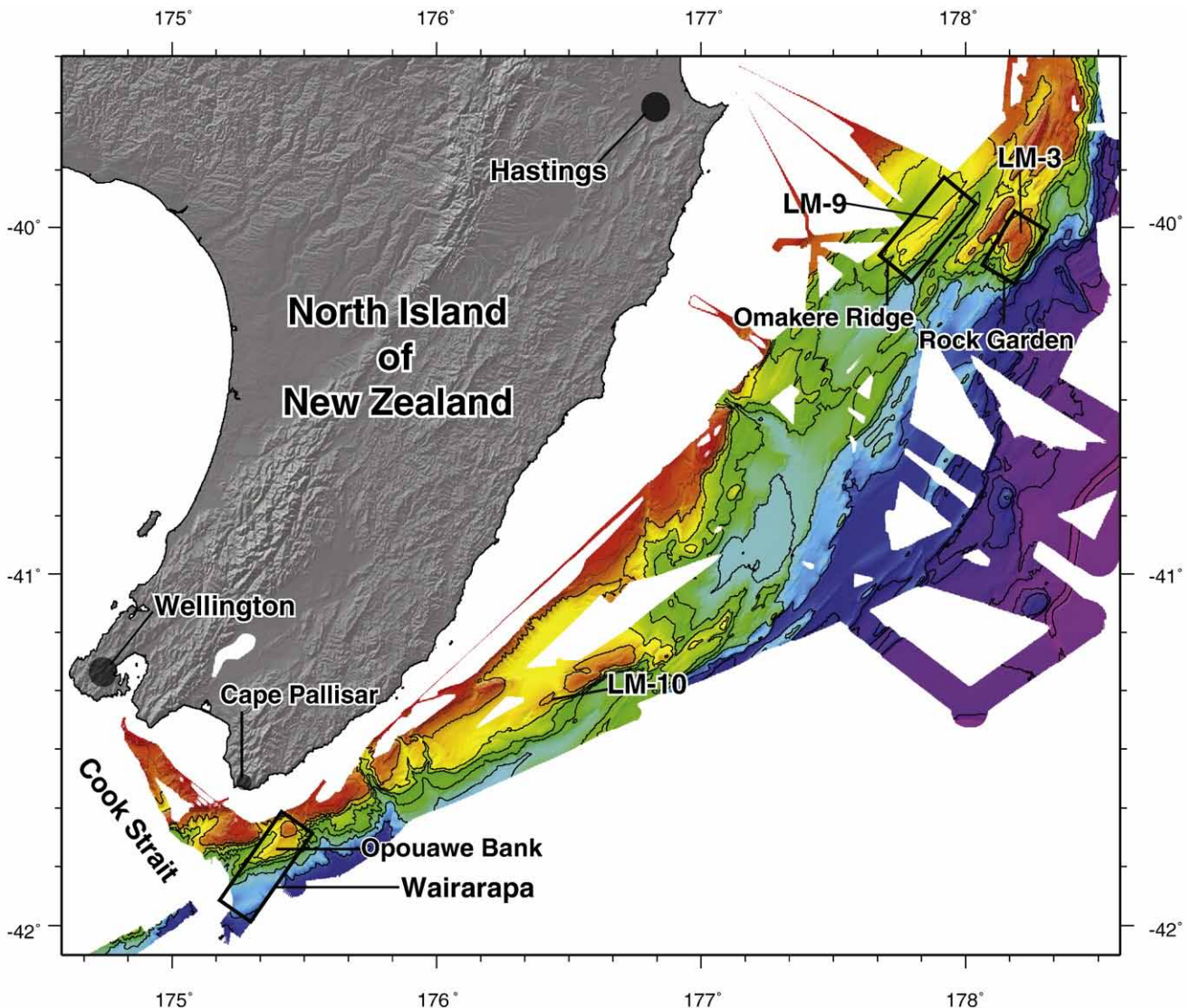
the Hikurangi Margin is described in Barnes et al. (2010–this issue). A general overview of these cruises and, e.g., naming of seep sites, is given in Greinert et al. (2010–this issue).

## 2. Methods

### 2.1. Sample collection

Gas chromatograph (GC) based methane analyses, CTD casts, GC–mass spectrometer isotope measurements and ADCP-based current measurements were employed for this study. Physical parameters such as temperature and conductivity, as well as CH<sub>4</sub> data, measured by a METS sensor (formerly by CAPSUM, now Franatech GmbH, Lüneburg, Germany), were collected during CTD casts using a Seabird 911 plus system.

The CTD was deployed in two ways, as vertical casts and in short towed casts close to the seafloor. Tow casts are shown on the bathymetric maps with an additional letter added to CTD station numbers (e.g., CTD42a, 42b, etc. see Appendix Fig. 1). The positions indicate where the NISKIN bottles were closed. The underwater position of the CTD during the towed casts was determined by an IXSEA Posidonia (2nd Leg) and GAPS system (3rd Leg).



**Fig. 1.** Bathymetric map of the Hikurangi Margin showing the three study areas, Rock Garden, Omakere Ridge and Wairarapa. Also shown are the locations of the seep sites (named LM) reported by Lewis and Marshall (1996). LM-1 is not shown, because it is outside the area depicted here.

Water samples were collected during CTD casts using twenty four 12 l Niskin bottles. Sampling depths were determined by monitoring the voltage signal of a METS sensor as an indication of CH<sub>4</sub> concentration on the downcast and adjusting the water sampling interval on the upcast based on the sensor's response. The METS used in this study was very sensitive to change in CH<sub>4</sub> concentration and had an exceptionally quick response time of 2–5 s, which enabled us to focus on sampling the areas of high interest and to differentiate thin layers (~10 m thick) of variable methane concentrations. Appendix Fig. 2 demonstrates the change in METS voltage (during down-cast) and the measured CH<sub>4</sub> concentration of samples collected in the up-cast.

## 2.2. Methane measurement of water samples

The concentration of dissolved CH<sub>4</sub> was measured using a modified, helium stripping method described in Faure et al. (2006) on all the cruises discussed in this work. A few (5) selected samples with high CH<sub>4</sub> concentration were re-analysed for dissolved methane, ethane, propane, n-butane, n-pentane and n-hexane concentration. Calibration was done using various concentrations (0.05–20 ppm) of a 100 ppm each Scott Specialty Gases standard mixture (methane to hexane) and He as diluent. Extraction efficiency of the gases were all assumed to be 88% for a 100:40 H<sub>2</sub>O:He mixture as was determined for CH<sub>4</sub> (Faure et al., 2006). During SO191 an additional system using vacuum extraction (Lammers and Suess, 1994; Rehder et al., 1999; Keir et al., 2009) was used mainly to extract gas for later isotopic analyses, but also to measure the concentration of dissolved CH<sub>4</sub> of selected samples. The two methods showed very good agreement (Bialas et al., 2007). The helium stripping method has a quicker sample turn-around time and is easier to use and therefore all samples were measured for CH<sub>4</sub> concentration using this method. The gases from the vacuum extraction system were stored in 20 ml headspace vials that were filled with 4 ml of degassed, NaCl supersaturated water as a gas-exchange barrier. After closing the vials with a butyl rubber stopper, the vials were stored top-side down and kept cool until further processing.

During Leg 3 of SO191 (2007) a remotely operated vehicle (ROV), "Genesis", was deployed for closer surveying of the seafloor and also for collection of water samples as close as possible to active venting (Bialas et al., 2007). The concentration of dissolved CH<sub>4</sub> was measured immediately onboard ship and gas extracted for later δ<sup>13</sup>C value measurement.

## 2.3. δ<sup>13</sup>C<sub>CH4</sub> method

Gas samples collected by the vacuum extraction method were analysed at IFM-GEOMAR for their δ<sup>13</sup>C<sub>CH4</sub> values using a GC-IRMS system with a ThermoFinnigan MAT 253 mass spectrometer. The isotope analysis involved removal of water and carbon dioxide on a NaOH/Ascarite trap, double cryofocussing at –100 °C (ethanol/nitrogen) on Hayesep D and Poraplot S columns, methane separation on a 30 m, 0.32 I.D. Poraplot Q capillary column at 50 °C, combustion to CO<sub>2</sub> using a Ni catalyst run at 1150 °C, removal of combustion water using a Nafion trap supplemented by a small P<sub>2</sub>O<sub>5</sub> filled inlay, re-focusing of the CH<sub>4</sub>-derived CO<sub>2</sub>, and injection into the mass spectrometer using continuous flow. The δ<sup>13</sup>C<sub>CH4</sub> values are expressed in the familiar delta (δ) notation in permil (‰) relative to VPDB (Vienna Peedee belemnite). Calibration of the system was performed daily using a CO<sub>2</sub> standard that has a known isotopic value. The average precision of stable isotope analyses has been determined to be less than ±1‰.

## 2.4. CH<sub>4</sub> equilibrator

The methane concentration of the surface water and the overlying air were continuously measured during SO191 using a fully

automated, semi-continuous seawater-air equilibrator system based on gas chromatography. Technical description and physical principles of this equilibrator are described in detail by Rehder and Suess (2001). The average precision of the system is better than 2% (Rehder et al., 2002). Surface water was pumped from 6.5 m water depth using purpose installed pump and tubing; air was sucked in ca. 10 m above the sea surface above the bridge of the ship. The sea surface temperature and salinity were recorded from the thermosalinograph installed on RV SONNE (Salinometer-OTS-Sonde; ME – Meerestechnik Elektronik GmbH) together with GPS data (position, heading, speed) and weather information (air pressure, wind direction, wind speed). The water temperature inside the equilibration vessel was measured continuously (Thermometer P650, Dossmann) for a later temperature correction between surface water and equilibrator (for details, see Rehder and Suess, 2001).

The gas chromatographic analysis provides the mole fraction of CH<sub>4</sub> in dry air. The concentration of dissolved methane and the expected equilibrium values derived from the temperature and salinity measurements are calculated according to the equation of Wiesenburg and Guinasso (1979). See also Rehder and Suess (2001) and Schmale et al. (2005) for a more detailed method description.

## 2.5. ADCP measurements

Acoustic Doppler Current Profiler (ADCP) deployments were undertaken during SO191 when the device was mounted to an *in situ* observatory (FLUFO) at all three of the areas under discussion (see also Linke et al., 2010–this issue). Here only the results from the deployments at Rock Garden (Faure Site) and Opouawe Bank (North Tower) are presented, others are shown in Linke et al. (2010–this issue). The device was an upward looking 300 kHz RDI ADCP mounted about 2.5 m above the seafloor with a range of 60 to 70 m. The bin cell size was set to 1 m and the burst interval was between 1 and 2 min. The data were analysed for current direction and magnitude.

## 2.6. Data processing and visualisation

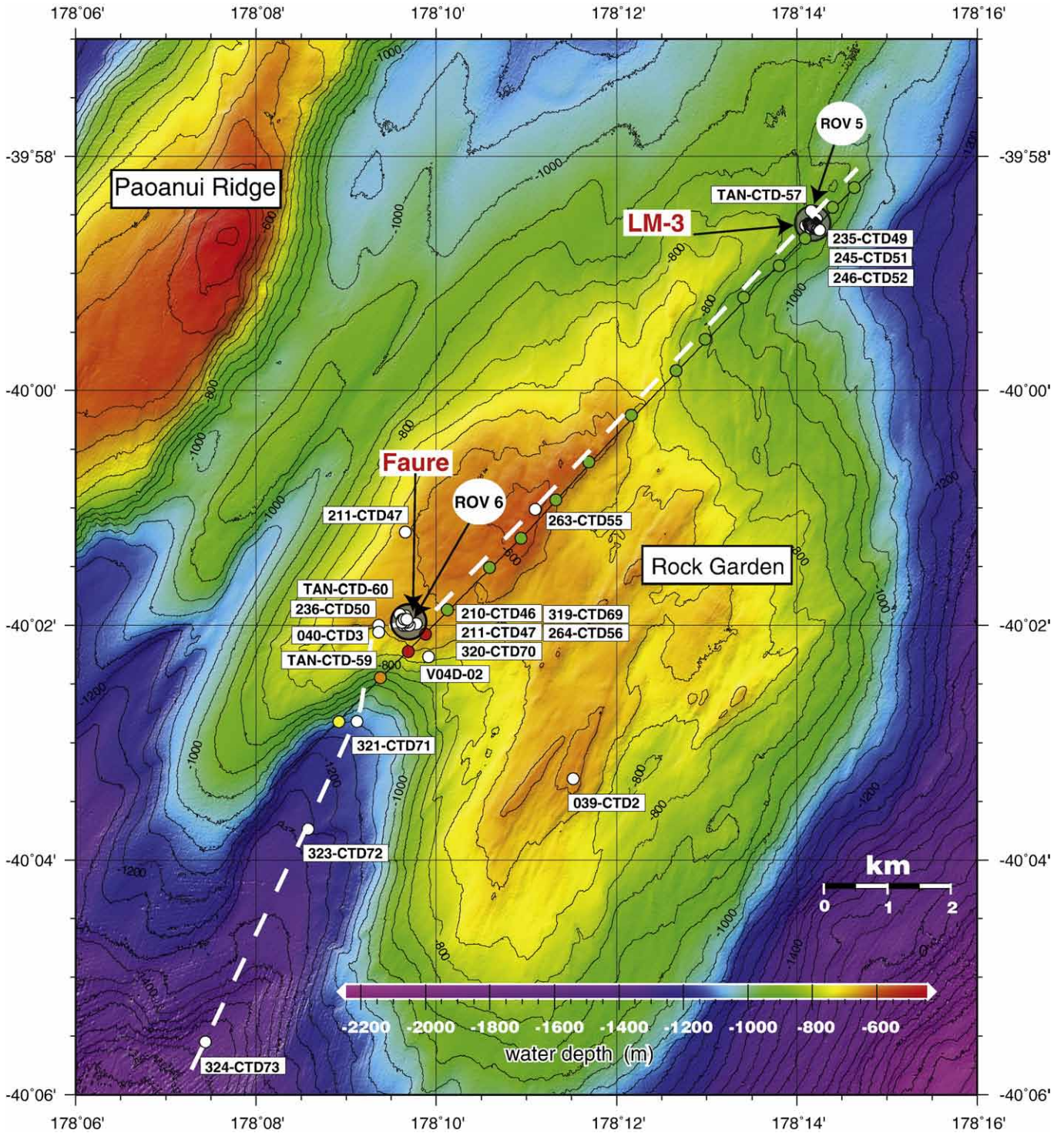
CTD data were processed using the Seabird processing software (Vers. 7.12) and averaged to 1 m depth intervals. The geochemical data (e.g., CH<sub>4</sub> concentrations and δ<sup>13</sup>C<sub>CH4</sub> values) were added to the processed CTD data in Ocean Data View (ODV, Version 3.4; Schlitzer, 2008). ODV was also used for displaying oceanographic cross sections of various data, using DIVA Gridding with *x* and *y* cell sizes set to 65. Contour plots (e.g., Figs. 7, 12, 17) do not represent precise distributions of CH<sub>4</sub> concentrations, but a two dimensional visualisation of data. The contouring is dependent on the number of samples and grid settings. In keeping the contour plots as realistic as possible 'white spaces' are created on the plots that indicate that there is too little information for ODV to interpolate. Processing of the ADCP was by dumping the raw data with BBLIST (RDI software) and plotting them using the processing capabilities from GMT 4.3.1 (Generic Mapping Tool; Wessel and Smith, 1998). The location (longitude–latitude), date and final depth of all CTD casts that are presented in this manuscript are listed in Appendix Table 1.

## 3. Results

### 3.1. Rock Garden

Rock Garden exposes morphologically a relatively flat, plateau-like seafloor (575–790 mbsl) on top with several slump sites of varying sizes on its flanks that rise up from 2700 m (Fig. 2; Faure et al., 2006; Kukowski et al., 2010–this issue). During the survey in 2004, Faure et al. (2006) observed no seep activity at the LM-3 site (no flare and no elevated CH<sub>4</sub> concentrations), but higher methane concentrations and a flare were seen on the southern edge of Rock Garden plateau,





**Fig. 2.** Bathymetry map of Rock Garden and Paoanui Ridge. Locations of casts deployed during TAN0607 (TAN-CTD#) and SO191 (#-CTD#) and ROV dives are indicated by white dots. The line with coloured dots is the location of samples collected in a horizontal tow (about 50 m above sea floor) by Faure et al. (2006). The coloured dots indicate the CH<sub>4</sub> concentrations (green < 4 nM, yellow ca. 6, orange ca. 8 nM, and red ca. 10 nM). The tow line of Faure et al. (2006) passed about 30 m to the east of Faure seep site. The dashed white line is the section-line for contour plots (Fig. 7).

now referred to as Faure Site (Fig. 2, Appendix Fig. 3). Here, the CH<sub>4</sub> concentrations were elevated (up to about 10 nM), but still relatively low compared to the highest concentration (~3500 nM) from the same area presented in this study. In total, three vertical casts were deployed during TAN0607 and 12 vertical and 4 towed casts were performed during SO191. Additional sampling was undertaken with a ROV at the LM-3 and Faure Site (Naudts et al., 2010-this issue).

Methane concentrations and  $\delta^{13}\text{C}_{\text{CH}_4}$  values from the ROV dives are presented here as well.

3.1.1. Physical setting (temperature, salinity and currents)

Temperature and salinity from CTD casts collected at Rock Garden during SO191 (31 January–23 March 2007) and TAN0607 (20 June–2 July 2006; Fig. 3). The figure shows pronounced seasonal variation,

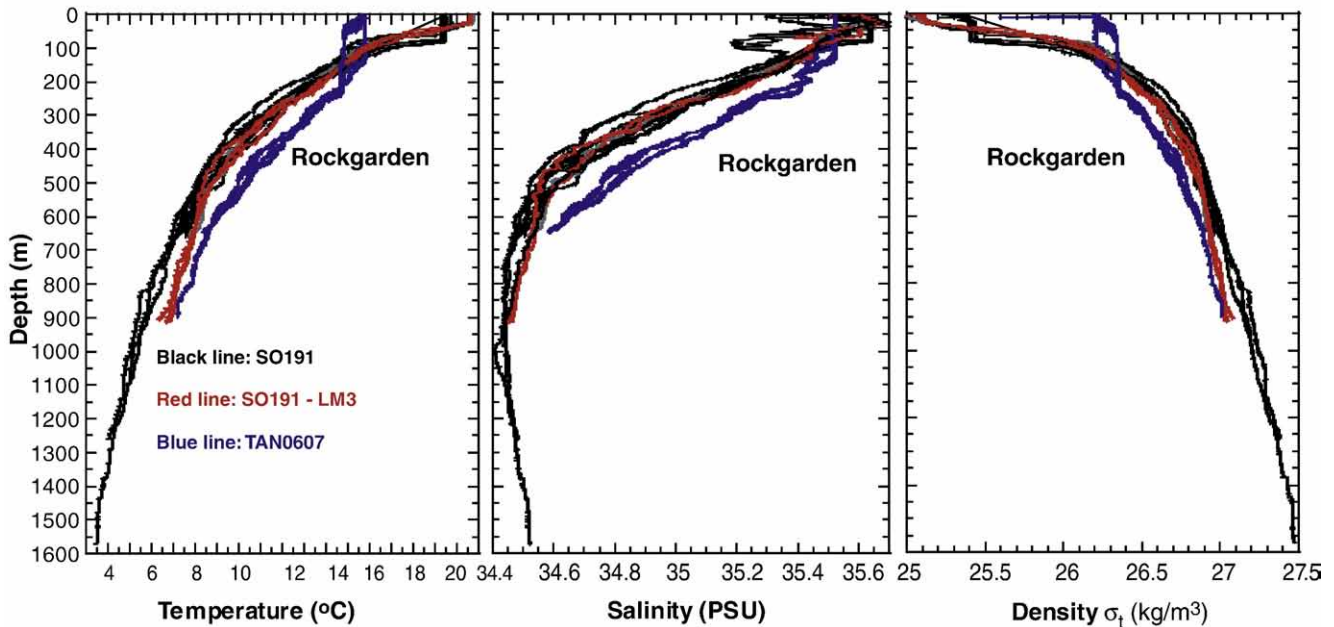


Fig. 3. Plot of temperature, salinity and density at Rock Garden. All data are from the SO191 cruise, except for blue lines which are from the TAN0607 cruise. The temperature and salinity variability during SO191, appears to be related to temporal differences when they were measured.

especially in the surface waters between the winter (TAN0607) and the summer cruise (SO191), down to 900 m water depth. At 600 mbsl the temperature varies by more than 2 °C (Fig. 3), which is a significantly greater range than the ~0.9 °C reported by Pecher et al. (2005). The water between 200 and 900 mbsl is colder, less saline and denser in summer (January) than in winter (July). Seawater at depths shallower than 500 mbsl becomes increasingly more saline and warmer, and above about 300 mbsl the density rapidly decreases (Fig. 3).

Analysis of the two upward looking ADCP deployments at Rock Garden (FLUFO-4 and -5) show currents flowing south to southeast within during the 1.5 to 2 day deployments in the bottom 60 m (Fig. 4). Current speeds vary, but are mostly below 35 cm/s [see also Linke et al. (2010-this issue) for other information from landers].

### 3.1.2. Methane concentration

One vertical cast was deployed during the TAN0607 cruise at the LM-3 Site, and only very low CH<sub>4</sub> concentrations were obtained (highest 5.3 nM at 650 m), which are similar to the low concentrations obtained by Faure et al. (2006; Fig. 5). Based on the Faure et al. (2006) and TAN0607 results, it seemed that the LM-3 Site was not considerably active. This is contrary to geophysics results which suggest that gas chimneys are pinching out near LM-3 (Crutchley et al., 2010-this issue) and a flare that was observed during TAN0607 (Greinert et al., 2010-this issue).

During SO191 a more thorough investigation was done and two towed CTD transects were executed to study the lateral distribution of methane at the LM-3 Site. Despite observing a mussel field of living *Bathymodiolus* sp. and the very high CH<sub>4</sub> concentrations measured in water sampled by ROV (Naudts et al., 2010-this issue), the water

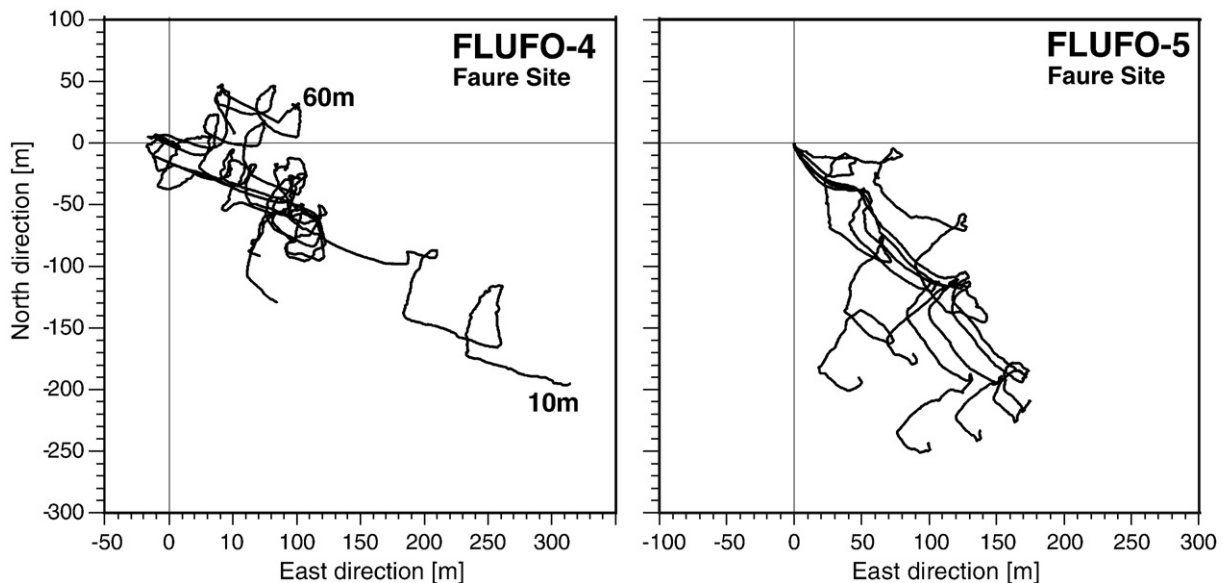


Fig. 4. Progressive vector plots from FLUFO-4 (1.5 days) and -5 (2 days) deployed at the Faure Site. The numbers indicate the distance of the respective vector above the seafloor.



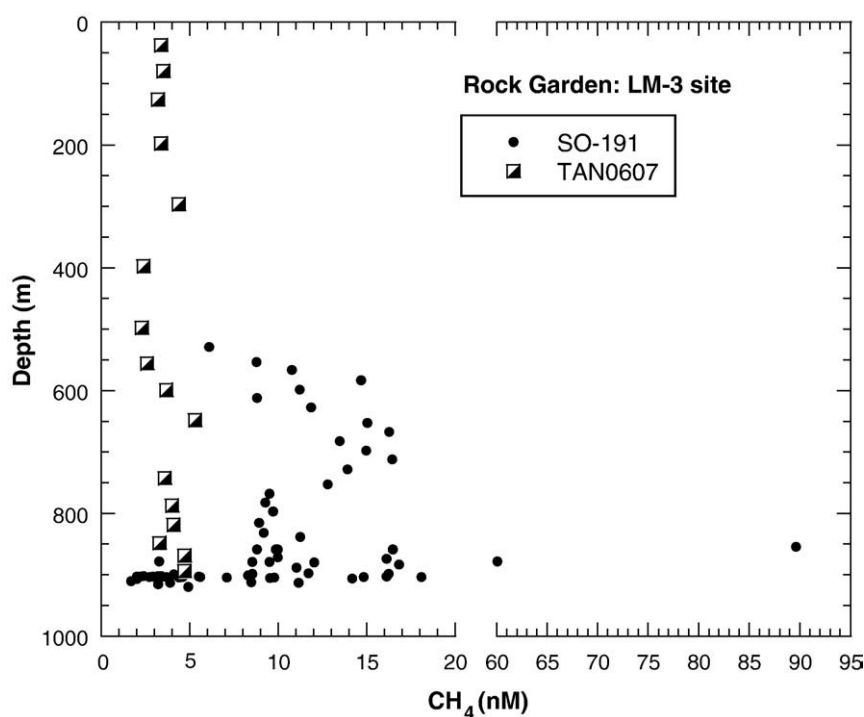


Fig. 5. Plot of CH<sub>4</sub> concentrations measured during SO191 and TAN0607 at LM-3.

samples from these two tows did not yield very high concentrations. Only two samples had concentrations of 90 and 60 nM with the rest below 20 nM. During ROV dive #5, one weak bubble stream was discovered above the *Bathymodiolus* field. Water was sampled near the bubble stream with a horizontally mounted Niskin bottle and had a CH<sub>4</sub> concentration of nearly 17,000 nM (Table 1). This ROV sample indicates that very high CH<sub>4</sub> concentrations occur only very close (decimetres) to the sea floor at active seep sites, which is not possible to be sampled by CTD operations.

Concentrations of up to ~30 nM (at 650 mbsl) were obtained close to Faure Site during TAN0607, supporting the measurements by Faure et al. (2006) and the conclusion that active methane seepage is taking place. During SO191 an intensive survey revealed that Faure Site was very active with pulsing bubble release at several places (Naudts et al., 2010-this issue). Methane concentrations as high as 3500 nM were measured at the site with the majority of these high concentrations occurring between 550 and 650 mbsl (Fig. 6). Based on this new information it is now apparent that the tow-line over Rock Garden described by Faure et al. (2006) was off to the south-west and the TAN0607 vertical cast (CTD-59) was to the south-east of the main venting location (Fig. 2). During SO191 the CH<sub>4</sub> concentrations measured down the southwest flank of Rock Garden were still high, with concentrations of up to 395 nM at 1078 mbsl (CTD 71). Faure et al. (2006) also observed slightly elevated CH<sub>4</sub> concentrations at this location and depth, but concentrations were near background (~5 nM).

**Table 1**  
Carbon isotope values and CH<sub>4</sub> concentrations of water samples collected by ROV.

Location	Details	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰, VPDB)	CH <sub>4</sub> (nM)
LM3			
SO191 ROV 5	Clam site	-66.3	Not measured
SO191 ROV 5	Raindrop site	-66.2	16,542
Faure Site			
SO191 ROV 6	A	-66.4	1268
SO191 ROV 6	B	-66.5	44,316

ROV water samples taken just above the bubble streams at Faure Site had CH<sub>4</sub> concentrations between 1300 and 44,000 nM (Table 1). It is possible that some bubbles were captured in the sampling bottle of sample "B" which caused these high concentrations. However, 44,000 nM is still below the equilibrium concentration of seawater at atmospheric pressure in presence of a 100% methane gas phase (1.4 mM at 20 °C and 34.5 psu).

The contour plot of CH<sub>4</sub> at Rock Garden reflects the high concentration in the southern part on the Faure site (~600 mbsl) and also down-slope at about 1100 mbsl (Fig. 7). The oceanographic profile at Rock Garden that is presented in Fig. 7 is drawn in a NNE–SSW direction, parallel to the shoreline and main current direction (southerly) of the East Cape Current (Chiswell, 2002, 2003).

### 3.2. Omakere Ridge

The Omakere Ridge is located west of Rock Garden (Fig. 1) and although it is closer to land it occurs in greater water depth (1100 to 1200 m). Similar to Rock Garden, Omakere Ridge is characterised by a series of northeast–southwest orientated anticlinal ridges associated with major thrust faults along the Hikurangi Margin (Fig. 8). Lewis and Marshall (1996) reported that flares had been observed by fishermen in the area now known as LM-9, however, dredging yielded no seep associated faunal species before the observations undertaken during TAN0607 in 2006.

Detailed bathymetric mapping of the Omakere Ridge was completed during SO191 and additional side scan sonar surveys revealed four more active seep sites (Bear's Paw, Kea, Kakapo and Kaka) to the southwest of LM-9 (Fig. 8; Jones et al., 2010-this issue). Knowing the exact location of these sites was very useful for guiding the 28 CTD casts at Omakere Ridge during SO191. The CTD operations mainly focussed on these new sites and along the ridge in a northward direction. Only one cast was deployed near LM-9 during TAN0607 and SO191 each.

#### 3.2.1. Physical properties (temperature, salinity and currents)

Temperature and salinity values down to about 700 mbsl are lower in profiles from SO191 than those recorded during TAN0607, was

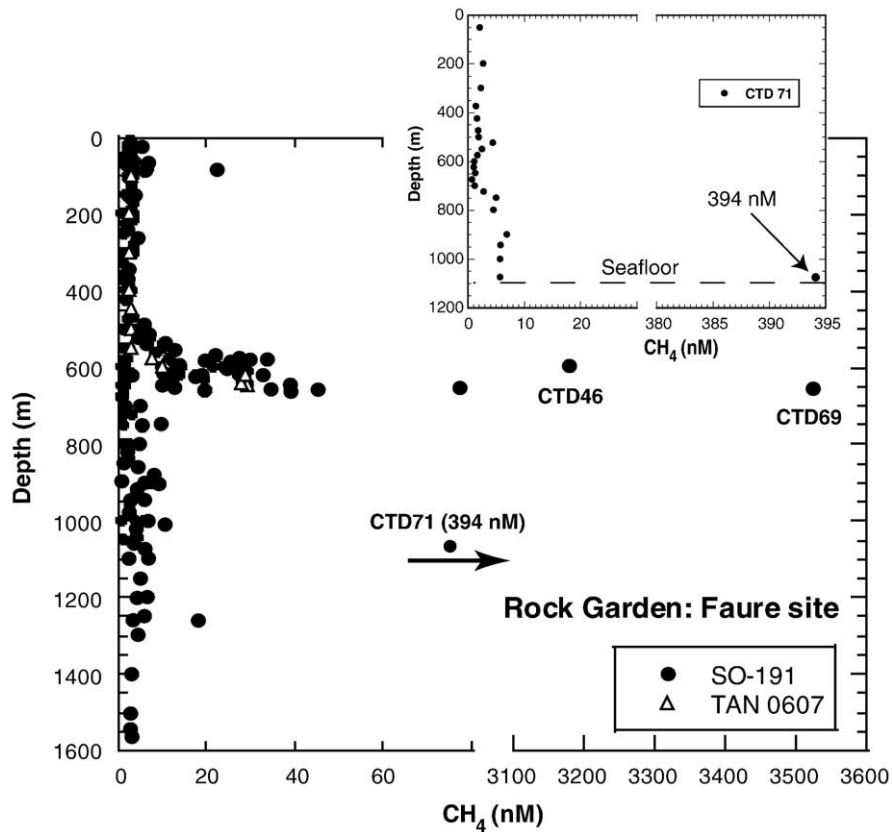


Fig. 6. Plot of  $\text{CH}_4$  concentration at Faure Site. Inset shows CTD 71 which is to the south of Faure Site with one very high  $\text{CH}_4$  value just above the seafloor (Fig. 2).

observed at Rock Garden (Fig. 9). The large variations in temperature and salinity above 400 mbsl during SO191 are most likely related to the 2–3 weeks time span between their recording and different water masses transported to the area by the Wairarapa Eddy and/or Wairarapa Coastal Current (Chiswell, 2002, 2003). Similar to Rock Garden, seawater shallower than 500 mbsl becomes increasingly more saline and warmer and shows rapidly decreasing densities above 300 mbsl (Fig. 9).

### 3.2.2. Methane concentration

Casts deployed at LM-9 during TAN0607 (CTD53) and SO191 (CTD4) had similar  $\text{CH}_4$  concentrations of up to 40 nM at the same depth (~1100 m; Figs. 8 and 10). These results suggest that LM-9 has

been active for at least 10 years, as flares were observed prior to 1996 (Lewis and Marshall, 1996). In contrast to Rock Garden, the CTD survey along the Omakere Ridge showed  $\text{CH}_4$  discharge over most of the area (Figs. 11, 12). The most active site in this area is Bear's Paw in the southern part of the longitudinal ridges (Fig. 8). Concentrations of up to 100 nM were very common along Omakere Ridge and one cast (CTD 18) showed  $\text{CH}_4$  concentrations up to 227 nM very high in the water column (~627 m above the seafloor), with the highest concentration of 380 nM near the sea floor (Fig. 11). Other sites with high  $\text{CH}_4$  concentrations are at CTD 7, 10 and 11 (Kea, Kaka and Moa); at CTD 12, 17 and 23; as well as in the southernmost (CTD5) and northernmost part (CTD 6) of the surveyed area (Fig. 8). Many casts showed that  $\text{CH}_4$  concentrations >5 nM occur exclusively deeper

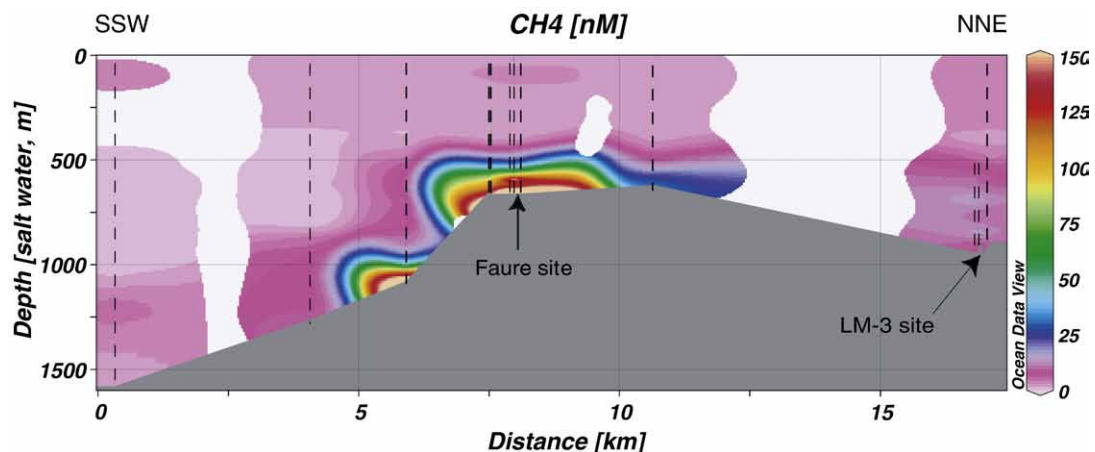
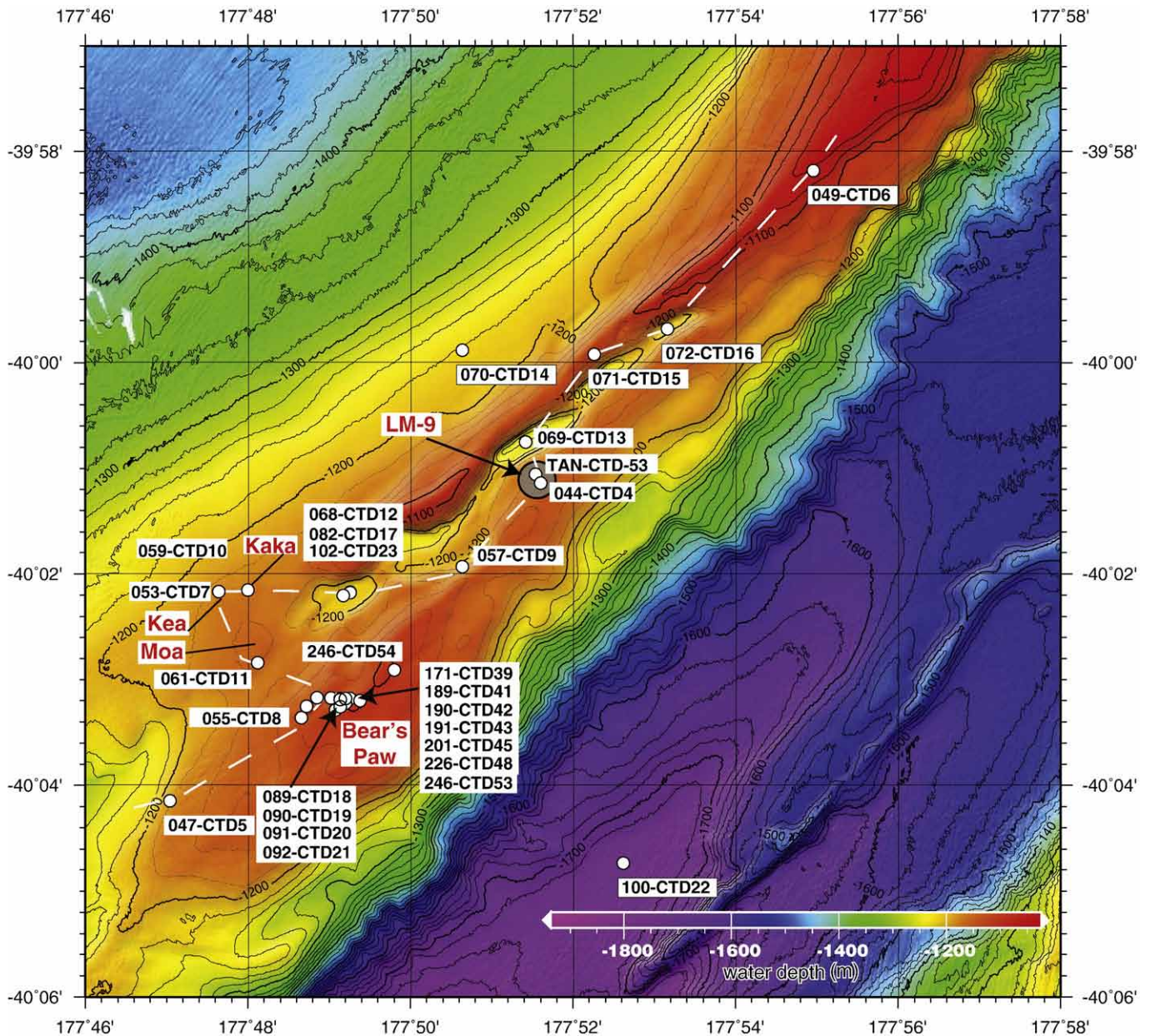


Fig. 7. Distribution of  $\text{CH}_4$  concentration at Rock Garden. Dashed lines indicate CTD casts. The section line is shown in Fig. 2. The 'white spaces' represent areas where there is too little information for ODV to interpolate (see Section 2.6 Data processing and visualisation).





**Fig. 8.** Bathymetry map of Omakere Ridge. Locations of casts deployed during TAN0607 (TAN-CTD-#) and SO191 (#-CTD#) are indicated by white dots. The dashed white line is the section-line shown in Fig. 12.

than 500 m, which is the same as for the other areas. As both the northern- and southernmost CTD stations of this section still contain samples with more than 100 nM of methane it is assumed that the surveyed section did not cover the entire seep-influenced area at the Omakere Ridge.

### 3.3. Wairarapa

The Wairarapa area (Fig. 1) is located at the southern end of the Hikurangi Margin. The seabed in the area surveyed varies from 810 mbsl at the top of Opuawe Bank to about 2500 mbsl in the deeper waters of Cook Strait (Figs. 1, 13). The location within the Cook Strait implies that the Wairarapa area is exposed to different and more complex oceanographic conditions compared to the other two sites. A new seep site named Tui at the northern top of Opuawe Bank was the most intensely studied (Fig. 13, Appendix Fig. 4). Fifteen vertical and four towed casts were deployed on Tui to identify the source and extent of the methane venting. A further 13 casts were deployed along a 43 km

long oceanographic section over Tui, the southern part of Opuawe Bank (crossing the North Tower seep) and into Cook Strait (Fig. 13).

#### 3.3.1. Physical properties (temperature, salinity and currents)

Similar to what was observed at Omakere Ridge, temperature and salinity vary over the two month sampling period between February and March 2007. Salinity data are very variable above 500 mbsl and densities become rapidly lower above 300 mbsl, but start to get less dense already from 500 m upwards. The temperature data indicate changes at 770 mbsl possibly reflecting its proximity to the Cook Strait (Fig. 14).

ADCP data from FLUFO-2 and -6 show again tide dependent current variations. The general current direction is towards the south which becomes progressively more west 60 m above the seafloor (Fig. 15A, B).

#### 3.3.2. Methane concentration

Results indicate that the Tui seep site on Opuawe Bank is very active with respect to CH<sub>4</sub> venting. Concentrations of up to ~920 nM between 640 and 840 mbsl were measured (Fig. 16). At the North



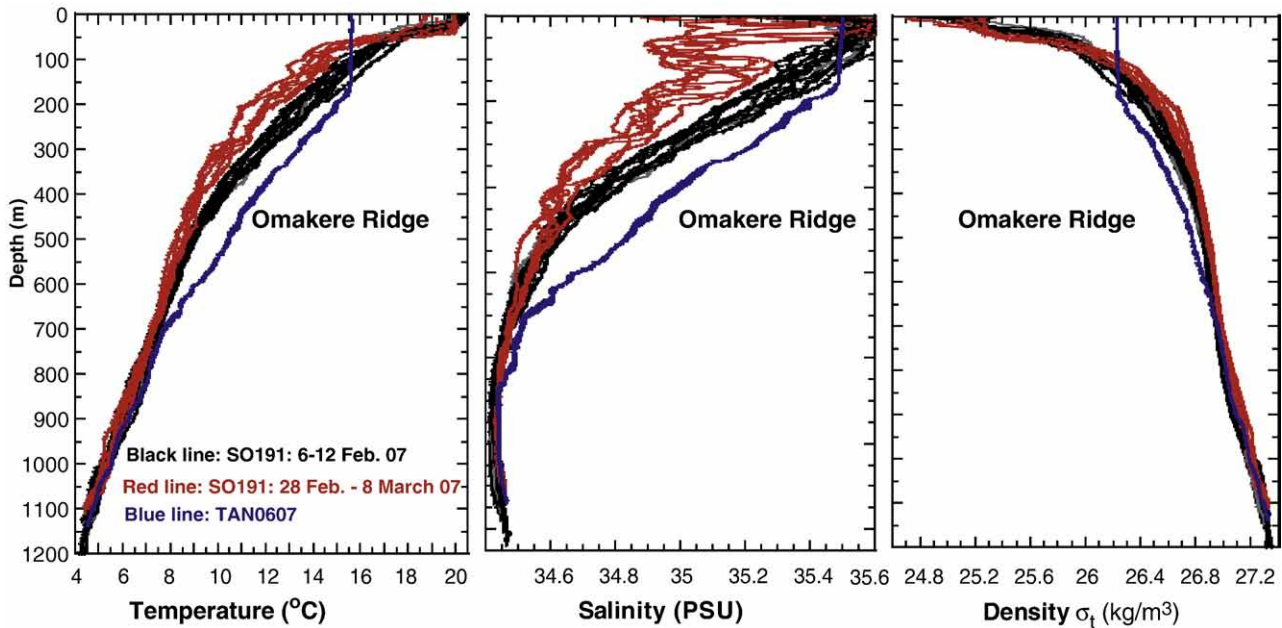


Fig. 9. Plot of temperature, salinity and density at Omakere Ridge. All data are from the SO191 cruise, except for blue lines which are from the TAN0607 cruise. The temperature and salinity variability during SO191 appears to be related to temporal differences.

Tower Site, 8 km towards the southwest of Tui (Fig. 13), CH<sub>4</sub> concentrations of up to 120 nM (1000 mbsl) indicate that this area also injects methane into the water column and supports the findings of the benthic studies by Sommer et al. (2010-this issue) and the hydroacoustic work by Greinert et al. (2010-this issue) and Klaucke et al. (2010-this issue). The ~500 m CH<sub>4</sub> boundary, above which CH<sub>4</sub> concentrations are typically at background levels, is clearly demonstrated at Tui (Fig. 16; Appendix Fig. 2).

CTD casts deployed southwest of Tui towards the 2400 m deep abyssal plain also showed elevated CH<sub>4</sub> concentrations down to 2100 mbsl

(~30 nM) and 700 mbsl (~20 nM; Figs. 16 and 17). At ~700 mbsl 3 samples over a 100 m vertical depth interval had CH<sub>4</sub> concentration that were ~5 times background (CTD61, max. concentration 27.3 nM) and 5 samples over 200 m vertical depth had concentrations that were ~3 times background concentration (CTD 62, max. concentration 11.2 nM).

#### 3.4. Sea surface and atmospheric methane

Results of the equilibrator measurements show that the sea surface temperature and salinity changes considerably along the Hikurangi

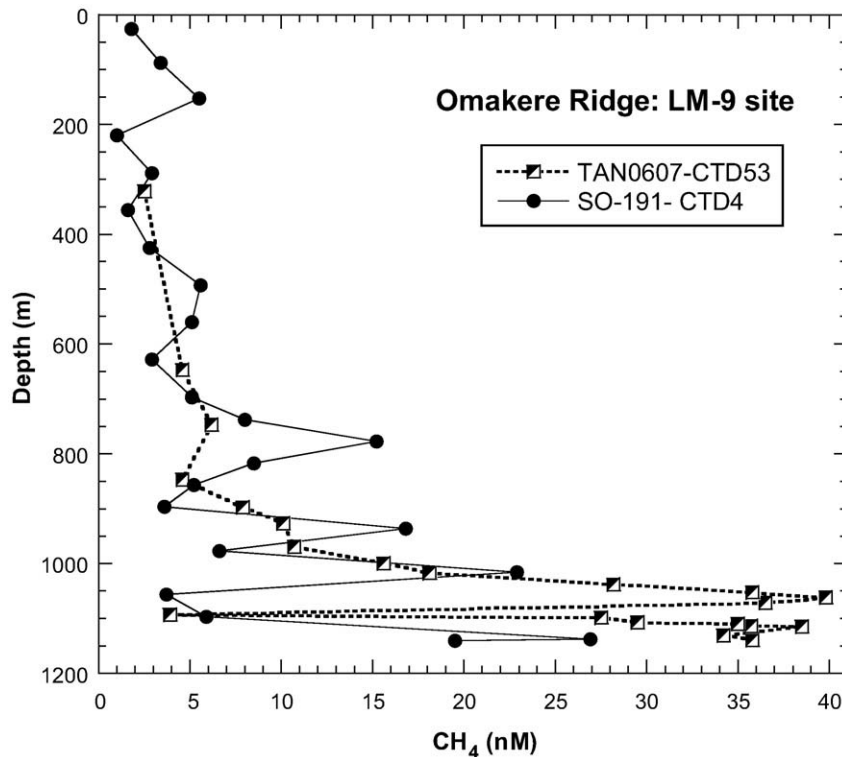


Fig. 10. Plot of CH<sub>4</sub> concentrations collect from LM-9 site at Omakere Ridge.

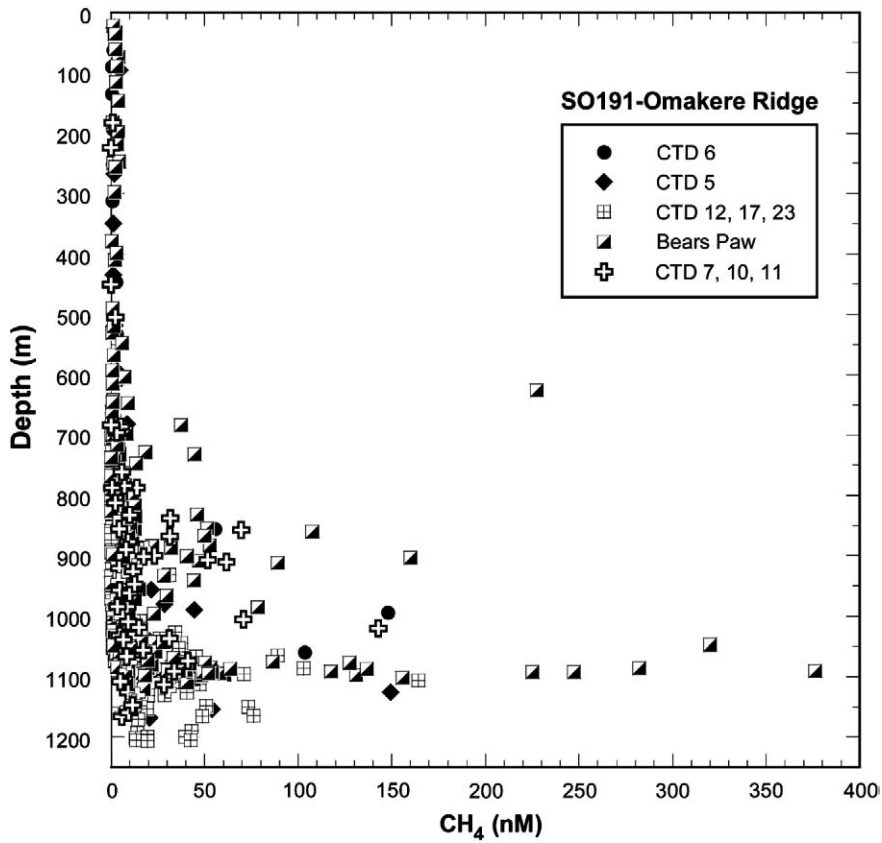


Fig. 11. Plot of CH<sub>4</sub> concentrations from the entire Omakere Ridge area.

Margin with higher values for both parameters at the Rock Garden and Omakere Ridge area compared to Wairarapa (Appendix Fig. 5). At Wairarapa in particular, a strong increase in temperature was observed between mid-January and mid-March, starting with temperatures around 15.1 °C and rising up to 18.6 °C. At the same time salinity values also increase from 34.7 to 35 psu.

Atmospheric methane concentrations along the Hikurangi Margin were found to scatter around 1.7 ppmV. This is in good agreement with the long term measurement station (1.75 ppmV) made at Bearing Head (NIWA, 2008). No systematic or region-specific changes were observed. The concentration of 1.7 ppmV was used to calculate the equilibrium concentration of the seawater according to Wiesenburg and Guinasso (1979).

Methane concentration of the sea surface water changes throughout the surveyed area (1.75 to 4 nM). Most prominent are the highest concentrations closest to land and shallow water which reach up to 4 nM (Wellington Bay, offshore Hastings and Napier; Appendix Fig. 6A). Calculations of the over saturation (OS) show a wide spread, but weak OS for most of the area, with a median value of 10% and most of the area being less than 40% oversaturated (Appendix Fig. 6B).

3.5. δ<sup>13</sup>C values CH<sub>4</sub>

The results of CH<sub>4</sub> carbon isotope analyses from SO191 samples indicate that samples with CH<sub>4</sub> concentrations above 100 nM have the

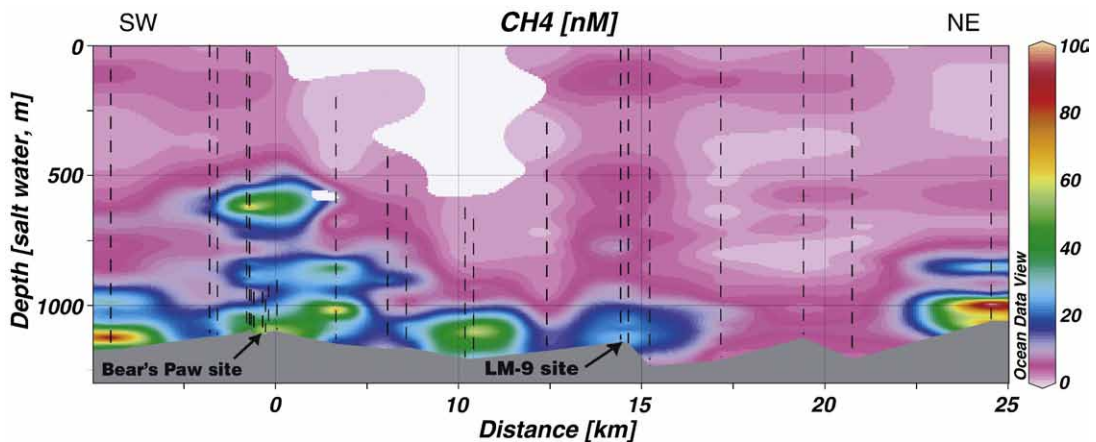


Fig. 12. Distribution of CH<sub>4</sub> at Omakere Ridge. Section line is shown on Fig. 8. The highest concentration of CH<sub>4</sub> were measured in the southern and northern-most casts, suggesting that other seep sites extending along the ridge may be present. Dashed lines indicate CTD casts. The 'white spaces' represent areas where there is too little information for ODV to interpolate (see Section 2.6 Data processing and visualisation).



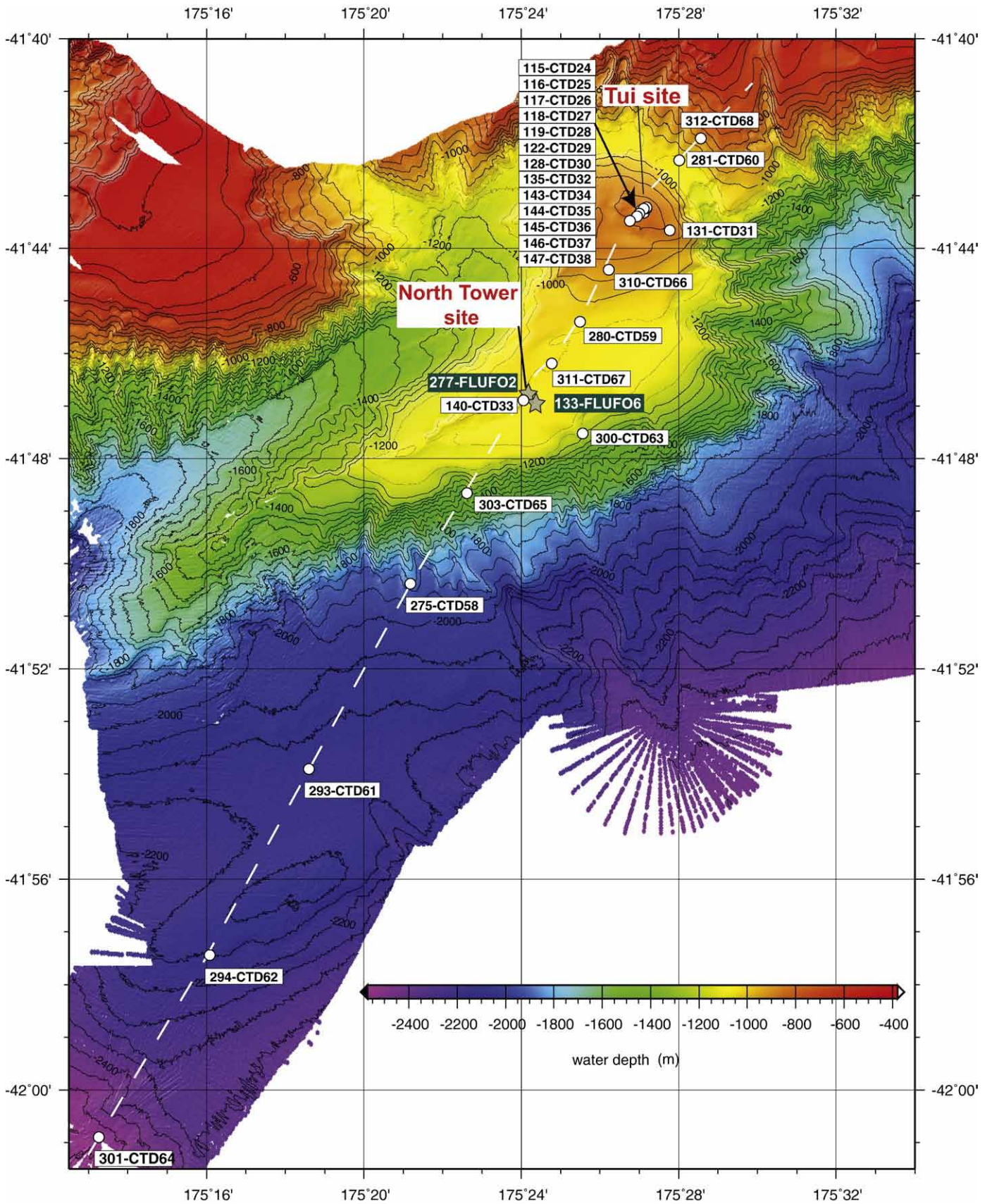


Fig. 13. Bathymetry map of the Wairarapa area. Locations of casts deployed during SO191 (#-CTD#) are indicated by white dots and ADCP locations are grey stars (#-FLUFO#). The dashed white line is the section-line drawn in Fig. 17. The majority of casts were deployed on Opouawe Bank, and 4 casts in the deeper waters of the Cook Strait.

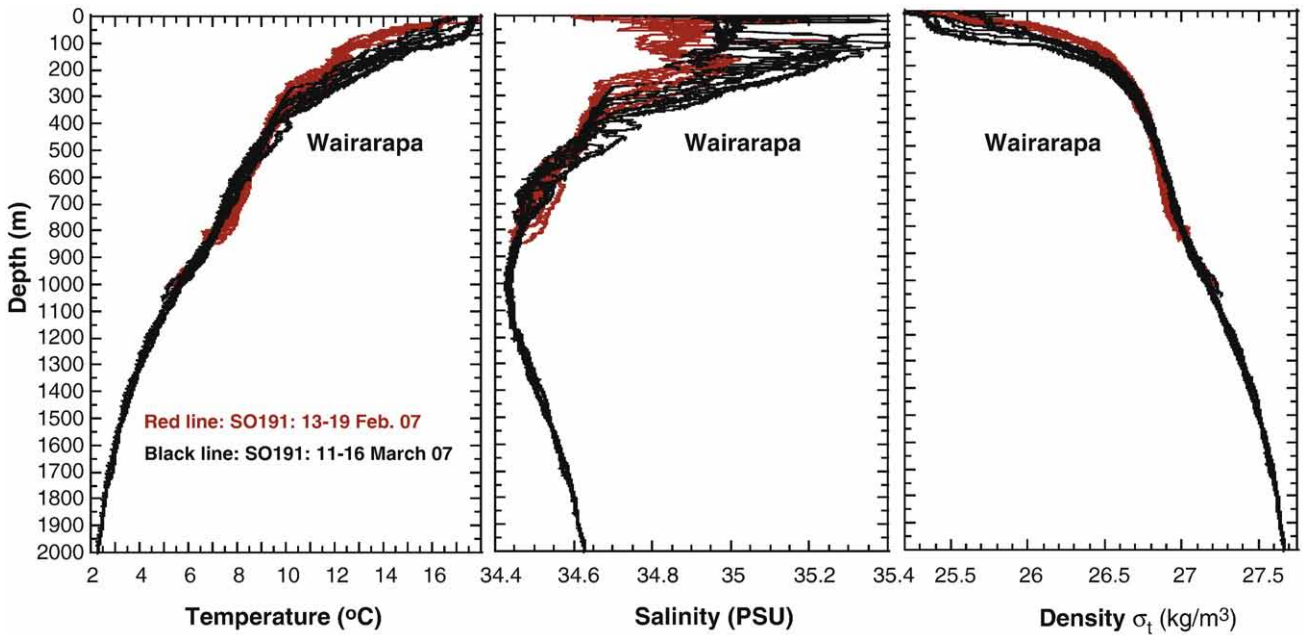


Fig. 14. Plot of temperature, salinity and density at Wairarapa. All data are from the SO191 cruise.

lowest  $\delta^{13}\text{C}_{\text{CH}_4}$  values, ranging from  $-71.3\%$  to  $-68\%$  VPDB (Appendix Table 2, Fig. 18A). Samples recovered by ROV at Rock Garden have much higher  $\text{CH}_4$  concentrations but slightly more positive  $\delta^{13}\text{C}_{\text{CH}_4}$  values ( $-66.3\%$ ; Table 1). There is no systematic variation of  $\delta^{13}\text{C}_{\text{CH}_4}$  values with depth when all the data are combined (Fig. 18B) and casts taken close to each other, but at different times, show different values. For example at Omakere Ridge CTD 9 has  $\delta^{13}\text{C}_{\text{CH}_4}$  values from  $-39$  to  $-31\%$ , but in CTD 17, which is close to CTD 9, the  $\delta^{13}\text{C}_{\text{CH}_4}$  values are about  $-70\%$  at the same depths (Appendix Table 2). Two samples that are clearly different to all the rest are those from the deepest part, in Cook Strait at 2524 mbsl. With values of  $-20\%$ , they have the highest  $\delta^{13}\text{C}_{\text{CH}_4}$  values measured in this study (Fig. 18B).

4. Discussion

4.1.  $\text{CH}_4$  distribution in water column

Methane is actively released as free and dissolved gas at all three areas studied (Naudts et al., 2010-this issue; Sommer et al., 2010-this issue). At Rock Garden and Wairarapa, the highest  $\text{CH}_4$  concentrations were measured at localised sites – Faure Site at Rock Garden and Tui Site on Opouawe Bank in the Wairarapa area. At Omakere Ridge seepage is more wide-spread, almost continuously over the 25 km long ridge.

It can be seen from Figs. 6, 10, 11, 16 and Appendix Fig. 2 that concentrations of  $\text{CH}_4$  greater than 5–10 nM do not occur at depths

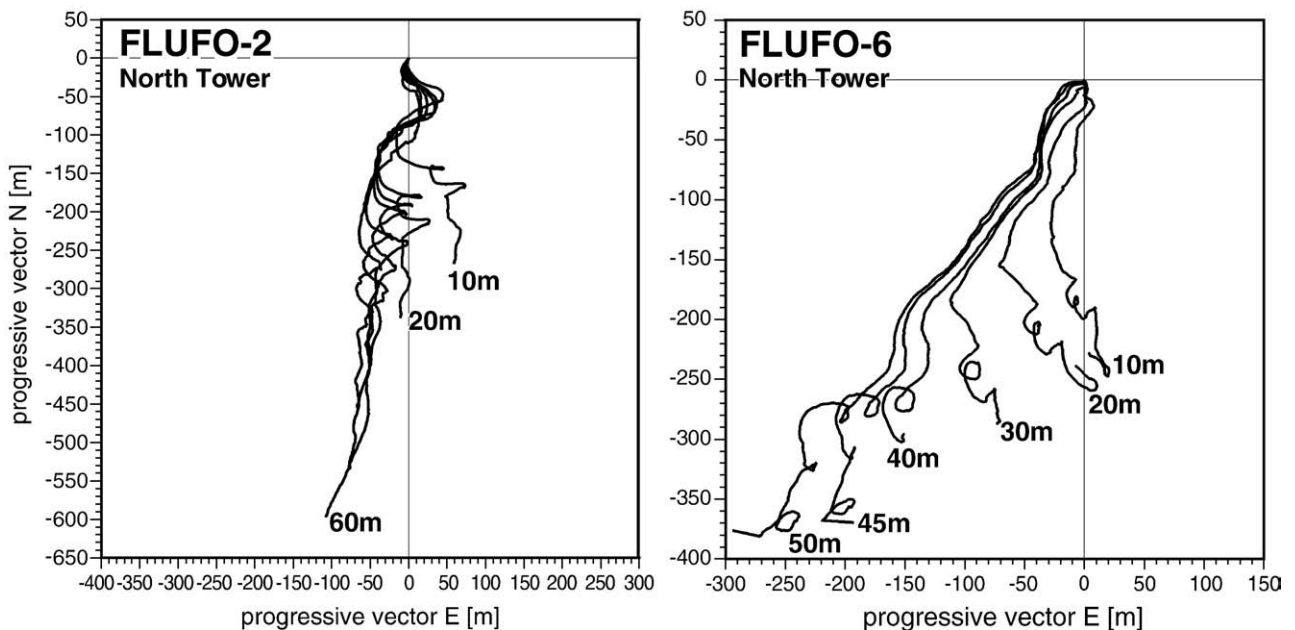
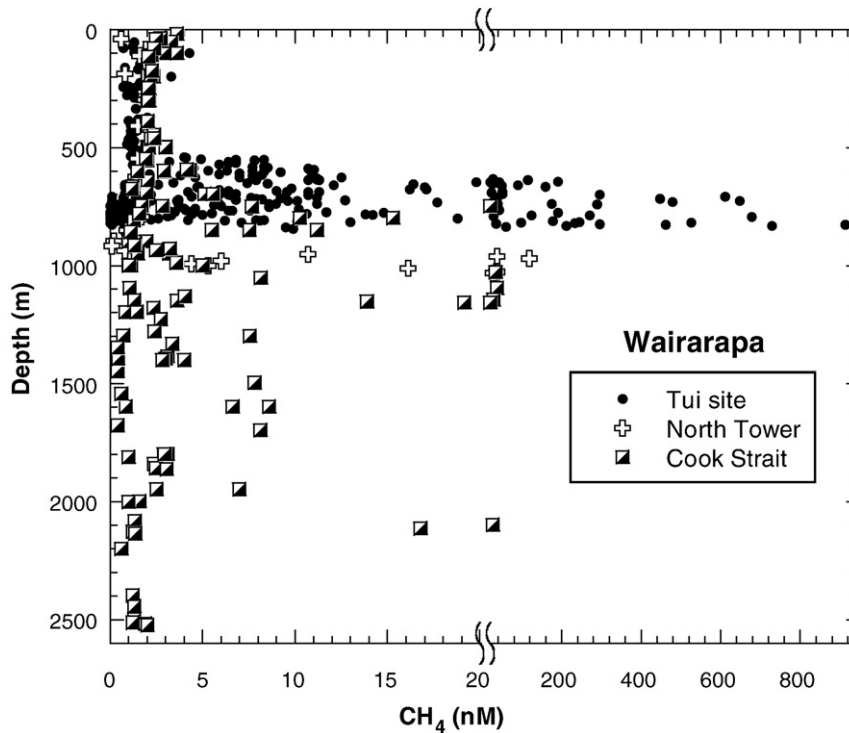


Fig. 15. Progressive vector plots from FLUFO-2 (2.5 days) and FLUFO-6 (3.5 days) on Opouawe Bank. The numbers indicate the distance of the respective vector above the seafloor. A clear change in current direction with increasing distance is seen for FLUFO-6.





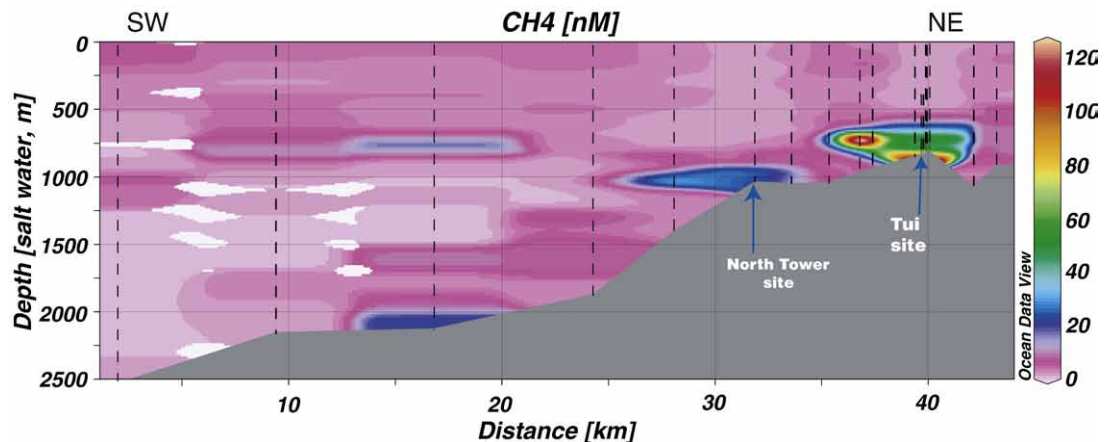
**Fig. 16.** Plot of  $\text{CH}_4$  concentrations at Wairarapa area. The highest concentrations are from the Tui seep site. The plot illustrates the  $\text{CH}_4$  boundary at about 500 m depth (coincides with seawater  $\sigma_t$  26.85  $\text{kg/m}^3$ ) above which seep  $\text{CH}_4$  is not present. This boundary is observed at all areas studied.

shallower than about 500 m. This minimum depth coincides with a seawater  $\sigma_t$  density of 26.85 ( $\text{kg/m}^3$ ). The reason for this  $\text{CH}_4$  boundary is not clear. It does not coincide with the thermocline, which is less than 100 m below surface at summer, or an abrupt change in water density. The stability zone for pure methane hydrate is deeper than 600 mbsl and a rapid dissolution of gas hydrate coated bubbles, as hypothesised by Heeschen et al. (2003), can thus be ruled out for the 500 m depth interval observed here.

In general, methane can be transported as dissolved or free gas phase and in reality  $\text{CH}_4$  is vented into the water column in a combination of these two ways. The ROV dive at Faure Site determined that bubbles were released from the seafloor at 680 m water depth and that the maximum size of the bubbles was 9 mm (Naudts et al., 2010-this issue). Based on the (single) bubble dissolution model (McGinnis et al., 2006; Greinert and McGinnis, 2009), at the ambient  $P$ ,  $T$  values and

dissolved gas concentrations, a pure methane bubble of 9 mm diameter will be dissolved at 495 mbsl, and a bubble of 15 mm at 366 m, but less than 10% of the initial amount of methane exists in the bubble above 480 mbsl. The rising height of up to 500 mbsl fits with the hydroacoustically detected flares (Greinert et al., 2010-this issue). In both cases, 50% of the methane will be dissolved within 60 m above the seafloor. Thus, the highest concentrations should be expected close to the seafloor, which is the case for Faure Site.

The vertical extent of elevated  $\text{CH}_4$  concentrations above background ( $>5$  nM) occurs mainly between 500 and 1200 mbsl. However, within this range, high  $\text{CH}_4$  anomalies were identified up to ~20 km away from the nearest known seep sites at Wairarapa (Fig. 17). The  $\text{CH}_4$  anomaly at about 700 mbsl is consistent with an overall southwest current direction (Fig. 15A,B), assuming the source was the North Tower, the nearest known seep site. At Rock Garden the lateral extent



**Fig. 17.** Distribution of  $\text{CH}_4$  concentration at Wairarapa. Section line is shown on Fig. 13. The highest concentrations of  $\text{CH}_4$  were measured in at the Tui site, one of the most active vent sites along the Hikurangi Margin. Note the "remnant"  $\text{CH}_4$  plume (~750 m depth) that has most likely been shifted from the seep sites by southerly currents. The source of the elevated  $\text{CH}_4$  at about 2200 m depth is uncertain, but may be of hydrothermal origin. The 'white spaces' represent areas where there is too little information for ODV to interpolate (see Section 2.6 Data processing and visualisation).

of anomalous CH<sub>4</sub> concentration is restricted to about 1 km south of the ridge, again consistent with the current flow direction (Figs. 4, 7). At Omakere Ridge the lateral distribution of CH<sub>4</sub> has not been explored as we did not sample consistent background concentrations north and south of the sample section.

At station CTD 61, within the deep waters of the Cook Strait, ~20 km from the nearest known seep site at Wairarapa, concentrations of 27 nM were measured at 2110 mbsl near the seafloor (2125 m) and concentrations of 7, 3 and 9 nM were measured up to about 500 m above the seafloor (Fig. 17). Typical CH<sub>4</sub> concentrations at this depth are much lower than 1 nM. The depth at which this CH<sub>4</sub> was measured precludes a source from the seeps at Opuawe Bank. A possible source of the CH<sub>4</sub> is fluids being expelled from faults and fractures that are associated with the Hikurangi Trough (see figures in

Barnes et al., 2010-this issue and Law et al., 2010-this issue), however, these CH<sub>4</sub> anomalies should be further explored.

In general, the CH<sub>4</sub> concentration diminishes laterally over relatively short distances as a consequence of mixing with seawater which has low CH<sub>4</sub> concentration (<1 nM), however, our results also show that CH<sub>4</sub> anomalies can be preserved in the water column over long distances (~20 km), carried by currents and diminish as a function of the original concentration, efficiency of the mixing process and to a minor extent by aerobic oxidation of CH<sub>4</sub> by bacteria (see discussion below).

4.2.  $\delta^{13}C_{CH_4}$  values: CH<sub>4</sub> source and destiny in water column

The  $\delta^{13}C_{CH_4}$  values (and CH<sub>4</sub> concentrations) indicate the source of methane, but it also provides a means of establishing if methane is

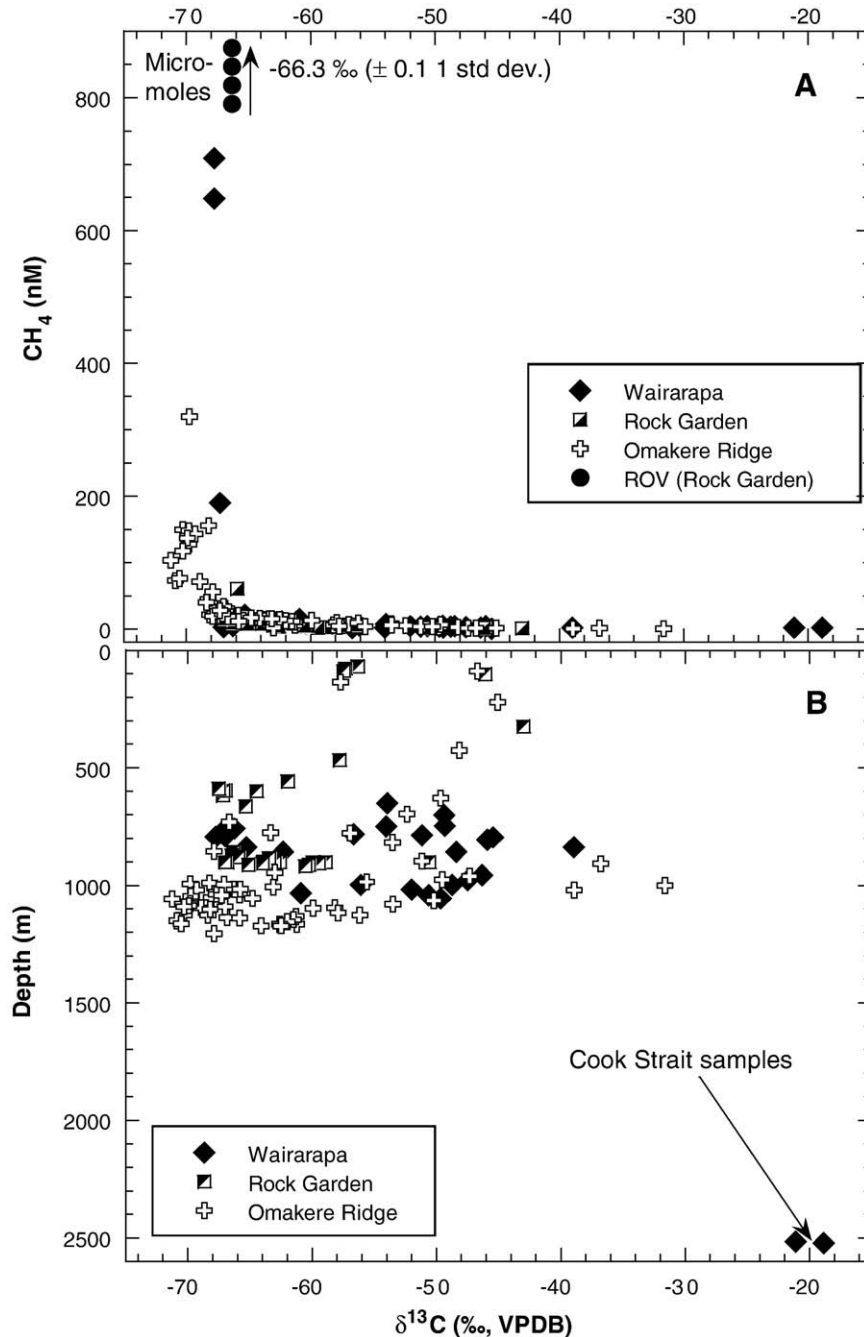


Fig. 18. A. Plot of  $\delta^{13}C$  values versus CH<sub>4</sub> concentration of selected samples collected during SO191. B. Plot of  $\delta^{13}C$  values of CH<sub>4</sub> versus depth.



oxidised in the water column or if isotopic changes are caused due to mixing.

The only published  $\delta^{13}\text{C}$  values of  $\text{CH}_4$  from offshore New Zealand are those from Botz et al. (2002) who reported that  $\delta^{13}\text{C}_{\text{CH}_4}$  values in hydrothermal gases range from  $-24.6$  to  $-28.9\text{‰}$ , from shallow hydrothermal vents in the Bay of Plenty, in the Taupo Volcanic Zone. These values are consistent with a predominant high-temperature source, with  $\text{CH}_4$  from magmatic origins averaging about  $-20\text{‰}$  (Botz et al., 2002; Proskurowski et al., 2008 and references therein). The values obtained during our study range from  $-18.9$  to  $-71.3\text{‰}$ , with the majority being lower than  $-45\text{‰}$  (Fig. 18A). There are two values of about  $-20\text{‰}$  ( $\text{CH}_4 < 2$  nM) from samples that were collected near the seafloor (2525 m; CTD 64) in Cook Strait in the south of the Wairarapa area. No report of hydrothermal activity has been documented from this region nor was any temperature deviation observed at this depth, so a hydrothermal origin seems unlikely. It has been speculated here that the presence of a large number of faults and fractures associated with the margin might be the source of fluids enriched in  $\text{CH}_4$  (deep waters of Cook Strait), which may have a thermogenic origin at depth and be consistent with the high  $\delta^{13}\text{C}_{\text{CH}_4}$  values. On the other hand, the relatively high  $\delta^{13}\text{C}_{\text{CH}_4}$  values may reflect the remaining  $\text{CH}_4$  fraction after bacterial oxidation in the water column (discussed below).

Excluding these two samples and those with  $\delta^{13}\text{C}_{\text{CH}_4}$  values more positive than  $-50\text{‰}$ , all other samples point to a biogenic methane formation. In this study, five samples with high  $\text{CH}_4$  concentrations were analysed for higher hydrocarbons (ethane, propane, n-butane, n-pentane and hexane). Only one sample from the Tui Site (CTD 34 at 818 m) had measurable ethane concentrations of 0.9 nM, with a  $\text{CH}_4$  concentration of 519.4 nM. The C1/C2 of this sample is 576 and does not entirely exclude a thermogenic methane origin (Whiticar, 1999). Unfortunately no hydrogen isotopic analyses could be undertaken

which would have provided additional information on the source of the  $\text{CH}_4$ . Whether the methane has been “recently” formed and is transported due to active (and possible deeper derived) fluid flow or if the  $\text{CH}_4$  is released from decomposing gas hydrate cannot be answered here.

A plot of  $\text{CH}_4$  versus  $\delta^{13}\text{C}_{\text{CH}_4}$  values indicates that the samples with the highest concentrations of  $\text{CH}_4$  have values of about  $-66\text{‰}$  at Rock Garden,  $-68\text{‰}$  at Wairarapa and range between  $-72$  and  $-68\text{‰}$  at Omakere Ridge (Fig. 18A). These values are consistent with those determined by Law et al. (2010-this issue) at North and South Tower in the Wairarapa area ( $-70$  to  $-63\text{‰}$ ). Similar  $\delta^{13}\text{C}_{\text{CH}_4}$  values (between  $-72$  and  $-62\text{‰}$ ) were obtained, for example, from the Cascadia convergent margin (Suess et al., 1999; Heeschen et al., 2005), which are also considered to have a biogenic origin. Fig. 18A shows an increase in  $\delta^{13}\text{C}_{\text{CH}_4}$  values with decreasing  $\text{CH}_4$  concentrations, but a heterogeneous increase in  $\delta^{13}\text{C}_{\text{CH}_4}$  values occur with decreasing water depth (Fig. 18B). A plot of  $\delta^{13}\text{C}_{\text{CH}_4}$  values versus the reciprocal of the corresponding methane concentrations shows that the majority of values plot along a mixing line between a primary cold seep end-member and atmospheric equilibrated seawater with much lower  $\text{CH}_4$  concentration (Fig. 19). This suggests that dilution has an important control on the distribution of methane and its  $\delta^{13}\text{C}$  values. A simple mixing model was used to generate a mixing curve between the two end members: 1) cold seep fluids with  $\text{CH}_4$  concentrations from 10 to several 1000 of nM and  $\delta^{13}\text{C}_{\text{CH}_4}$  values of about  $-70\text{‰}$  and; 2) “normal” seawater with  $\text{CH}_4$  concentrations of about 2 nM methane that has been equilibrated with the atmosphere ( $\delta^{13}\text{C}$  of  $-47\text{‰}$ ; Heeschen et al., 2005). Fig. 20 shows the different mixing curves and end-member values for all three areas.

There are some values which are shifted to the right of these mixing lines (Fig. 19, 20). These are, in particular, the  $\delta^{13}\text{C}$  values that have values higher than atmosphere, which indicates that some

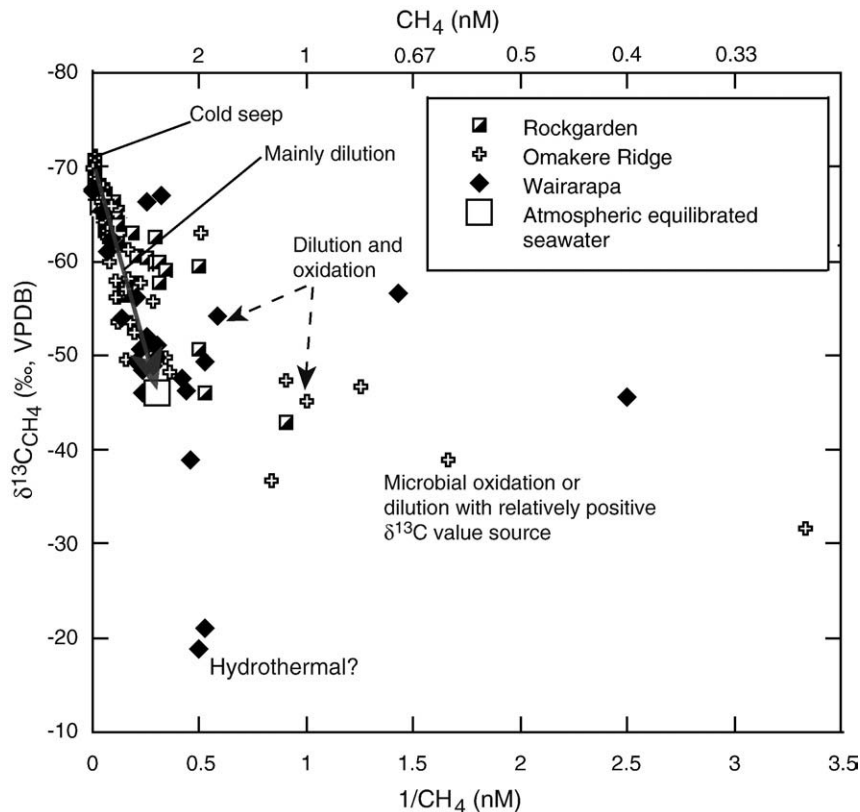


Fig. 19. Plot of  $\delta^{13}\text{C}$  values versus  $1/\text{CH}_4$  illustrate that most of the samples are positioned on a mixing line between a seep and atmospheric equilibrated end-member. Samples that plot away from the seep and atmospheric equilibrated mixing line indicate that bacterial oxidation of  $\text{CH}_4$  has occurred, which increases isotope values and decrease  $\text{CH}_4$  concentrations, or that mixing between another unknown source with  $\delta^{13}\text{C}_{\text{CH}_4}$  values more positive than  $-47\text{‰}$  has occurred.

microbial oxidation, or mixing with a source which has  $\delta^{13}\text{C}_{\text{CH}_4}$  values that are more positive than  $-47\text{‰}$ , must have taken place in addition to dilution of seep fluids and marine water. It has been demonstrated in many studies that aerobic oxidation of methane by bacteria in the water column will result in the residual methane becoming successively enriched in  $^{13}\text{C}$  as the bacteria preferably consume the  $^{12}\text{C}$ -enriched methane (e.g., Barker and Fritz, 1981;

Whiticar and Faber, 1986). A Rayleigh distillation model (Coleman et al., 1981) can be used to determine the fraction  $f$  of  $\text{CH}_4$  remaining, where  $\alpha$  is the kinetic isotope fractionation factor, and  $(\delta^{13}\text{C}_{\text{CH}_4})_i$  the starting stable isotope composition.

$$\delta^{13}\text{C}_{\text{CH}_4} = 1000 \times \left(\frac{1}{\alpha} - 1\right) \times \ln f + (\delta^{13}\text{C}_{\text{CH}_4})_i \quad (1)$$

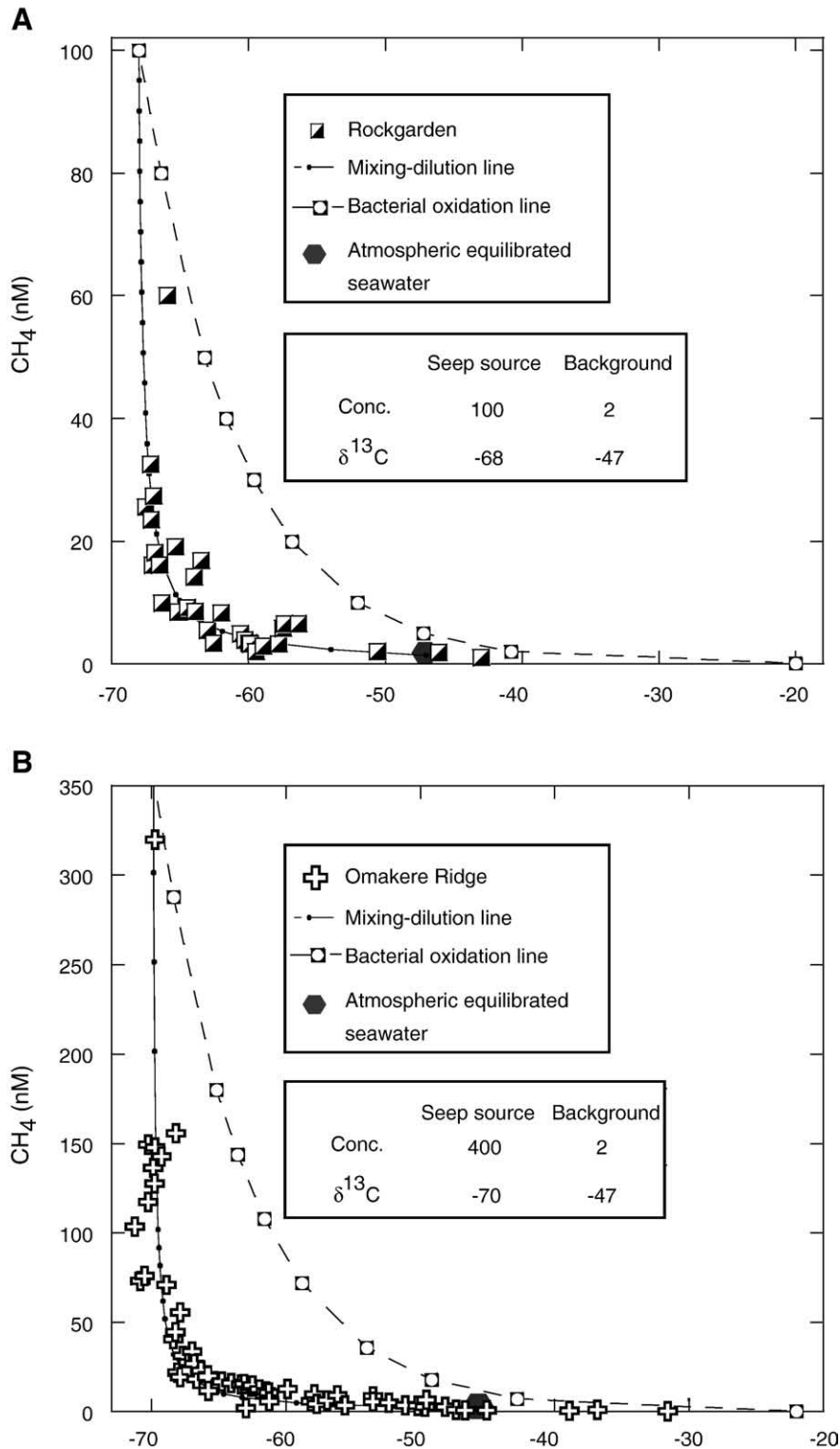


Fig. 20. Simple mixing plots between seep source and background seawater (atmospheric equilibrated) and Rayleigh isotope fractionation of seep  $\text{CH}_4$  compared to measurements from (A) Rock Garden, (B) Omakere Ridge, and (C) Wairarapa. Details of values used in calculations are shown on each plot.

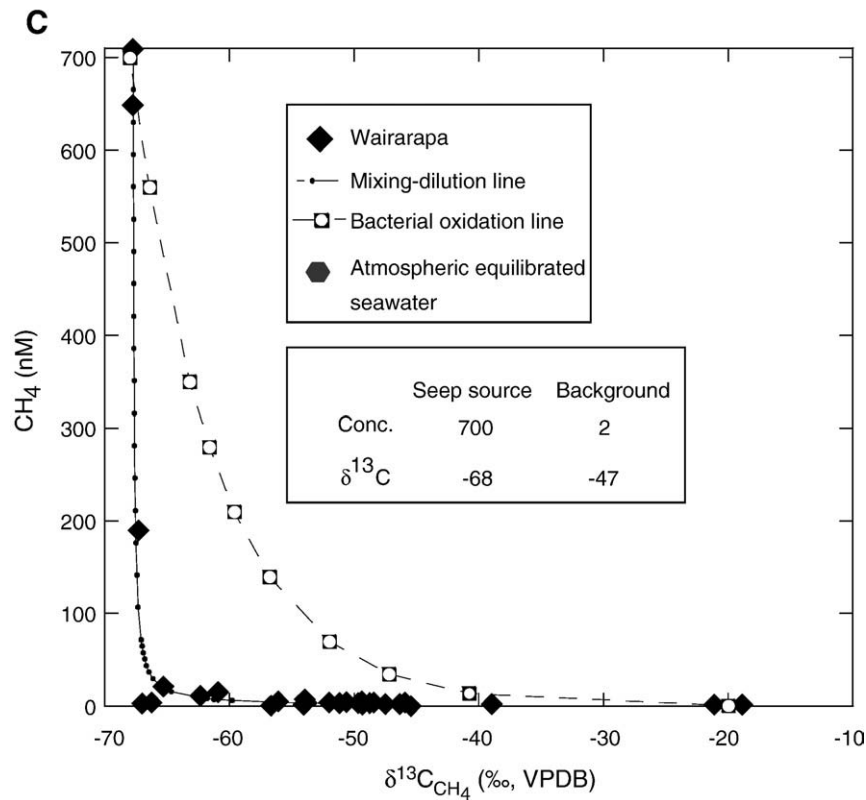


Fig. 20 (continued).

The Rayleigh model assumes that the methane reservoir has one sink (bacterial oxidation), no further inputs and that the isotopic composition is not affected by mixing. The isotope fraction  $\alpha$  that has been used here is 1.008 that is similar to the value commonly determined in other marine systems (Faber et al., 1994; Sansone et al., 1999; Grant and Whiticar, 2002). Utilisation of Eq. (1) demonstrates that aerobic methane oxidation has a minor control on the fate of cold seep  $\text{CH}_4$  in the water column and that simple dilution is the dominant process (Fig. 20), but some samples must have undergone bacterial oxidation or mixing with a source which has  $\delta^{13}\text{C}_{\text{CH}_4}$  values that are more positive than  $-47\%$ .

#### 4.3. Sea surface methane concentrations

During SO191 in 2007 (January to March) the  $\text{CH}_4$  over saturation (OS) of the surface seawater, with respect to the atmospheric concentration, had a median value of about 10%, with a range from about 5% to 45%. The OS values reported here are consistent with OS of open ocean ( $<10\%$ ; Bates et al., 1996). In our study methane OS increased up to 80% locally where the ship was close to land and where these higher OS values can be associated with methane-enriched sources near shore, rather than from seep sites (Appendix: Fig. 6B). This is again consistent with other studies which show the importance of coastal sources of methane from rivers and methane produced in shallow water (Bange et al., 1994). No CTD casts were deployed at shallow water sites close to land. Further offshore at our main working areas,  $\text{CH}_4$  concentrations are the lowest between 400 and 200 m water depth with maximum concentrations of 4.4 nM. From the sea surface down to 160 m water depth higher values occur in all areas but are typically less than 7.5 nM. Only one sample at Faure Site had a concentration of 22 nM (Fig. 6), but repeated sampling could not confirm this value. There is no evidence from our measurements that  $\text{CH}_4$  from cold seeps is reaching surface waters and escaping into the atmosphere.

The data represent a baseline for comparison for future studies and with the regionally limited dataset presented by Law et al. (2010-this issue), this is the first data of such kind offshore New Zealand.

#### 5. Summary

The cruises TAN0607 and SO191 increase our knowledge about methane seepage along the Hikurangi Margin due to the discovery of new seep sites and the first detailed geochemical studies at seeps that have been known to be active for more than 10 years (LM-3 and LM-9).

The Faure Site in the Rock Garden area, which was discovered only in 2004 (Faure et al., 2006) had the highest  $\text{CH}_4$  concentrations (3500 nM at 660 mbsl), but overall the concentrations here were generally lower than 50 nM. Down-slope from Faure Site our measurements confirmed another source of  $\text{CH}_4$  ( $\sim 400$  nM) at about 1100 mbsl (Faure et al., 2006), but higher concentrations were limited to 5 m just above the seafloor.

Evidence is ambiguous as to whether venting at LM-3 on Rock Garden is waning, but measurements during the latest cruise (SO191) showed that  $\text{CH}_4$  concentrations were generally low ( $<20$  nM) and higher concentrations could be only observed just above seep sites (decimetres) in samples collected by ROV.

The seeps at Omakere Ridge have been shown to be actively venting and the newly discovered Bear's Paw Site is particularly active. Overall, seepage in this area is widespread and is occurring over most of the 25 km long studied section (Fig. 12). The northern and southern limit of the seepage still has not been defined.

Seepage is occurring in the Wairarapa area at several sites but particular at the newly discovered Tui Site with many  $\text{CH}_4$  measurements having values  $>500$  nM. Only one cast was deployed at the North Tower Site, which had relatively elevated concentrations (up to 120 nM). A zone of elevated  $\text{CH}_4$  ( $\sim 20$  nM at  $\sim 700$  mbsl) was identified in Cook Strait, about 20 km to the south of the nearest



known vent sites. We propose that the CH<sub>4</sub> has been transported by the southerly drifting currents from the nearest possible source, the North Tower Site.

No evidence was found in the water column or sea surface to indicate that seepage-mediated CH<sub>4</sub> is currently reaching the sea surface at any of the studied areas. An upper depth limit for elevated CH<sub>4</sub> background is well-defined and occurs consistently at about 500 mbsl at the three areas studied. This 500 m boundary does not correspond to an obvious density gradient or the gas hydrate phase boundary. We speculate that the density at this depth coincides with the density of methane-charged fluids that rise as geochemical plume through the water column until its final termination at this depth. Measurements of surface seawater support that no methane from seeps is reaching the surface water and atmosphere. The slight over saturation in methane of about 10 to 40% is typical for normal ocean conditions.

Maximum CH<sub>4</sub> concentrations associated with minimum  $\delta^{13}\text{C}_{\text{CH}_4}$  values indicate that the CH<sub>4</sub> released from seeps has isotopic values between  $-71$  and  $-68\%$ . These values, together with the absence of higher hydrocarbons clearly point to a biogenic process for the methane formation within the sub-seafloor. Overall, there is a heterogeneous decrease in CH<sub>4</sub> concentration and increase in  $\delta^{13}\text{C}_{\text{CH}_4}$  values with decreasing depth. Mixing and isotope fractionation calculations show that CH<sub>4</sub> concentrations and isotopic composition change predominantly by dilution of the seep fluid with 'normal' seawater. Oxidation of CH<sub>4</sub> by bacteria and/or dilution by water which has  $\delta^{13}\text{C}_{\text{CH}_4}$  values more positive than atmospheric equilibrated seawater, is occurring, but to a much lesser degree.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.margeo.2010.01.001](https://doi.org/10.1016/j.margeo.2010.01.001).

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