GEOMAR REPORT

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Helmholtz-Zentrum für Ozeanforschung Kiel

RV CELTIC EXPLORER
EUROFLEETS Cruise Report
CE12010

– ECO2@NorthSea -

20.07. – 06.08.2012
Bremerhaven - Hamburg

Berichte aus dem Helmholtz-Zentrum
für Ozeanforschung Kiel (GEOMAR)

Nr. 4 (N. Ser.)

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1 Summary

Carbon capture and storage (CCS), both on- and offshore, is expected to be an important technique to mitigate anthropogenic effects on global climate by isolating man-made carbon dioxide (CO_2) in deep geological formations. In marine environments, however, the potential impacts of CO_2 leakage, appropriate detection methods, and risk and pathways of atmospheric emissions are poorly defined even though CO_2 has been stored in the North Sea (Sleipner) for more than 15 years and for 3 years in the Barents Sea (Snøhvit). In this regard, the EU project ECO2 will assess the likelihood and impact of leakage on marine ecosystems, apply novel monitoring techniques to detect and quantify the fluxes of formation fluids, natural gas, and CO_2 from storage sites, and, finally, develop a best practice guide for the management of sub-seabed CO_2 storage sites considering the precautionary principle and estimate the costs of monitoring and remediation. Therefore, the project partners study existing sub-seabed storage sites in the Norwegian sector of the North Sea and the Barents Sea as well as natural gas seeps at the seafloor.

The oceanographic survey ECO2@NorthSea included both facets of the project and was performed aboard the Irish R/V Celtic Explorer from 20 July – 6 August 2012 (Bremerhaven – Hamburg). The project's ship time and transportation was funded by EUROFLEETS, with work being conducted in the framework of the ECO2 project. Interdisciplinary measurements were performed at the Norwegian Sleipner storage site and the Blowout site in the UK sector of the Central North Sea. Large amounts of data and samples have been collected during the cruise which will be analysed and interpreted in the coming months, with preliminary results detailed here. Of particular importance was the successful employment of a CO_2 release experiment to test the sensitivity of the sensors and to trace the near-field dispersion processes of a limited amount of CO_2 in the sea water as input parameters for the environmental studies and numerical model simulations. Together with the dedication of the vessel's captain and crew and favorite weather conditions, we were able to obtain excellent scientific results during this cruise.

Fig. 1.1: Scientific crew from R/V Celtic Explorer cruise CE12010 (photo Denis Rowden).

2 Research Programme/Objectives

On this cruise, when proposed in 2010 – one year before the official start of the ECO2-project in May 2011, we wished to investigate the Sleipner CO_2 storage site operated by Statoil, the natural shallow water CO_2 seep offshore Juist Island and the Tommeliten methane seep area as a reference site. The Norwegian gas field "Sleipner" has been used since 1996 to inject CO_2 into a saline aquifer (Utsira formation) at ~900 m sediment depth in parallel to gas production. Our objectives were to quantify fluxes of key chemical parameters and potentially toxic metals and study the mechanisms determining the migration of CO_2, CH_4, and formation waters through the sedimentary overburden by a variety of novel monitoring techniques. Included in this plan were investigations of seawater chemistry together with the near-field dispersion processes as key input parameters for our environmental studies and numerical model simulations. Furthermore, we planned to perform an assessment of the distribution of sensitive megafauna and wanted to use fingerprinting of microbial community diversity as a key indicator of environmental impacts.

In the meantime, several expeditions have been conducted in the framework of the ECO2-project to the sites mentioned above. During 2012, there were four expeditions scheduled for the Sleipner working area: a cruise of the MPI Bremen with R/V Heincke in spring 2012, in the beginning of July an expedition with the Norwegian R/V G.O. Sars, the expedition CE12010 in July-August, and in September another expedition with the British R/V James Cook. As the expeditions complement each other to efficiently use valuable ship time, the research programme of this cruise had to be adapted to the discoveries and results obtained during the previous cruises. One of these discoveries is a large fracture, 3 km in length and 25 km north of the Sleipner storage site. The discovery was made with the aid of an autonomous underwater vehicle (AUV) in 2011, deployed by the University of Bergen from the research vessel G.O. SARS. The AUV was equipped with a synthetic aperture sonar (SAS) measuring the acoustic back-scatter intensity of the seafloor. The intriguing, large branched seabed feature and abandoned wells in the vicinity of the subsurface CO_2 plume were revisited on 3 subsequent cruises. Primary objectives of these cruises at Sleipner were:

(1) to determine whether shallow gas and fluid seepage has increased or old pathways have been reactivated,

(2) to search for formation water displaced by the injected CO_2 plume that might be seeping out.

Thus, fluid and gas seepage will be studied as a potential precursor of CO_2 leakage from the storage site. Therefore, on this cruise the prime investigation methods for leakage detection were hydroacoustic techniques, sensitive to observe single gas bubbles emitted from the seafloor, subsequently followed by video observation (ROV and towed cameras) and instruments to measure seepage fluxes (benthic lander systems, CTDs) and coring devices to study biogeochemical gradients at the seep sites.

Furthermore, a CO_2 release experiment was conducted at the seafloor in the vicinity of the Sleipner storage site to test the sensitivity of the sensors and to trace the near-field dispersion processes of a limited amount of CO_2 in the sea water as input parameters for the environmental studies and numerical model simulations.

In addition to the Sleipner storage site, the so-called blowout crater in the British sector of the North Sea was investigated, where high quantities of methane have been emitted for more than 20 years following a failed drill attempt. Ideally, this unplanned long-term release experiment can be used to estimate how much methane is emitted from the seafloor and its resultant distribution in the water column. Furthermore, it can be used as a natural laboratory to study the establishment of microbial communities, which are capable of consuming this methane and may hinder the emission of the green house gas into the atmosphere.

3 Narrative of the Cruise

On 19 July seven containers where shipped to the berthing place of RV Celtic Explorer and a part (7 of 19 persons) of the scientific crew boarded the vessel in the fishery harbor of Bremerhaven. In the morning of the next day after a short familiarization tour on the vessel, we started unloading the containers on the pier and loading the equipment on the vessel. During the afternoon the rest of the scientific crew arrived and helped loading the equipment on board the ship. During the next day the equipment was installed on deck and in the laboratories on board the vessel.

On 22 July, a tool box meeting for deployment and recovery of ROV KIEL 6000 was commenced on the aft deck of the vessel followed by a wet test of ROV and last preparations for sailing. At 13:30 the Celtic Explorer left the fishery harbor through the locks of Bremerhaven and went on transit to the main working area "Sleipner" with preparation of the instrumentation on deck and in the laboratories on board the vessel.

In the afternoon of the next day, a science meeting was conducted to talk about the program ahead. The speed of the vessel was slowed down to arrive in the working area in the morning of the next day. In the evening at 20:00, a meeting with the officers and bosun was commenced at the bridge to present this program and explain the deployment of the different instrumentation and the work program of the next day. The work program was send by email to the Sleipner control room. This procedure was conducted every evening during the following days.

Upon arrival at Sleipner on 24 July (Fig. 3.1), pre-dive preparations for the first ROV dive at the abandoned well 15/9-13 were made. At the abandoned well sampling of the emanating methane and sampling of sediments covered by bacterial mats was performed by the ROV. Later in the afternoon the BIGO lander was deployed at this site. During the night the first cast with the video-guided CTD was conducted. A submersible pump was attached to the wire to pump water from depth into the laboratory. The hose is connected with a membrane inlet mass spectrometer and a CO_2 analyser.

During most of the following day ROV dive 2 at the "fracture" about 20 km in the northeast of the Sleipner platform was conducted. The fracture was clearly visible in the scanning sonar of the ROV and covered by bacterial mats. During the dive sampling of water by Niskin bottles and sediments by push corer at bacterial mats was performed. Within one large circular field of bacterial mats slaps of carbonate crusts were recovered. Following the dive the vibro corer was deployed for sampling sediments.

On 26 July the BIGO Lander was recovered from well 15/9-13 and the ROV dive at the fracture in the north was continued, followed by sediment sampling with the vibro corer.

On the next day the first gas release experiment was conducted on the Elevator Lander with subsequent ROV dive. During the dive an ADCP was deployed in about 20 m distance to the Lander to monitor the current regime during the experiments. By arrival at the lander gas the discharge of CO_2 und Krypton on top of the Lander was observed with HD video and sonar in different distances and elevations above the Lander. The impact of the discharge was monitored by a CO_2 and pH sensor mounted on the ROV. Unfortunately, the dive had to be terminated due to technical problems with one node of the ROV. However, the ROV was safely recovered with only 3 of 7 thrusters working. A subsequent video CTD cast started right on top of the lander and investigated the spreading of the gas plume by chemical sensors onboard the CTD and by on-line analysis of the water flow pumped into the laboratory.

In the morning of 28 July, the Elevator Lander was recovered and the vessel transited to the fracture in the northeast of the working area. Here, two vibro corers were deployed for sediment recovery before the ROV was used for detailed push coring at the bacterial mats covering the fracture. During the night, the pump CTD was towed above a seismic chimney south of the Sleipner platform. As this survey did not show any signs for seepage plans to deploy the ROV here were changed and the ROV was deployed at the abandoned well 16/7-02. At this site with active methane gas emission, a detailed sampling program was commenced. After this dive, the BIGO Lander was deployed at a bacterial mat at the fracture followed by another deployment of the vibro corer.

In the morning of 30 July, the second gas release experiment was started. The Elevator Lander was deployed with a constant rate of gas release. Subsequent to the deployment the ROV was launched carrying an eddy correlation system (ECS) on the porch. The ECS was deployed in 10 meters distance to the Lander. During the dive several measurements with the CO2 and pH-sensor were conducted in the near field CO_2 plume released by the Lander. This deployment was followed by a CTD cast starting right above the Lander and a CTD transect across the subsurface CO_2 plume, which replicated a transect, which had been commenced during last year's cruise AL374.

On the next day, the BIGO Lander was recovered, followed by the last deployment of the vibro corer at this site. After this, the vessel steamed to the gas release site and the Elevator Lander was recovered. During the subsequent ROV dives all equipment left on the seafloor was recovered. During the evening a dense grid above the abandoned well 15/9-13 was performed by video-guided CTD. During the night the vessel left the Sleipner working area and steamed towards the "Blowout" site (well 22/4b) in the UK sector of the North Sea.

Upon arrival on 1 August, the ROV was launched to conduct sampling of gas, water, sediments and carbonates within the blowout crater. This was followed by sampling of surface sediments in the vicinity of the crater by the mini corer. In the evening a CTD grid was conducted in three different layers above the crater. Water sampling was accompanied by air sampling in close distance to the sea surface by the Picarro mass spectrometer.

In the morning of the next day, a ROV dive was commenced at a secondary crater in the SE of the main crater. Unfortunately, the crater was not found. Therefore, a short survey with the echo sounder was conducted, which helped to find the acoustic flare of the emitted gas. During the second dive the crater was sampled in detail. A background CTD terminated our work in the UK sector of the North Sea and the vessel steamed back to Sleipner.

During the last day in this working area, the third gas release experiment was performed. It started with a deployment of the Elevator Lander and a subsequent ROV dive to deploy the ADCP and ECS in 20 m distance to the Lander. Later on, the ROV conducted profiles in various heights and distances to the gas efflux to study the spreading of the plume in the near-field. This was continued by CTD-transects away and perpendicular to the plume. The experiment was terminated with the recovery of the Lander and the last ROV dive to recover the ADCP and the ECS. After this, station work was finished and the vessel steamed towards Tommeliten.

In the morning of 4 August, the vessel arrived at the last station at Tommeliten, which has been visited during cruise CE0913 in 2009. Two sediment cores were taken to obtain missing geochemical data of the sediments. The station work was terminated and the equipment was packed during the transit to Hamburg. The vessel arrived at the Elbe pilot station at 09:00 and in the port of Hamburg at 16:20, where the cruise ended. During the next day all equipment was packed and unloaded and all scientists (Fig. 1.1) disembarked the vessel.

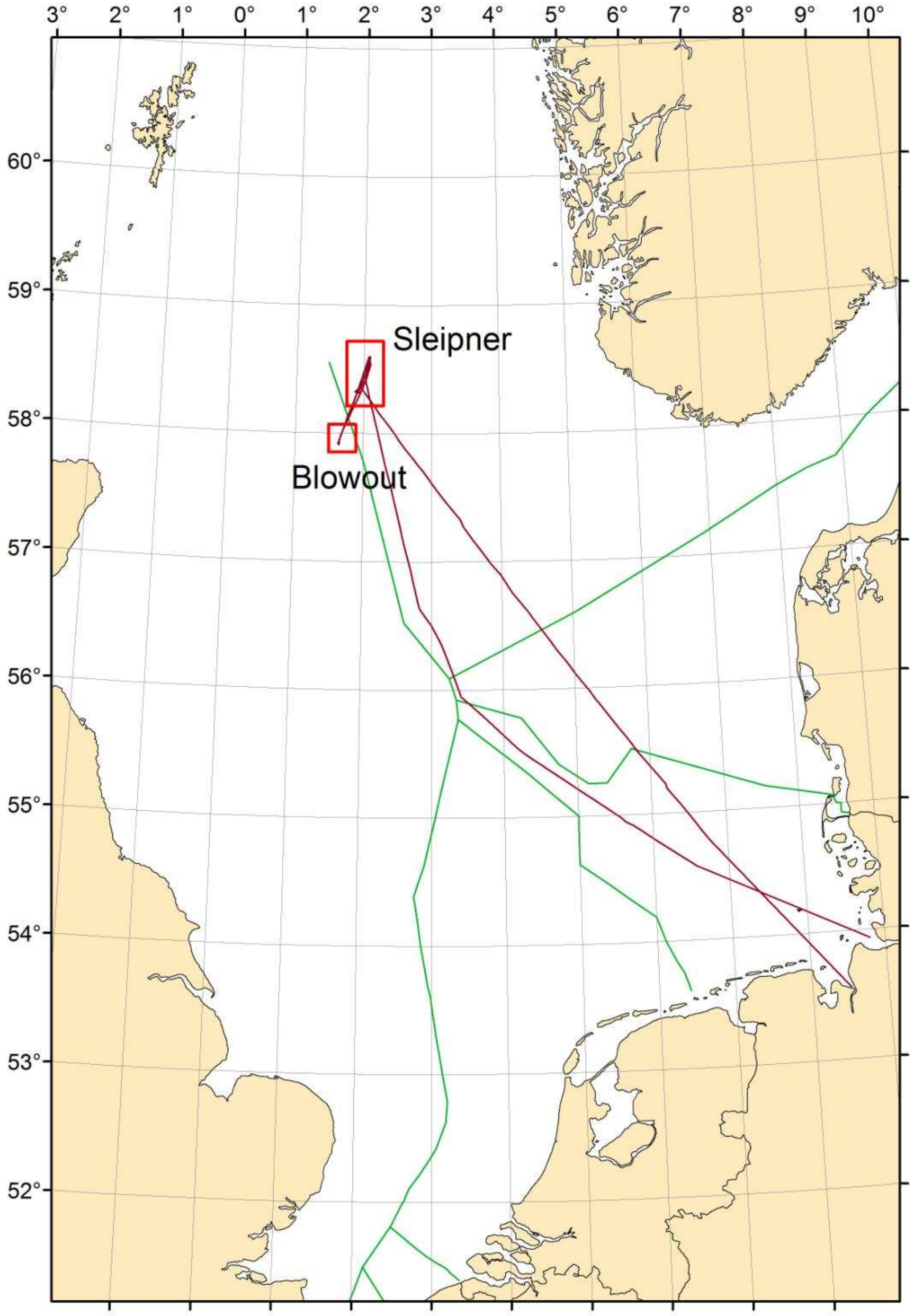

Fig. 3.1: Working areas and track chart of R/V Celtic Explorer cruise CE12010. EEZ borders of the coastal countries are indicated as green lines.

4 Preliminary Results

4.1 Water Column and Sediment Gas Geochemistry

M. Schmidt, S. Sommer, P. Linke, S. Cherednichenko, A. Bodenbinder, L. Bryant

4.1.1 Introduction and Overview of Data

Main objectives of gas geochemical investigations during CE12010 cruise (Sleipner and Blowout area, North Sea) were to identify seepage areas at the seafloor, to indicate sources of dissolved and free gas, and to quantify gas release rates from natural and artificial seeps. Main natural gas components which were characterized in porewater and seawater are methane, nitrogen, oxygen, argon, CO_2, and higher hydrocarbons (C1-C6). In addition krypton was used as a tracer during CO_2-release experiments. Therefore conventional water sampling was conducted by using a Niskin Water Sampler Rosette and by using ROV-mounted Niskin samplers. Moreover, water continously pumped from the Water Sampler Rosette to the wet lab of RV Celtic Explorer was measured online by using membrane inlet mass spectrometry. In situ gas sensors (pCO_2, CH_4) mounted to ROV6000 and the Niskin Water Sampler provided additional continously recorded gas data. Furthermore, atmospheric trace gas concentrations (i.e. CH_4, CO_2) were determined in real-time along the ship's track.

In total 12 CTD stations were performed with 115 Niskin bottles fired (Tab. 4.1.3.1). Most of the CTD stations were conducted in the Sleipner area (Fig. 4.1.1.1), however, CTD 8-11 are located in the «Blowout» area (well 22/4b, UK).

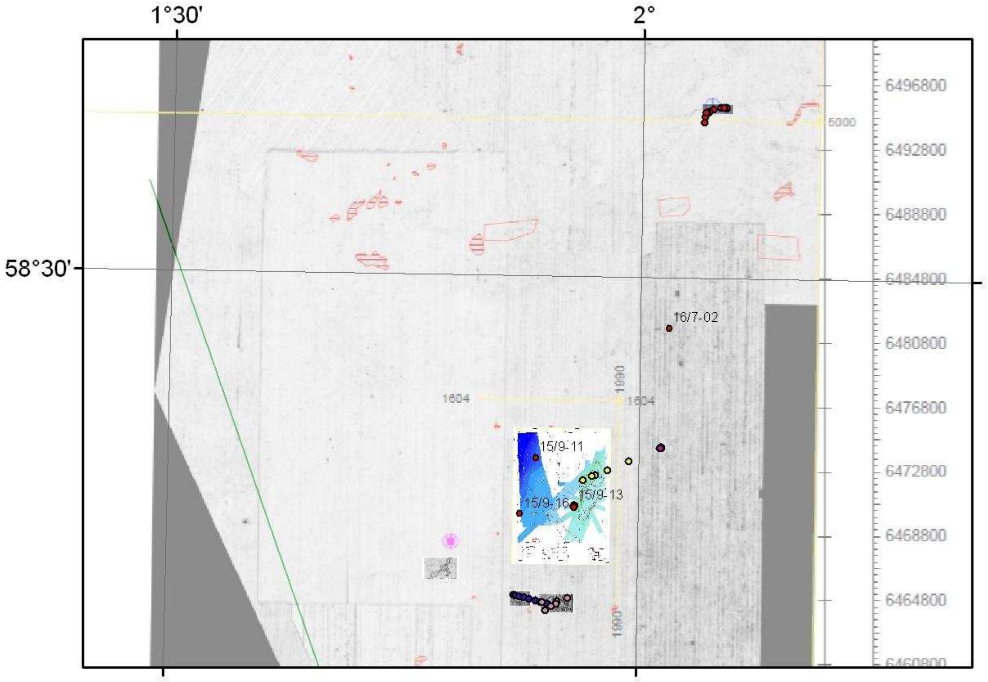

Fig. 4.1.1.1: Bathymetric map of the «Sleipner» area (blue color). Un-labeled colored circles mark positions of water column samples taken by Niskin bottles. Labeled red circles mark selected abandoned wells. The gray-shaded area provides background data from seismic data evaluation (red polygones mark burried shallow gas and seismic chimney structures).

4.1.2 Methods

Video-guided water sampler rosette

Water samples were mainly retrieved during cruise CE12010 by using hydrocasts or tracks with a towed water sampler rosette (12 x 10 L Niskin bottles) equipped with Seabird 9plus CTD. The CTD is providing temperature, pressure, conductivity, and additionally pH data (SBE 27). Moreover, an external pCO_2 sensor (Contros, Kiel) was connected via serial cable to the subsea CTD unit (see below).

A newly designed subsea telemetry and video system (Sea and Sun Technology "SST", Trappenkamp) is adapted to the water sampler rosette. The main video camera looking downwards to the seafloor is placed below the Niskins aside the Seabird 9plus CTD (Fig. 4.1.2.1). The camera consists of a full HD camcorder which can be controlled via telemetry (zoom, start/stop internal recording with a resolution of 2.3 Mpixel). The telemetry unit is placed within the rosette frame above the SBE9plus. The unit is connected to the power unit aboard with a 200 m Ethernet cable. By using the integrated Ethernet interface several IP cameras could be controlled and their video data transmitted in parallel. Light is provided by 3 LED lights (Bowtech) which can be dimmed according to the required light conditions and turbidity. All data/videos displayed in the dry lab of RV Celtic Explorer on a laptop are recorded by using SST software.

In situ gas sensors (HydroC-CO2, HISEM)

Up to two additional in situ gas sensors are connected to the Seabird CTD's analogue channels during hydrocasts or towed CTDs (HydroC-CO2 and HISEM; Figs. 4.1.2.1 a,b).

The HydroC-CO_2 sensor determines partial pressure of CO_2 in seawater by measuring infrared absorption in an inner absorption cell separated from seawater by a membrane. The system is designed for water depths up to 2000 m and calibrated between 0 and 1000 and 3000 µatm pCO_2, respectively. The actual precision is about ±10 and 30 µatm, respectively.

HISEM (high sensitive methane sensor) is based on tuneable diode laser technology. The prototype system was designed by Contros GmbH and measures dissolved CH_4 concentrations down to 1 ppm.

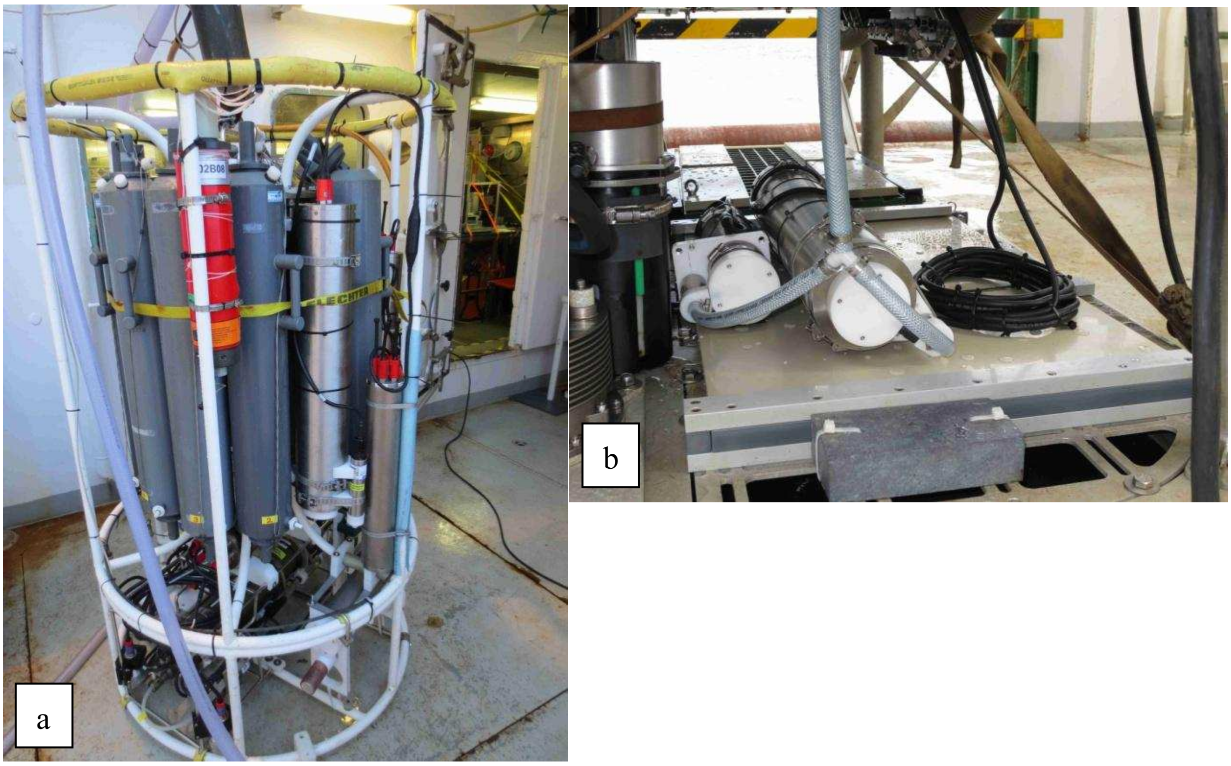

Fig. 4.1.2.1: (a) Video-guided water sampler rosette, equipped with Seabird SBE9plus CTD, 10 L Niskin bottles, SBE27 pH sensor, Contros HydroC-CO_2 (1000 μatm version), and HISEM (CH_4) gas sensors. (b) Contros HydroC-CO_2 (3000 μatm version, left side) and HISEM (right side) gas sensors mounted on the ROV chassis.

Gas bubble sampler

Pressure retaining gas samplers (see Rehder and Schneider von Deimling, 2008 for details) were used to collect gas bubbles at the seafloor at ambient pressure (~9bar). The sampler (inner tube volume of 62 ml) is submerged with an open valve (green handle). The water filled sampler is placed on top of a bubble stream and is hold in position by the main manipulator arm until the funnel is filled with gas (Fig. 4.1.2.2). The valve is then closed by using the second arm of the ROV.

After recovery of the pressure retaining sampler it is connected by the SwageLok adapter to a vacuum apparatus equipped with pressure gauge. Subsamples of high-pressured gas are released into pre-evacuated sample volumes (i.e. 20 and 100 ml glass vials), under controlled pressure (i.e. ~1020 mbar).

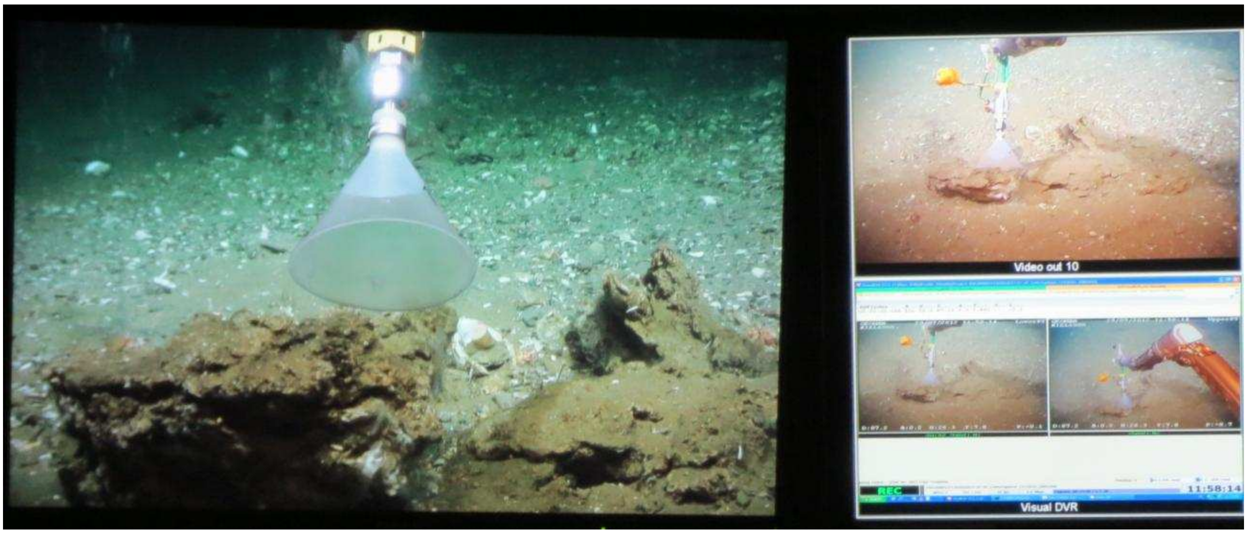

Fig. 4.1.2.2: The gas bubble sampler filled with gas emanated from the seafloor is operated by ROV KIEL 6000.

CO_2-release Lander

A CO_2 release experiment was designed to test CO_2 plume distribution during a continuous bubble flux emanating from the seafloor in the North Sea (i.e. Sleipner area). Moreover, suitability of different analytical methods (MIMS, HydroC/CO_2-sensor, pH sensor) and different techniques (ROV, Video-CTD) were tested by using the artificial release site.

Main part of the release experiment is a pressure/flow-control unit for gases under high pressure (up to 250 bar) and up to 50 L/min flow rate (Fig. 4.1.2.3a). The system works up to 100 m water depth at in situ flow rate of 5 L/min CO_2 and 0.5 L/min noble gas (i.e. Krypton), respectively. The flow rate is controlled by a tiger microcontroller and variable flow rates can be programmed for one dive.

The release head is made of 1/8’’ stainless steel tubes connected by valves and captured by plastic heads. The plastic heads are pierced by up to four 0.5 or 0.8 mm holes (Fig. 4.1.2.3b).

The whole release experiment including pressure bottle, battery pack, control unit, release plate is mounted to a Lander system (“Ocean Elevator”, Linke et al., 2011). The three pressured bottles (50 L) of CO2 and one 10 L bottle of Krypton (250 bar) can produce bubble stream up to 12 hours at highest flow rates.

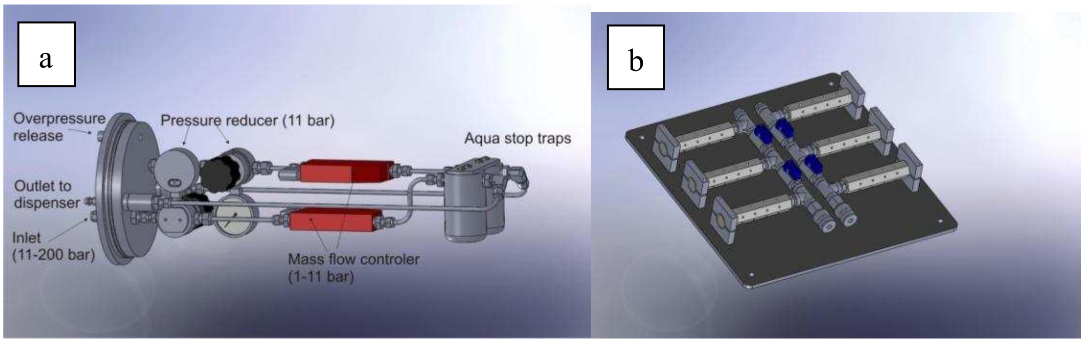

Fig. 4.1.2.3: (a) Sketch of the gas control unit (mass flow controllers, pressure reducers, circuit boards etc. are placed in a pressure housing). (b) The bubble release plate with replaceable release units (0.5-0.8 mm orifice outlets).

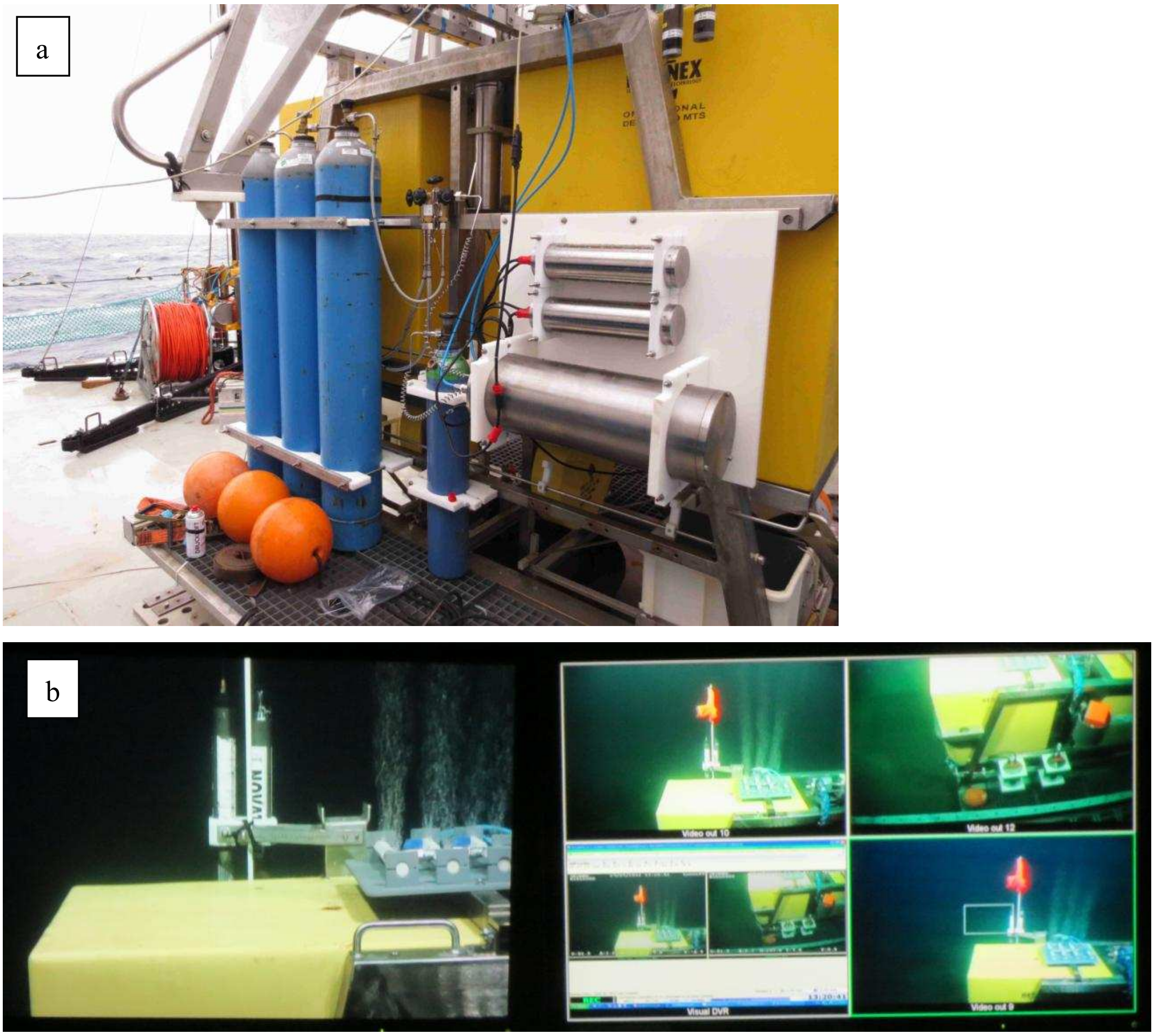

Fig. 4.1.2.4: (a) The gas release device includes three 50L CO_2 bottles (~55 bar), one 10L Kr bottle (200 bar), a mass flow control unit (large metal tube), two battery units (2 small metal tubes), and the release unit on top of the Lander. (b) The bubble streams venting from the release unit are monitored by ROV KIEL 6000.

Onboard atmospheric gas measurements

Atmospheric trace gas concentrations (CH_4, CO_2, H_2O) were measured by using a Cavity Ring-Down Spectrometer (CRDS) built by Picarro. Filtered air was pumped by an external pump, through a teflon tube, from above the vessels bridge and from 2 m above the sea surface, respectively, to the measuring device (Fig. 4.1.2.5). Concentration data is recorded with 2 Hz. Dry mole fraction of CH_4 and CO_2 is calculated and stored in 1 h-separated files. Precision of <3 ppb and <250 ppb is given for CH_4 and CO_2, respectively.

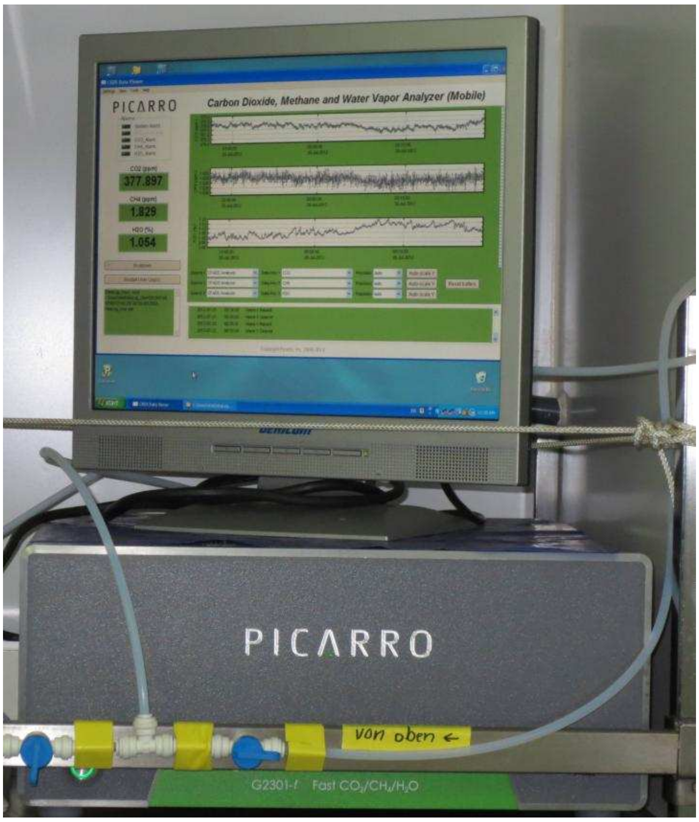

Fig. 4.1.2.5: CO_2, CH_4, H_2O gas analyser “Picarro G2301-f” installed onboard Celtic Explorer.

Onboard GC and MS analyses

Membrane Inlet Mass Spectrometry

Continuous gas measurements were conducted by using onboard mass spectrometry coupled with the Niskin Water Sampler Rosette. An immersion pump, attached to the Water Sampler Rosette, continuously pumped seawater 32 L/min through a hose (i.d.:2.5 cm) into the onboard laboratory. The tube on deck and throughout its way to the laboratory was insulated and wrapped into rescue cover sheets to reduce temperature changes. Continuous sub-sampling from the tube took place using a steel capillary that was connected to the membrane inlet. The distance between the location of sub-sampling and the inlet was about 100 cm. Along this distance the steel capillary was permanently cooled to in situ temperature of the bottom water. To guarantee best possible temperature stability of the inlet itself it was kept in a water bath using a Dewar vessel also at in situ temperature. Constant flow of 2 ml min^{-1} of the bottom water through the inlet was achieved using a peristaltic pump (Ismatec). The design of the glass membrane inlet followed that of G. Lavik (Max Planck Institute for Marine Microbiology, Bremen). Within the glass inlet the water was sucked through a permeable silicone tube (length 40 mm, i.d. 1.4 mm). Gas flow from the inlet to the mass spectrometer (GAM 200, InProcessInstruments, Bremen) was supported with Helium that was supplied through a fused silica capillary (i.d. 100 µm). An inline cryo-trap (– 35° C ethanol) between the inlet and the mass spectrometer was used to remove water vapour, Figure 4.1.2.6.

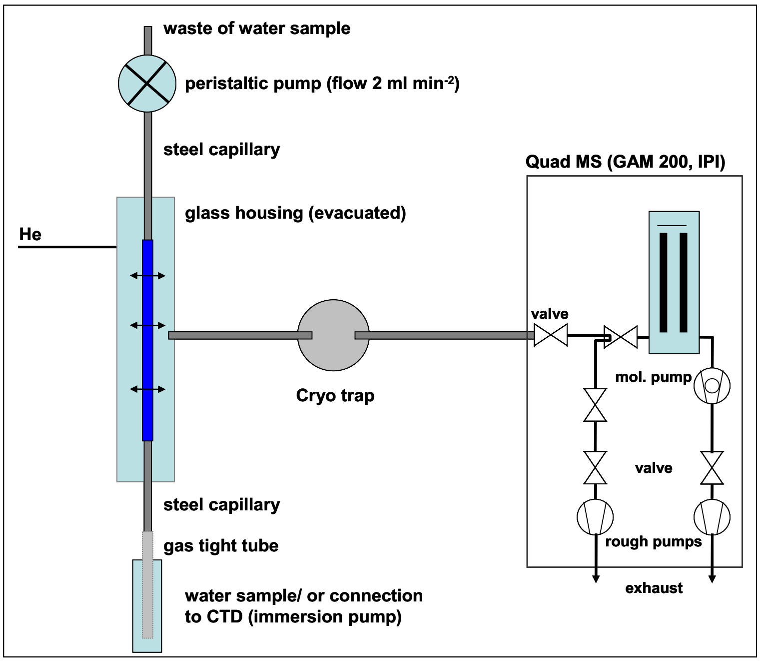

Fig. 4.1.2.6: Scheme of the setup of the Membrane Inlet Mass Spectrometer. For details see text.

Concentration of CO_2, CH_4, C_2H_6, N_2, Ar, and Kr were sequentially obtained from ion currents at mass to charge (m/e) ratios 44, 15, 29, 28, 40, and 84, respectively. Gases were detected using a Secondary Electron Multiplier (SEM). Instrument response time was typically less than 3 min, hence only "smeared" gas concentrations alongside the towed transects were obtained. Instrumental CO_2 ion current (44) was calibrated using equilibrated sea water standards. Standards were prepared by bubbling CO_2 standards (300, 500, 700, 1000, 5000 ppm) balanced with N_2 through filtered (0.2 µm) seawater kept in septum stoppered glass bottles (Schott). Ion currents of CH_4 (15) were calibrated in the same way by using 10, 100, 500 and 1000 ppm standards. Ion currents of N_2 (28), Ar (40), and O_2 (32) were calibrated using air equilibrated water samples at different salinities (0, 20, 35 psu) following the method of Kana et al. (1994). These standards consisted of 500 ml glass bottles containing filtered water (0.2 µm) gently bubbled with air through a diffusing stone. Whilst bubbling they were kept close to in situ temperature. The bottles were capped to reduce evaporation losses. The dissolved gas concentrations in the standards were calculated using the solubility equations of Hamme & Emerson (2004) and Garcia & Gordon (1992) for appropriate temperature and salinity. Before calculating the gas concentrations the ion currents were corrected for instrument drift and temperature fluctuations inside the cooler.

Headspace sampling and gas chromatography

Water samples for dissolved gas sampling were mainly taken during near-seafloor CTD-tracks in 10 L Niskin bottles. Subsamples were transferred bubble-free into 100 ml headspace vials immediately after recovery of the Niskin Water Sampler Rosette. Dissolved gases were released from the seawater samples by head space technique (headspace of 10 ml of Ar 4.5). After adding 50 µl of saturated HgCl2-solution the vials were stored at 4°C. Concentration determination of methane released into the headspace was conducted by using onboard gas chromatography (Shimadzu 2010). 100 µl of headspace gas was injected for hydrocarbon analyses (Poraplot, 30m; FID; isotherm at 50°C; N2-carrier gas).

Sediment samples from push cores and vibro cores were sampled for porewater gases according to Sommer et al. (2009). From each selected sediment depth, a 3 ml sediment sub-sample was transferred into a septum-stoppered glass vial containing 9 ml of saturated NaCl-solution and 1.5 g of NaCl (s) in excess. The vials were kept cold (4°C) during storage until hydrocarbon (C1-C4) concentration determinations of the headspace gases were performed in GEOMAR laboratories by using gas chromatography (CE8000top gas chromatograph, He carrier gas, FID, Poraplot Q capillary column, T-program).

4.1.3 Preliminary Results

CTD Measurements and water sampling at Sleipner

In total 12 CTD stations were performed with 115 Niskin bottles fired (Tab. 4.1.3.1). Most of the CTD stations were conducted in the Sleipner area (Fig. 4.1.3.1), however, CTD 8-11 are located in the «blowout» area. The Niskin water samplers were usually fired during slow (0.3-0.6 kn) towed CTD-tracks in bottom view mode. However, a few samples from the vertical water column have been taken during hydrocasts as well (Tab. 4.1.3.1). In figures 4.1.3.1, 4.1.3.2. 4.1.3.4 the locations of Niskin samples are plotted with bathymetric background data.

All Niskin samplers were subsampled into 100 ml headspace vials for subsequent determination of dissolved gas concentrations (i.e. CH_4, and higher homologues). 250 ml water samples for DIC analysis have been taken from selected Niskin bottles only (Tab. 4.1.3.2).

During the CTD casts CTD 1 (Sleipner, seismic chimneys), CTD 2 (Sleipner/fracture), CTD 4 (Sleipner, seisminc chimneys) and CTD 7 (Sleipner, well 15/9-13) MIMS gas analyes were conducted. Online MIMS gas measurements were further conducted during all three gas release experiments (CTD 3, 5/6, 12) using the same set up. For details of the gas release experiments see above and section 4.3. Presently, the raw data are post-processed.

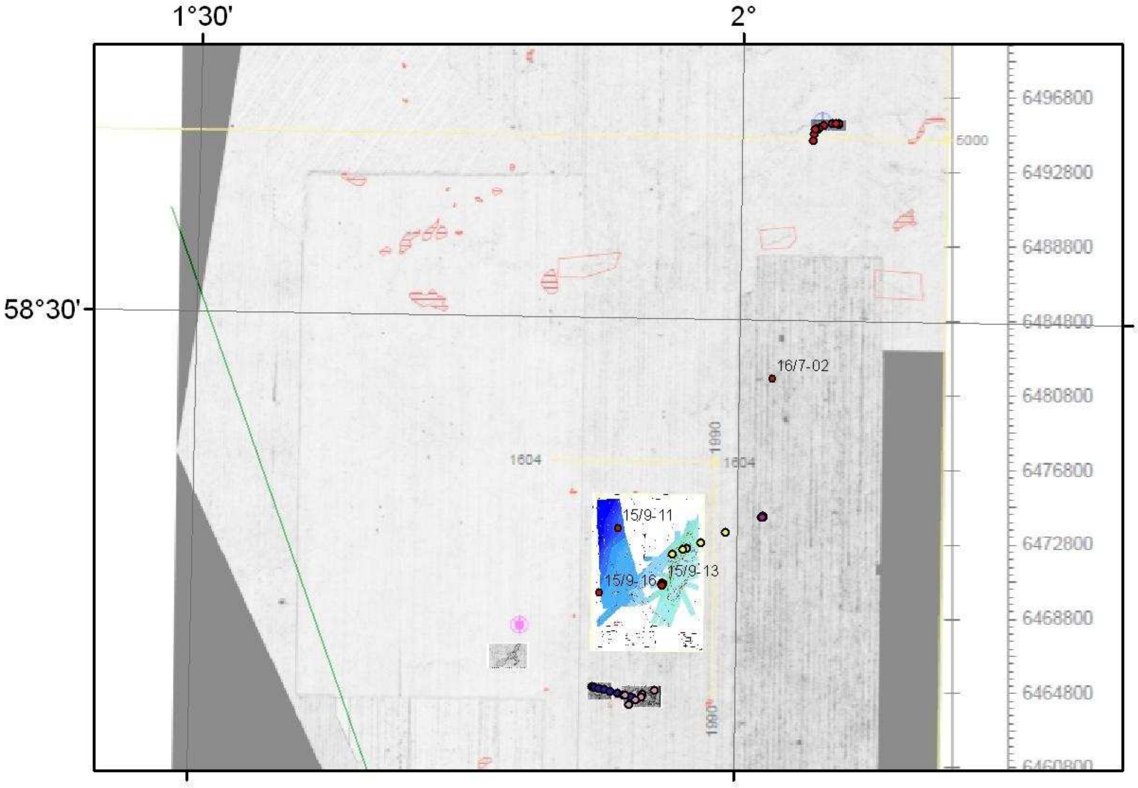

Fig. 4.1.3.1: Bathymetric map of the «Sleipner» area (blue color). Un-labeled colored circles mark positions of water column samples taken by Niskin bottles. Labeled red circles mark abandoned wells near Sleipner. The gray-shaded area provides background data from seismic data evaluation (red polygones mark burried shallow gas and seismic chimney structures).

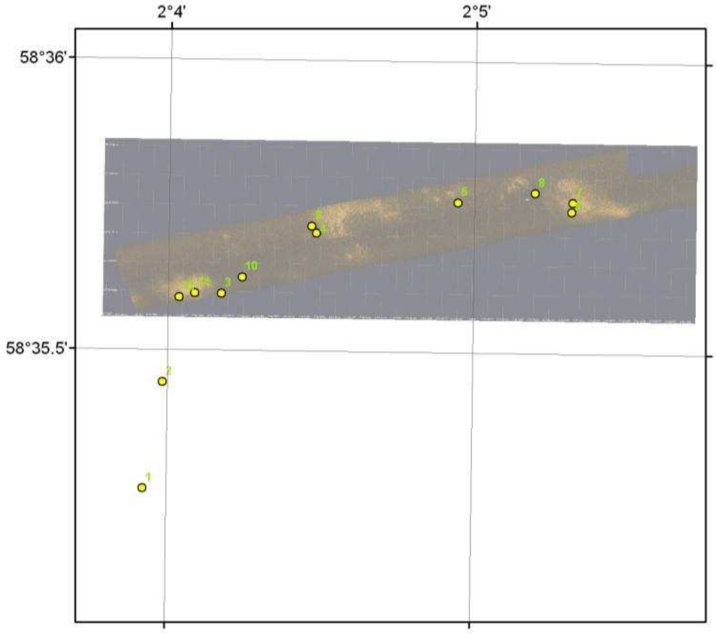

Fig. 4.1.3.2: Niskin water samples (yellow circles) sampled near the seafloor above the «fracture» structure, located 25 km NE of the Sleipner sub-surface CO_2 plume. The gray/brownish shaded image is produced from sidescan sonar data (Petersen, pers. comm.).

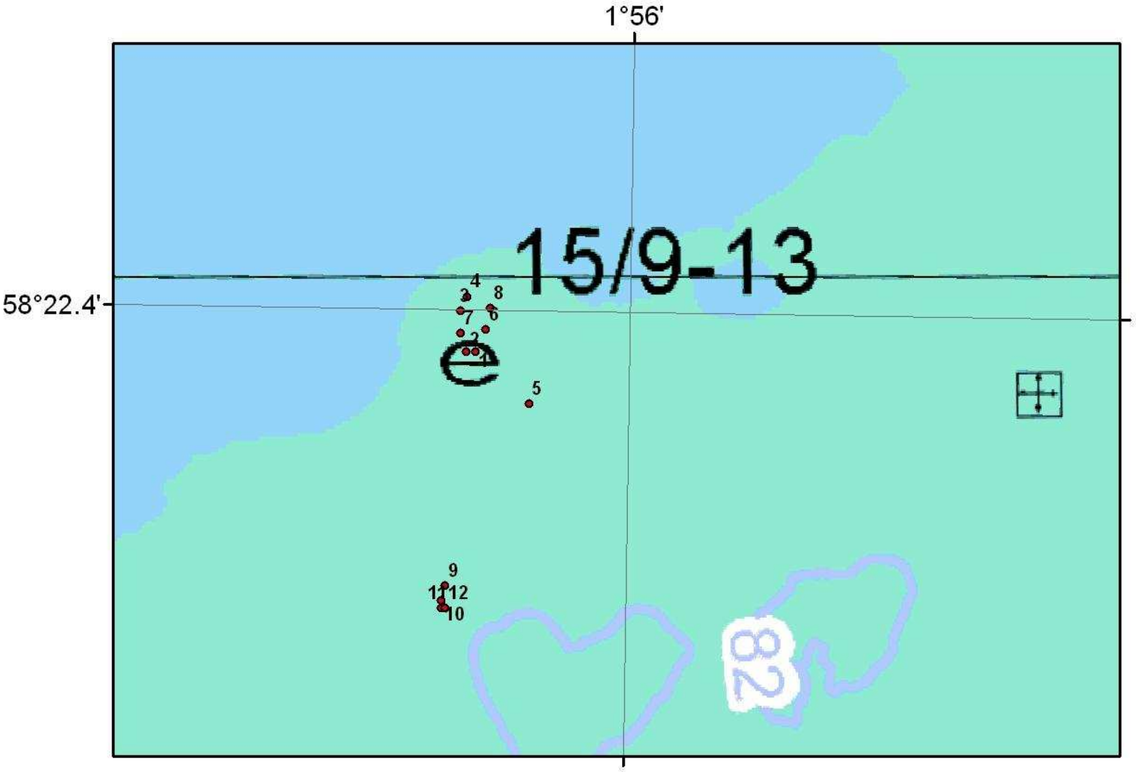

Fig. 4.1.3.3: Locations of niskin water samples (CTD 7: red circles) taken at the abandoned well 15/9-13.

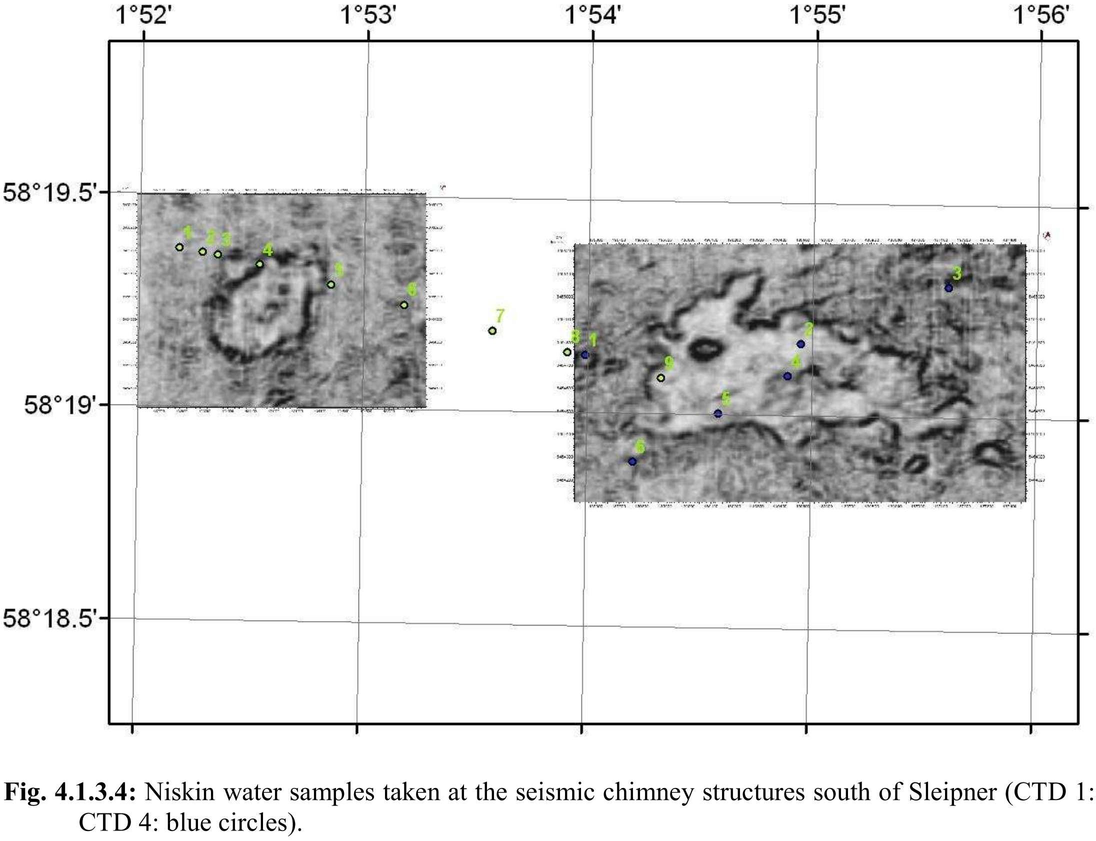

Fig. 4.1.3.4: Niskin water samples taken at the seismic chimney structures south of Sleipner (CTD 1: green circles; CTD 4: blue circles).

CTD measurement and water sampling at the Blowout area

A detailed sampling campaign for measuring dissolved gas concentrations and atmospheric methane concentrations at the «Blowout» site (well 22/4b, UK) was conducted on the 1st of August 2012. The aim is to quantify gas release from the seafloor, to monitor dissolved gas plume distributions, to identify (microbial) hydrocarbon degradation in the water column, and to estimate the methane contribution to the atmosphere at this site. Therefore 12 Niskin water samplers have been fired in each case at selected water depths in the vicinity of the blowout crater (Fig. 4.1.3.5). The selected depths are 84 mbsl (bottom view), 41 m (just below the thermocline), and 11 mbsl (above thermocline). Onboard gas release by head space extraction and subsequent gas chromatographic analyses showed concentrations ranging between 8 nM and 37 µM of CH_4 dissolved in seawater. Respective concentration patterns are plotted as colored contours in figure 4.1.3.6.

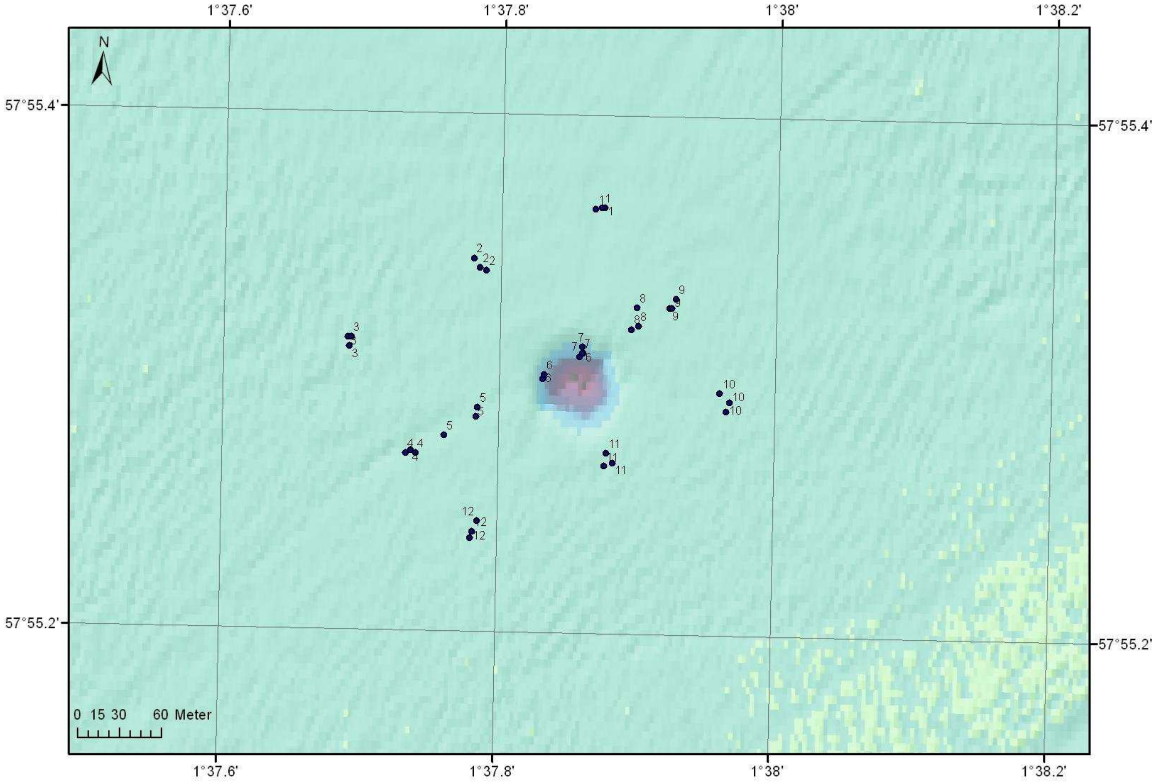

Fig. 4.1.3.5: Niskin bottles fired at the «Blowout» site (CTDs 8, 9, 10; Tab. 4.1.3.1). A hydrocast was conducted for background data 2200 m NE of the Blowout (CTD11).

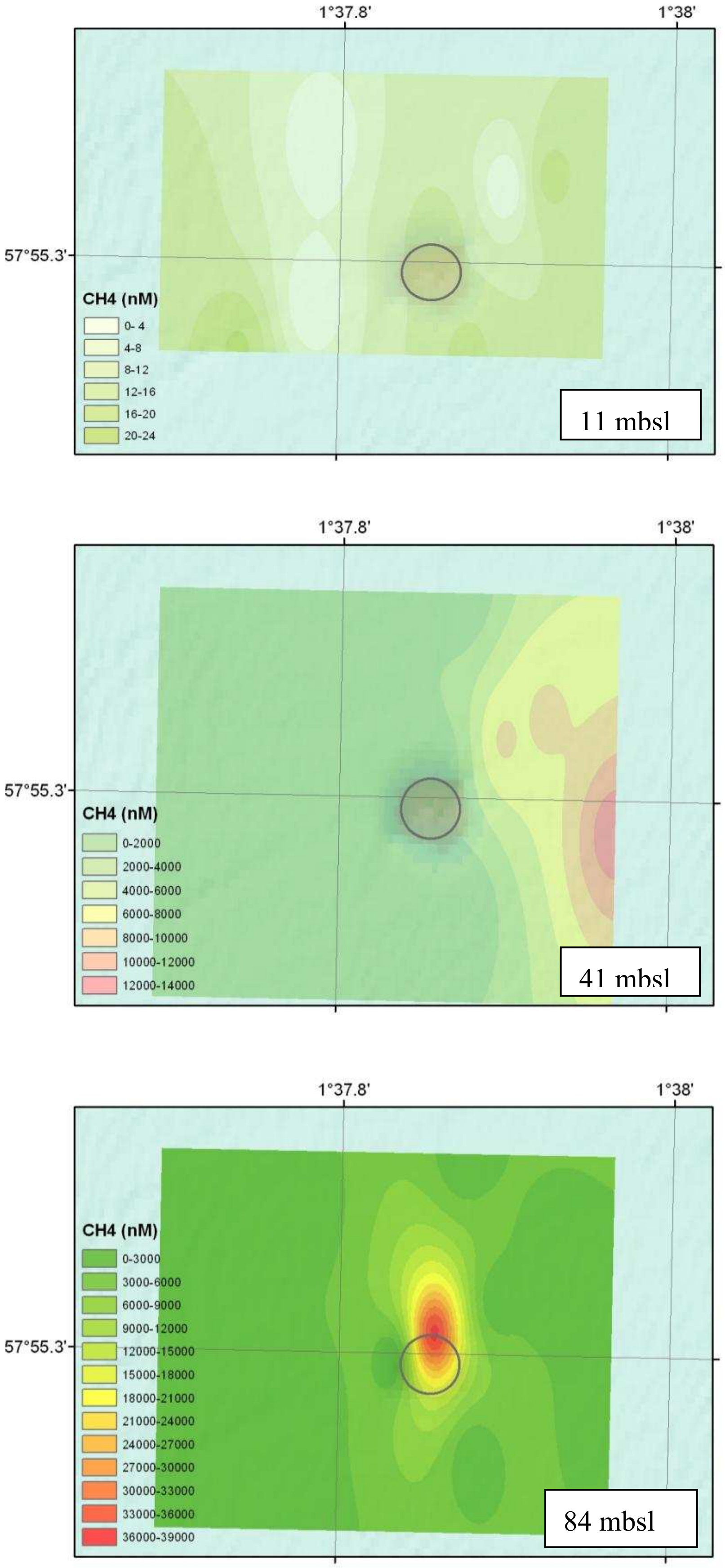

Fig. 4.1.3.6: Contour plots of dissolved methane concentration determined at about 84, 41, and 11 m below sea level («Blowout» site, UK).

In parallel to the Niskin sampling campaign atmospheric methane and CO_2 concentrations have been measured by using online cavity ring down spectrometry (Picarro). The range of measured methane concentration is shown in figure 4.1.3.7 (1.88-19 ppm). Highest atmospheric CH4 values were determined at various locations (Fig. 4.1.3.8). The complex pattern is probably controlled by the transport and mixing situation of the rising gas bubble plume (tides, currents) and the weather conditions. Fortunately, low wind and wave conditions occured during the sampling on the 1st of August.

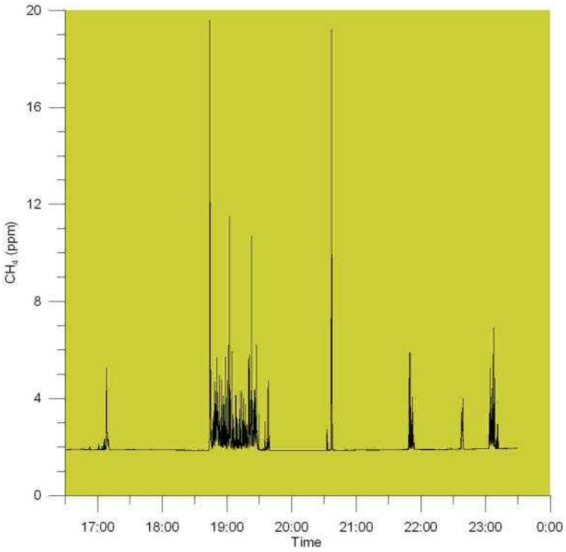

Fig. 4.1.3.7: Atmospheric methane concentration measured 2 m above sea level at the Blowout site (01.08.2012). Data is recorded in parallel to a water sampling campaign.

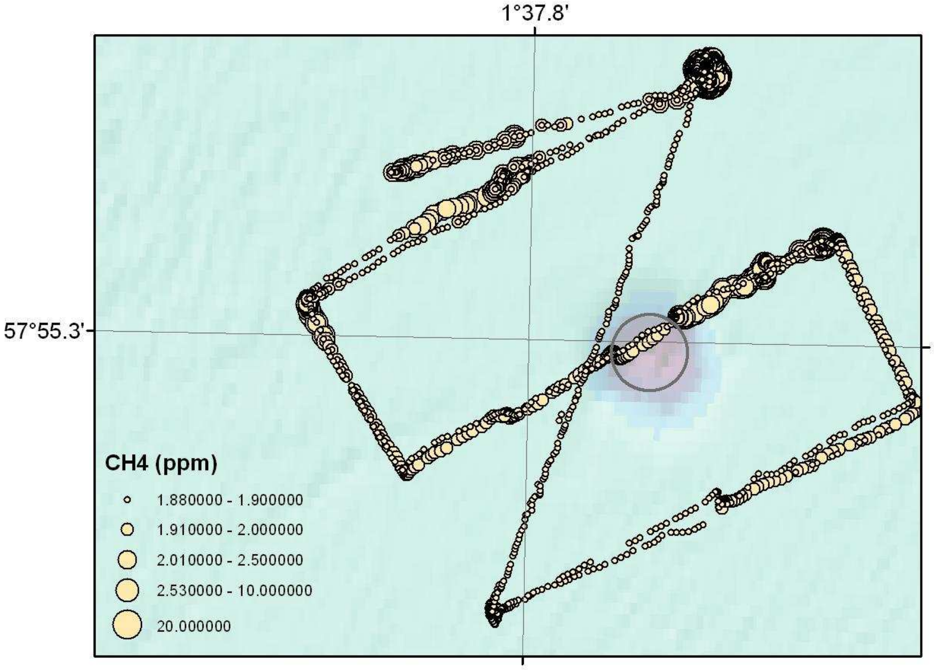

Fig. 4.1.3.8: Atmospheric CH_4 concentration (2 m above sea level) is plotted ontop of «Blowout» bathymetric map.

High Sensitive Methane Sensor (HISEM)

First results of the newly designed high sensitive CH_4 sensor (GEOMAR-Contros-Wintershall Noordzee joint project, MARTECH-program, BMWi funded) are presented in figures 4.1.3.9 and 4.1.3.10. CH_4 data was recorded by the sensor system during all ROV dives and one CTD station (Fig. 4.1.3.9). During ROV dives the sensor was connected to a flexible suction tube which was permanently pumped. The inlet of the suction tube was placed near the manipulator arm of the ROV6000.

The optical sensor shows a dynamic range of 1 ppm to ~30.000 ppm CH4. A selected detailed data set is plotted in figure 4.1.17. The ROV-mounted sensor system recorded data during ROV dive 6. The CH4 signal is increasing when approaching the «leaky» well (16/7-02) northeast of Sleipner. During gas bubble sampling and push core sampling on site the continuously recording sensor shows saturation. After leaving the seepage site the sensor shows nearly background methane data again. Considering the high sensitivity of the sensor even at low concentrations the HISEM was also used to select diffusive CH4 emanation sites at the seafloor (reproducable measured differences of ΔCH4 ~ 0.5 ppm). Therefor the suction tube inlet was placed near the seafloor (e.g. at bacterial mat). Selected sites were then sampled by using push cores for biogeochemical studies.

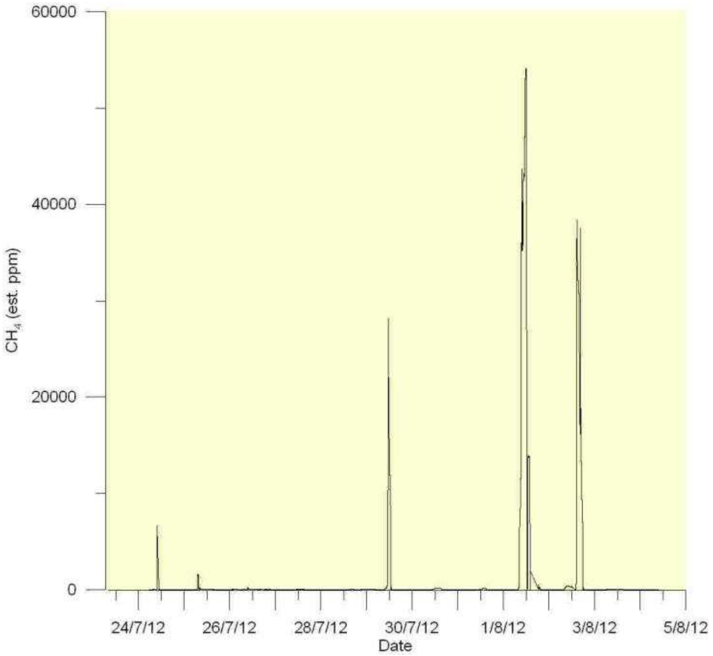

Fig. 4.1.3.9: CH_4 concentrations measured during CE12010 research cruise by using the ROV/CTD-mounted HISEM prototype.

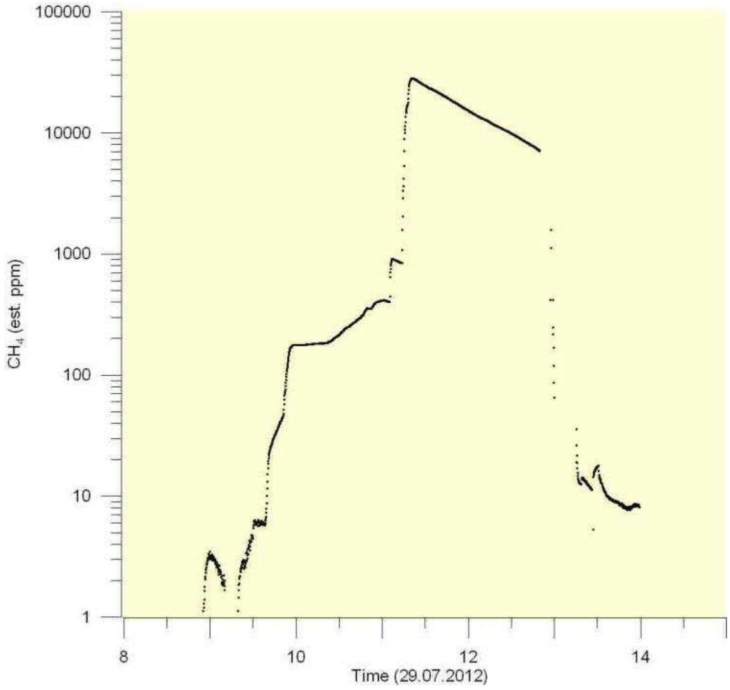

Fig. 4.1.3.10: CH4 concentration determined with ROV-mounted HISEM during ROV 6 dive (Station 20, 29.07.2012).

Porewater hydrocarbon composition at the fracture site

Headspace methane (C1) concentrations and higher homologues (C2+: ΣC2,C3,C4) were determined and plotted as ppmV ratios in figure 4.1.3.11. The variable (orders of magnitude) ratios at the different sampling sites probably indicate mixtures of hydrocarbons derived from thermogenic processes and methane formed by microbial processes. However, secondary microbial degradation and/or complex fluid migration superimpose the C1/C2+ ratios at the fracture site (Fig. 4.1.3.11; see also chapter 4.6).

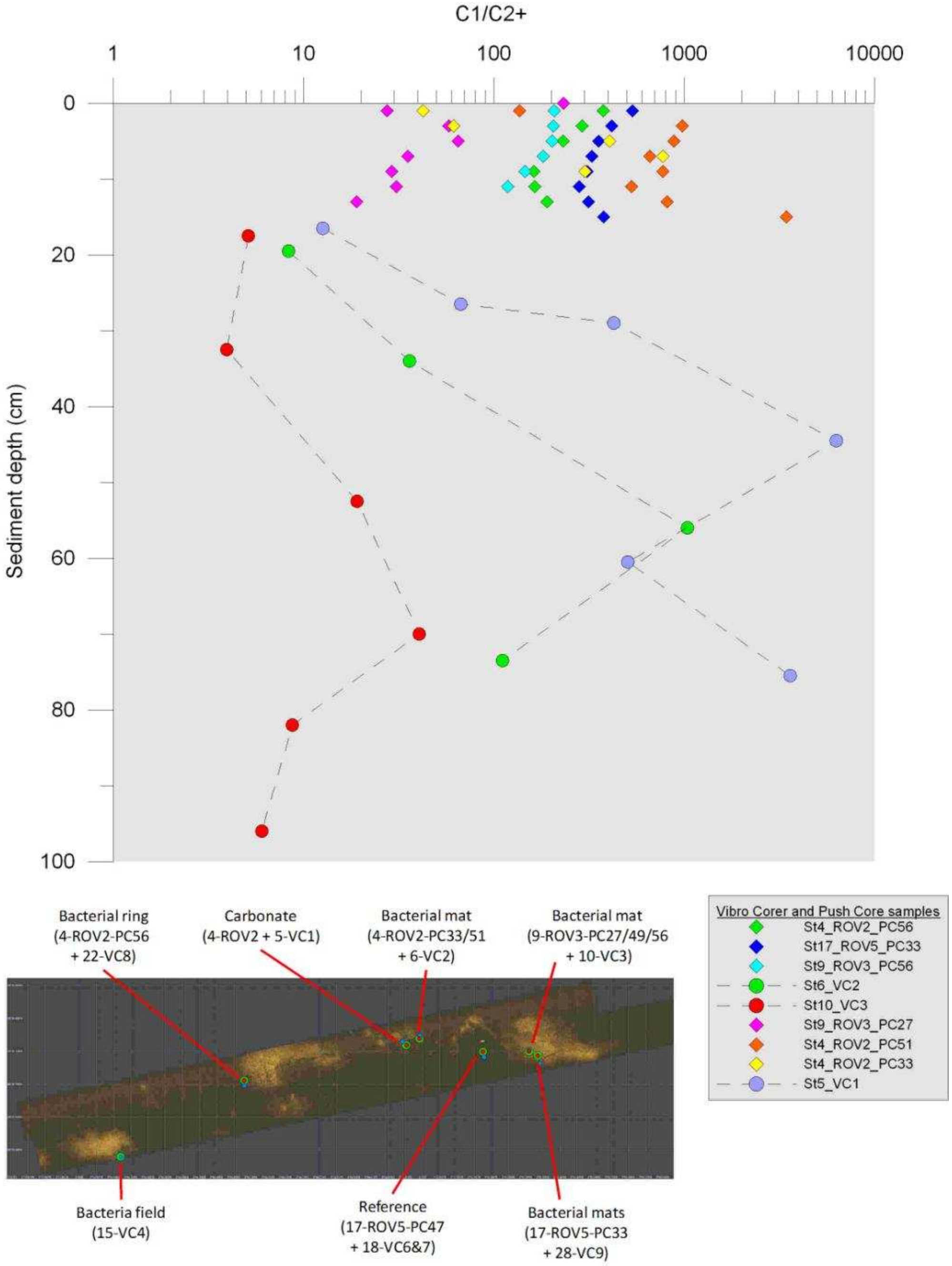

Fig 4.1.3.11: Preliminary data of hydrocarbon ratios (C1/C2+) of porewater samples from the fracture site, measured by head space gas chromatography.

Tab. 4.1.3.1: Niskin water samples taken during CTD-tracks and -hydrocasts (SBE9 recorded data set; «btl»-file data)

Station	CTD	Bottle	Time	Depth (m)	Temperature (°C)	Salinity (PSU)	Latitude (°N)	Longitude (°E)
3	1	1	23:56:13	83.2	7.7904	35.1310	58.32290	1.86960
		2	00:12:30	83.0	7.7899	35.1313	58.32274	1.87130
		3	00:23:55	82.8	7.7889	35.1315	58.32266	1.87242
		4	00:45:16	82.4	7.7868	35.1322	58.32230	1.87556
		5	01:06:45	81.4	7.7846	35.1333	58.32154	1.88092
		6	01:24:31	81.0	7.7822	35.1352	58.32080	1.88634
		7	01:46:11	82.9	7.7664	35.1478	58.31984	1.89295
		8	02:04:26	81.7	7.7625	35.1529	58.31906	1.89852
		9	02:27:16	81.8	7.7617	35.1573	58.31810	1.90550
7	2	1	21:21:16	90.6	7.6605	35.1925	58.58770	2.06542
		2	21:44:36	90.7	7.6597	35.1922	58.59074	2.06644
		3	22:12:15	89.9	7.6596	35.1914	58.59330	2.06960
		4	22:39:43	90.1	7.6589	35.1907	58.59506	2.07475
		5	23:13:32	91.2	7.6611	35.1897	58.59598	2.08246
		6	23:42:36	90.7	7.6651	35.1808	58.59574	2.08866
		7	00:41:54	90.8	7.6643	35.1893	58.59600	2.08874
		8	00:51:50	91.2	7.6640	35.1904	58.59626	2.08666
		9	01:45:25	91.0	7.6632	35.1920	58.59526	2.07448
		10	02:05:43	91.1	7.6649	35.1924	58.59378	2.07071
		11	02:16:49	91.4	7.6658	35.1924	58.59330	2.06815
		12	02:20:41	91.3	7.6667	35.1924	58.59318	2.06728
13	3	1	17:21:10	74.5	7.7911	35.1321	58.40620	2.02364
		2	20:26:06	76.1	7.8102	35.1558	58.40624	2.02392
		3	20:36:57	76.2	7.8100	35.1561	58.40618	2.02346
19	4	1	21:36:46	80.6	7.7694	35.1281	58.31894	1.89986
		2	23:54:05	80.3	7.7757	35.1258	58.31950	1.91587
		3	02:12:51	77.8	7.7953	35.1144	58.32180	1.92674
		4	03:04:26	77.8	7.7911	35.1153	58.31824	1.91492
		5	03:27:04	78.2	7.7941	35.1154	58.31672	1.90978
		6	03:55:01	79.0	7.8017	35.1156	58.31479	1.90345
25/26	5/6	1	17:03:37	76.5	7.8067	35.1357	58.40600	2.02358
		2	17:17:22	76.5	7.8068	35.1362	58.40604	2.02366
		3	20:41:59	76.8	7.8047	35.1348	58.40566	2.02278
		4	21:08:10	76.3	7.8012	35.1343	58.40594	2.02256
		5	00:02:57	76.7	7.8041	35.1307	58.39822	1.98978
		6	01:36:26	75.3	7.8067	35.1382	58.39324	1.96702
		7	02:27:47	74.1	7.7940	35.1196	58.39050	1.95454
		8	02:41:05	73.4	7.7912	35.1204	58.38972	1.95128
		9	03:21:44	73.7	7.7974	35.1154	58.38748	1.94150
31	7	1	17:47:28	80.3170	7.82270	35.1237	58.37322	1.93256
		2	18:23:08	80.47100	7.8284	35.1196	58.37322	1.93251
		3	18:26:48	80.53400	7.8278	35.1183	58.37333	1.93248
		4	18:27:41	80.52800	7.8278	35.1193	58.37337	1.93251
		5	19:56:26	80.77500	7.8324	35.1168	58.37308	1.93284
		6	20:03:31	80.52400	7.8289	35.1174	58.37328	1.93261
		7	20:15:23	80.61700	7.8289	35.1183	58.37327	1.93248
		8	22:07:40	80.61300	7.8135	35.1194	58.37334	1.93263
		9	22:45:39	58.31000	7.7985	35.1154	58.37258	1.93242
		10	22:46:36	44.55200	7.8244	35.1131	58.37254	1.9324
		11	22:47:54	24.40300	10.6457	34.9514	58.37252	1.9324
		12	22:49:05	4.60500	14.9725	34.5654	58.37252	1.93242

Station	CTD	Bottle	Time	Depth (m)	Temperature (°C)	Salinity (PSU)	Latitude (°N)	Longitude (°E)
37	8	1	16:50:48	85.12400	7.9739	35.149	57.92274	1.63127
		2	16:58:59	84.31200	7.9605	35.1458	57.9224	1.62971
		3	17:08:29	84.33600	7.9453	35.1413	57.92182	1.62822
		4	17:15:25	84.43400	7.9348	35.1391	57.92116	1.62898
		5	17:21:02	84.44700	7.944	35.1418	57.92138	1.62976
		6	17:26:25	84.61100	7.9368	35.1402	57.92163	1.63056
		7	17:30:43	84.74100	7.9474	35.1426	57.92178	1.631
		8	17:35:16	84.39200	7.9362	35.1404	57.92196	1.63162
		9	17:39:19	84.62600	7.9435	35.1426	57.9221	1.63208
		10	17:45:30	84.01900	7.9559	35.1462	57.92144	1.63278
		11	17:53:50	84.81000	7.9794	35.1535	57.9211	1.63142
		12	18:02:58	84.60100	7.9914	35.1577	57.92071	1.6298
38	9	1	19:35:38	43.4410	8.52580	35.1502	57.92274	1.63124
		2	19:57:26	42.98700	8.6633	35.1526	57.92234	1.62978
		3	20:07:37	40.94800	8.6653	35.1591	57.92188	1.6282
		4	20:15:01	41.22900	8.4376	35.1744	57.92114	1.62892
		5	20:18:34	41.26900	8.7662	35.1489	57.92126	1.62938
		6	20:28:53	41.23700	8.6971	35.1544	57.92166	1.63058
		7	20:34:44	41.31600	8.6934	35.1548	57.92184	1.63103
		8	20:40:02	41.06300	8.3823	35.1703	57.92198	1.6317
		9	20:48:07	41.36400	8.452	35.1698	57.9221	1.6321
		10	20:55:28	41.36500	8.5695	35.1536	57.9215	1.63282
		11	21:04:58	41.21400	8.7437	35.1531	57.92108	1.63132
		12	21:16:05	41.27400	8.3447	35.1596	57.9206	1.62972
39	10	1	22:27:29	12.75200	14.3517	34.8588	57.92273	1.63116
		2	22:36:35	10.61500	14.3814	34.8524	57.92232	1.62986
		3	22:45:58	10.97400	14.3875	34.8642	57.92188	1.62824
		4	22:53:58	10.80000	14.3705	34.8768	57.92114	1.62904
		5	23:00:03	10.85500	14.3853	34.8603	57.92144	1.62978
		6	23:11:35	11.08800	14.3937	34.8725	57.9218	1.63104
		7	23:11:46	10.95900	14.3895	34.8774	57.9218	1.63103
		8	23:17:54	10.49500	14.2926	34.9068	57.9221	1.63168
		9	23:22:52	10.45500	14.3935	34.8656	57.92216	1.63215
		10	23:29:15	10.86300	14.2002	34.9501	57.92156	1.6327
		11	23:38:17	10.72500	14.4005	34.8763	57.92116	1.63134
		12	23:47:46	10.59800	14.4018	34.883	57.92064	1.62974
42	11	1	18:24:28	85.1320	8.18100	35.2446	57.94016	1.64364
		2	18:24:30	85.00200	8.1814	35.2445	57.94016	1.64364
		3	18:28:38	40.68500	8.2949	35.1247	57.94014	1.64362
		4	18:28:39	40.61000	8.2991	35.1237	57.94014	1.64362
		5	18:30:34	10.65100	14.3407	34.9054	57.94016	1.64364
		6	18:30:36	10.59300	14.3406	34.906	57.94016	1.64364
45	12	1	14:52:14	78.5460	7.82720	35.1183	58.40624	2.02378
		2	14:53:37	78.50700	7.8253	35.1185	58.40624	2.0238
		3	15:15:25	78.81700	7.8239	35.1189	58.40619	2.02384
		4	15:19:58	79.58700	7.8252	35.119	58.40614	2.0238
		5	15:22:09	79.66800	7.8263	35.1184	58.40612	2.02372
		6	15:24:33	79.73900	7.8243	35.1185	58.40608	2.02378
		7	15:32:13	80.54100	7.8242	35.1185	58.406	2.02384
		8	15:38:41	80.35600	7.824	35.1188	58.4061	2.02382
		9	15:50:20	78.82300	7.8241	35.1187	58.40624	2.02378
		10	15:51:33	77.93900	7.8232	35.1187	58.40624	2.0238
		11	16:05:06	78.87800	7.8231	35.1187	58.40608	2.02384
		12	16:17:31	79.01200	7.8236	35.1184	58.40596	2.02378

Tab. 4.1.3.2: List of 250 ml water samples stored for DIC analysis.

CTD No/Niskin No..	Date	Station
CTD 4_NiBo2	28.07.2012	Sta.19
CTD 4_NiBo3	28.07.2013	Sta.20
CTD 4_NiBo4	28.07.2014	Sta.21
CTD 4_NiBo5	28.07.2015	Sta.22
CTD 4_NiBo6	28.07.2016	Sta.23
CTD 12_NiBo1	02.08.2012	Sta. 44
CTD 12_NiBo2	02.08.2012	Sta. 44
CTD 12_NiBo3	02.08.2012	Sta. 44
CTD 12_NiBo4	02.08.2012	Sta. 44
CTD 12_NiBo5	02.08.2012	Sta. 44
CTD 12_NiBo6	02.08.2012	Sta. 44
CTD 12_NiBo7	02.08.2012	Sta. 44
CTD 12_NiBo8	02.08.2012	Sta. 44
CTD 12_NiBo9	02.08.2012	Sta. 44
CTD 12_NiBo10	02.08.2012	Sta. 44
CTD 12_NiBo11	02.08.2012	Sta. 44
CTD 12_NiBo12	02.08.2012	Sta. 44

4.2. Lander Deployments

S. Sommer

4.2.1 Introduction

In order to assess whether carbon dioxide is released from a site at the abandoned well 15/9-13 (BIGO-II-1) and from a fracture located 25 km NE of the Sleipner CO_2 plume (BIGO-II-2) a BIGO type Lander (Biogeochemical Observatory) was deployed to measure fluxes of pCO_2, O_2 and CH_4.

4.2.2 Methods

The BIGO has been described in great detail by Sommer et al. (2009). In brief, the BIGO contained two circular flux chambers (internal diameter 28.8 cm, area 651.4 cm^2), herein referred to as chamber 1 (C1) and chamber 2 (C2). A TV–guided launching system allowed smooth emplacement of the observatories at selected sites on the sea floor. Approximately two hours after the observatories were placed on the sea floor the chambers were slowly driven into the sediment (~ 30 cm h^{-1}). During this initial time period, the water inside the flux chamber was periodically replaced with ambient bottom water. After the chamber was fully driven into the sediment, the chamber water was again replaced with ambient bottom water to flush out solutes that might have been released from the sediment during chamber insertion. From inside both chambers as well as from the ambient sea water water-samples were taken at defined time intervals using two different water sampling systems. Samples for the analysis of ions and total alkalinity were taken using glass syringes that were connected to each chamber and the ambient sea water using 1 m long Vygon tubes that prior to the deployment were filled with distilled water. Upon sampling this water dilutes the actual water-samples. During each BIGO deployment 8 syringe samples were taken from each chamber and the ambient sea water. For the gas analyses of pCO_2, CH_4, N_2 and Ar water was slowly pumped into about 1 m long glass tubes using peristaltic pumps. This method circumvents the problem of dilution delivering uncontaminated samples. During the BIGO deployments 4 samples were taken from each chamber at defined time intervals. Time series of oxygen inside and outside the chambers were measured using Aandera optodes that were calibrated prior to deployment. Gas analysis of pCO_2, CH_4, N_2 and Ar was conducted using Membrane Inlet Mass Spectroscopy (as described in section 4.1.2). The glass tubes were directly connected to the inlet avoiding any atmospheric contamination.

4.2.3 Preliminary Results

Preliminary results of oxygen and pCO_2 recorded during either BIGO deployment are depicted in Figure 4.2.3.1, indicating that all chambers operated successfully. The change of the slope of the oxygen recording during BIGO-II-1 chamber 1 (blue line) is likely caused by a failure of the stirrer. During the incubations the overlying water body did not become anoxic which otherwise could result in any artefacts. A linear decrease of oxygen was measured in all chambers whereat the sediments at the fracture were more reactive than at the abandoned well indicated by a steeper slope. As to expect pCO_2 increased with time conversely to oxygen.

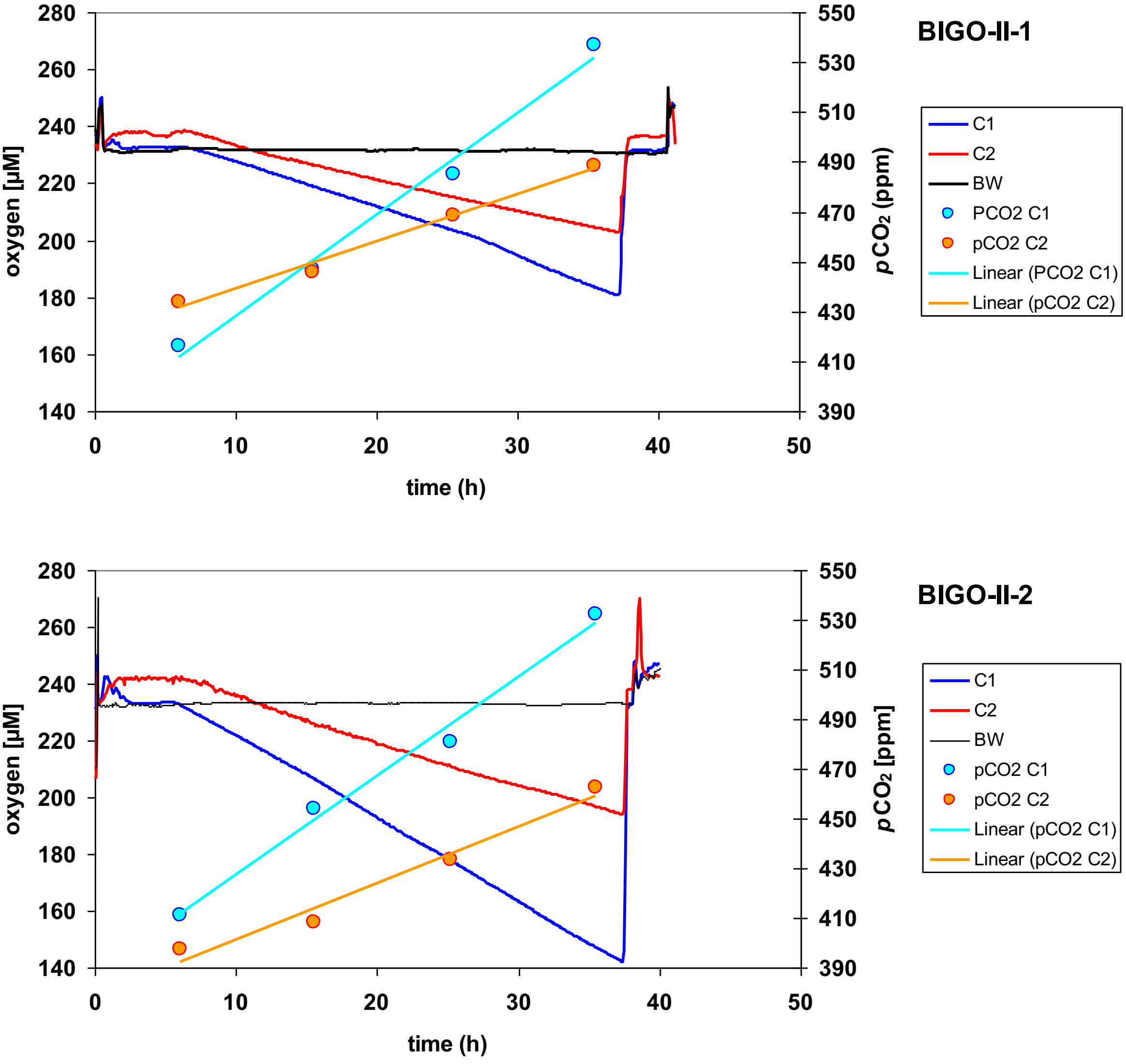

Fig. 4.2.3.1: Time course of pCO_2 (dots) and O_2 levels (lines) inside the benthic chamber 1 and 2 (C1, C2) and the bottom water (BW) during the deployment of BIGO-II-1 (abandoned well 15/9-13) and BIGO-II-2 (fracture 25 km NE to Sleipner CO_2 plume). Please note: the data are preliminary.

4.3 Gas Release Experiment

L. Vielstädte, S. Sommer, M. Schmidt, P. Linke, M. Haeckel

4.3.1 Introduction

With regard to potential leakage and monitoring of seabed CO_2 sequestration sites a gas release experiment has been deployed at the seafloor close to the "Sleipner West" platform. The objectives of the experiment were to quantify the dispersion of the dissolved CO_2 plume in the water-column and to test different geochemical monitoring devices at conditions present at "Sleipner" (MIMS, the Hydro-C sensor from CONTROS, and a pH-sensor). The collected data will be used for calibration of a newly developed Bubble Dissolution- and Plume Distribution Model, which aims to quantify gas fluxes and predict risk assessments on the marine ecosystem, depending on various leakage scenarios.

Three replications of the experiment were conducted during three days, where CO_2 and Kr (used as a tracer gas) were released on top of the elevator lander over 10 to 15 hours at varying flux rates (CO_2: 15- 50 L/min; Kr: 1- 3 L/min) and different initial bubble sizes (Tab. 4.3.1.1). The gas discharge was observed in-situ during ROV dives, equipped with HD video and a sonar system. The impact of the discharge was monitored geochemically in different distances and vertical heights downstream off the lander by a CO_2 sensor and pH sensor, both fixed on the ROV. Additionally, a video guided CTD investigated the spreading of the dissolved gas plume by chemical sensors onboard the CTD and by mass spectrometer analysis of the water flow pumped into the laboratory (MIMS). The local hydrodynamics were measured by a current measuring device (ADCP) and an eddy correlation device (ECM) deployed at the seafloor a few meters (10-20 m) from the lander.

Tab. 4.3.1.1: Conducted gas release experiments and engaged measuring devices.

Release Experiment	Date	Geographic position	Diffusor size	Release rate [L/min]	ADCP	MIMS	Hydro-C	pH	ECM	CTD
I	27.07.12	2°01.4" 58°24.4"	4 mm	CO_2: 15/25/50* Kr: 1	X	X	X	X	X	X
II	30.07.12	2°01.4217" 58°24.356"	4 mm	CO_2:25 Kr: 3	X	X	X	X	X	X
III	03.08.12	2°01.4300" 58°24.3599"	8 mm	CO_2: 30 Kr: 1.5	X	X	X	X	X	X

**Varying each 2h*

4.3.2 Material and Methods

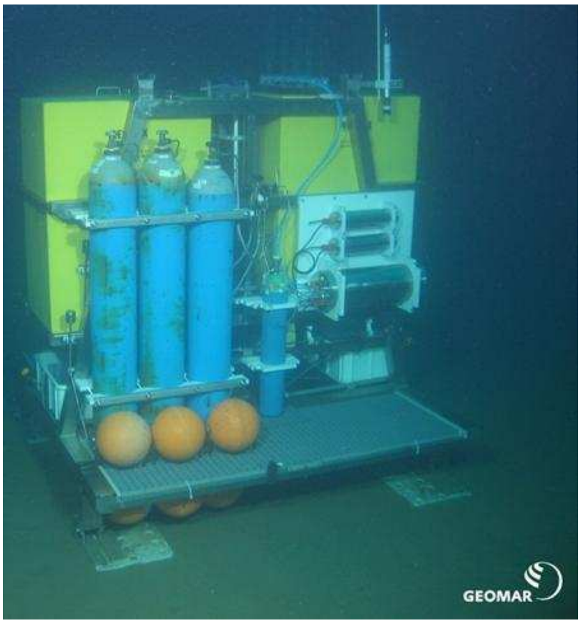

Fig. 4.3.2.1: Deployed Elevator Lander on the seafloor above the Utsira CO_2 storage formation.

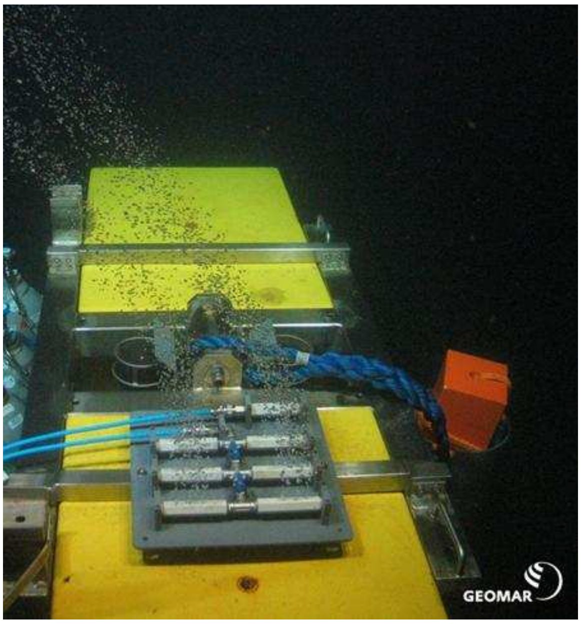

Fig. 4.3.2.2: Bubble streams of CO_2 and Kr released through perforated Teflon pipes on top of the Lander.

The Elevator Lander was used as platform for the experimental setup, which was equipped with a maximum of three CO_2 gas bottles and one smaller bottle of Kr (Fig. 4.3.2.1 and section 4.1.2). To reduce the pressure of the outflowing gas, the flow went through a spiral coil, which reduced the pressure from 57 bar inside the gas bottle to 20 bar, before the gas flow entered the heated pressure regulator, which further decreased the pressure to ~ 13 bar. Subsequently the gas was released through a heated flow controller (to avoid freezing of the system, due to the pressure decrease of CO_2) and six perforated Teflon pipes (CO_2) or rather one for Kr on top of the lander (Fig. 4.3.2.2). Each perforated pipe consisted of 3 holes acting as a bubble diffusor. The hole size of 4 mm in diameter remained constant during the first and second experiment and has been increased to a diameter of 8 mm before the third experiment started. The gas discharge rate of CO_2 changed every 2 hours from 15 to 25 to 50 L/min during the first experiment, while the gas release of krypton remained constant at 1 L/min. During the second and last experiment the gas flux remained stable for both, CO_2 and Kr (Tab. 4.3.1.1).
The local current regime was observed by a hydroacustic current meter (ADCP), which has been deployed at the seafloor a few meters away from the Lander (~20 m). During all experimental runs it measured the current direction and magnitude in 3-D, which is important for numerical modeling of the advective transport of the dissolved CO_2 plume in the water-column. The eddy correlation technique was used during the second and last experiment to measure turbulent fluxes, which are important for the dilution of the dissolved gas plume in seawater (see section 4.5).

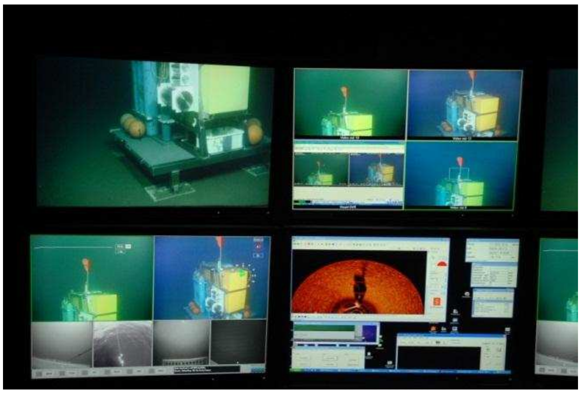

Fig. 4.3.2.3: Optical HD video and camera devices, as well as a sonar system on board the ROV enabled good navigation and tracking of the gas flare.

The gas discharge has been observed optically and geochemically during ROV dives and subsequent video guided CTD casts. The ROV "Kiel 6000" was equipped with geochemical (CO_2 and CH_4 sensor, and a pH sensor) and optical devices, which were used for in-situ geochemical surveying, as well as HD-video and camera observation of the bubble streams. The Hydro-C sensor from CONTROS was programmed to measure in 60 s intervals. The gained data of dissolved CO_2 and CH_4 values were transferred simultaneously into the ROV container onboard the research vessel. In addition to the sonar system of the ROV, the geochemical data enabled a good navigation and tracking of the plume (Fig. 4.3.2.3). For geochemical surveying of the near-field plume a horizontal and vertical grid was aligned downstream off the Lander (Tab. 4.3.2.1). The ROV abided at each measuring point for at least 10 minutes to ensure a true pCO_2 signal. Nevertheless, optimal positioning of the ROV directly downstream of the gas vent was temporally complicated, due to strong current activity, changing current directions (tidal shifts), and the limiting width of the plume. For detailed description of the plume surveying conducted by the MIMS, please look at section 4.1.2. For interpretation of the data it has to be kept in mind, that the thrusters of the ROV itself might have influenced the local hydrodynamics and thus, the dispersion and dilution of the dissolved gas plume.

Tab. 4.3.2.1 Points of measurement in meter above seafloor (asf) along the aligned horizontal and vertical grid downstream off the Lander by the pCO_2 sensor onboard the ROV (Red Cross = experiment I, blue cross = experiment II, and black cross = experiment III).

Distance to Lander [m]

Height asf [m]	1	2	3	4	6	7	8	9	10	11	12	13	15	20
0.3			x								x		x	x
1.5			x	x			x				x			
2.2		x	x											
2.7	x	xx	xx	x	x	x	x	x	x			x		
3			x				x				x			
3.2		x	xx											
3.7		x	x											
4			x											
4.20		x	x											
4.5							x				x			

4.3.3 Preliminary Results

The local current regime was strongly related to the tides with main directions to the NNE and SSW, whereas a net transport to the SW was predominant.

By optical observation generated initial bubble sizes of Kr and CO_2 could be roughly estimated to ~ 4- 8 mm in diameter (regarding to the different flow rates and diffusor sizes of the experiments).

The spatial extension of the dissolved gas plume was very limited and reached around 70-100 cm in width, which could be seen in the sonar. The Krypton bubble stream reached up to 27 m (sonar observation of Experiment III) from the bubble source, whereas the CO_2 bubbles disappeared optically between 1.50 m to 2.80 m above the Lander. CO_2 bubbles dissolve much faster than Kr bubbles, due to their higher solubility in seawater (CO_2 is ~ 18 times more soluble than Kr) explaining the different rising heights of the two gas streams. During ROV observations and downstream geochemical profiling maximal values of pCO_2 (up to 2320 μatm) were measured in 2.70 m height above the seafloor (50 cm above the gas source), decreasing with increasing distance to the gas source (Fig. 4.3.3.1 A). Close to the Lander enhanced pCO_2 values were also observed in 1.50 m height above ground (70 cm below the gas source), where the occurrence of a flow shade was likely to cause the downward suction of plume water. In 12 m distance enhanced bottom water values of pCO_2 were measured, which could be tracked up to 20 m away from the Lander. This observation might be either due to the density increase of CO_2 enriched plume water or is rather the effect of the Lander itself, which acted as a baffler in the local current regime. First numerical results of the local hydrodynamics, which have been realized with MULTIPHYSICS indicate that the Lander is likely reasonable for the observed down-welling of the plume, due to a reduction in the flow pressure field behind the Lander.

First bubble modeling results for pure CO_2 bubbles emerging with 4, 6, and 8 mm from the Lander indicate the rapid dissolution of CO_2 mostly within the first 1-2 m upon release, depending on the initial bubble size (Fig. 4.3.3.1 C). This generally coincides with the observed spread of the dissolved CO_2 plume. Bubbles at higher rising heights only contain N_2 and O_2, due to gas stripping from sea-water.

ROV observations of the third experiment were conducted during tidal shifting, where the current direction changed from 50° at the beginning of the measurement, to 190° at the end of the survey (Fig. 4.3.3.1 B). Thereby the whole plume rotated in the same direction without any significant changes in pCO_2 values or changes in the thickness of the plume. The interpretation of data gained by MIMS and video guided CTD casts is still in process.

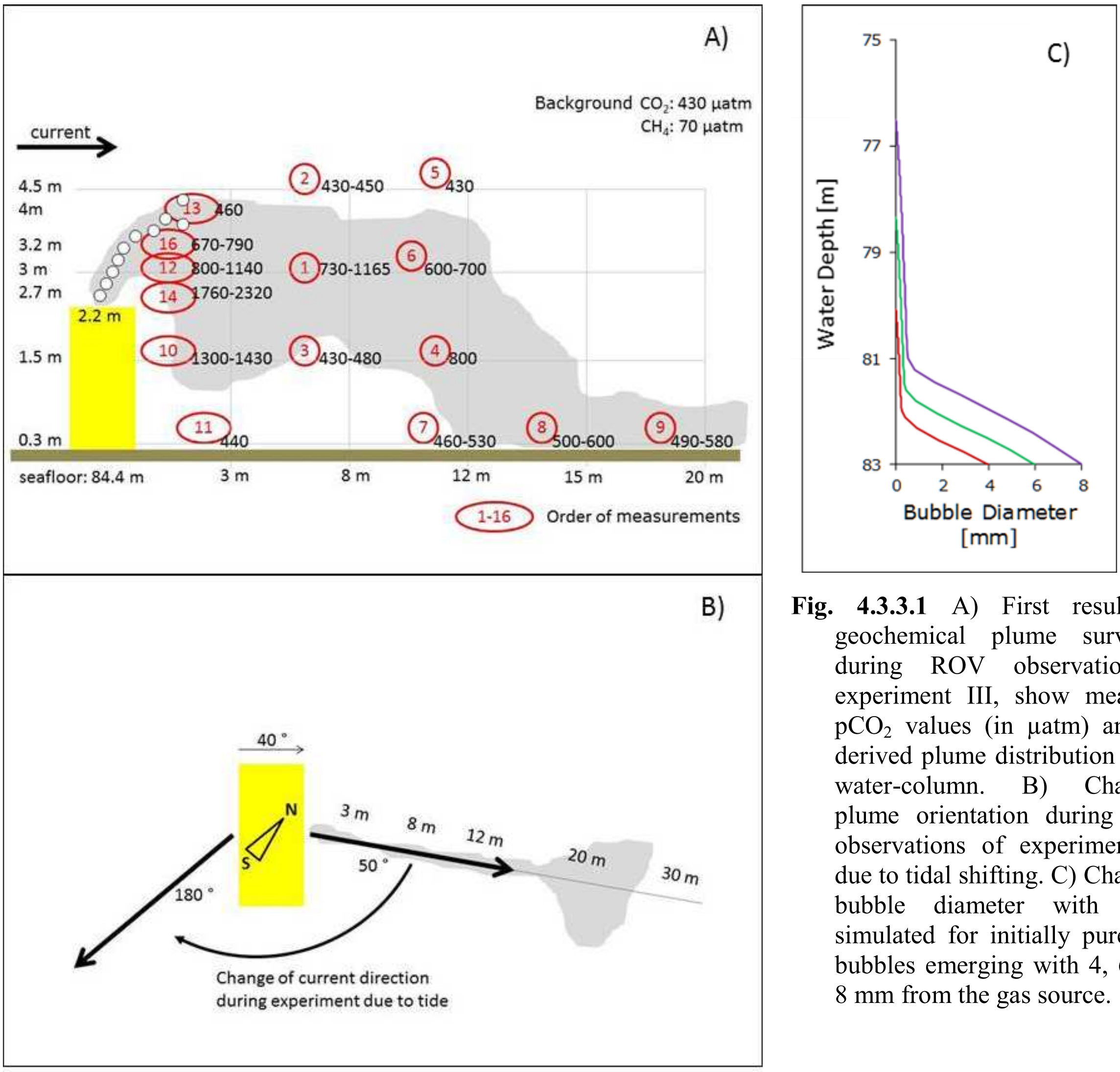

Fig. 4.3.3.1 A) First results of geochemical plume surveying during ROV observation of experiment III, show measured pCO_2 values (in µatm) and the derived plume distribution in the water-column. B) Changing plume orientation during ROV observations of experiment III, due to tidal shifting. C) Changing bubble diameter with depth simulated for initially pure CO_2 bubbles emerging with 4, 6, and 8 mm from the gas source.

Due to strong tidal currents and the fact, that the gas flux of each experiment was temporally limited to 10-15 hours, the dissolved gas plume occurred only in the near-field and did not developed a measurable far-field component, which is however likely to be expected in natural vent areas or during a long-term leakage scenario.

4.4. ROV Deployments

F. Abegg, M. Bodendorfer, P. Cuno, J. Hennke, M. Pieper, I. Suck

4.4.1 Introduction

The work class ROV KIEL 6000 was used for sampling of sediments, carbonates, bottom water, for obtaining on-line readings of a methane and CO_2-sensor, for observing a gas release experiment, and for deployment and recovery of autonomous instruments.

4.4.2 Methods

ROV KIEL 6000 is a 6000 m rated deep diving platform manufactured by Schilling Robotics LLC, Davis, USA. It is based on commercially available ROVs, but customized to our demands, e.g. being truly mobile. ROV KIEL 6000 has been operated from a variety of different national and international research vessels (RV Sonne, N/O l'Atalante, RV Maria S. Merian, RV Meteor, RV Celtic Explorer, RRS James Cook and RV Polarstern) until today. As an electric work class ROV of the type QUEST, this is build No. 7. ROV KIEL 6000 is based at GEOMAR in Kiel, Germany.

For shallow-water applications, like during this cruise, a 28 mm Aramid mantled cable (neutrally buoyant tether, 500m) is used, which is paid in and out manually, using a capstan winch (Fig. 4.4.2.1). For underwater navigation, the ship-based Sonardyne system was used with an autonomous transponder mounted on the light rack of the ROV. ROV KIEL 6000 is equipped with a tool skid containing 2 drawers onto which a variety of tools to customers demand can be mounted be equipped with (Fig.4.4.2.2).

Fig. 4.4.2.1: Decks-setup of ROV KIEL 6000 system using a 500 m tether cable (see right on capstan winch).

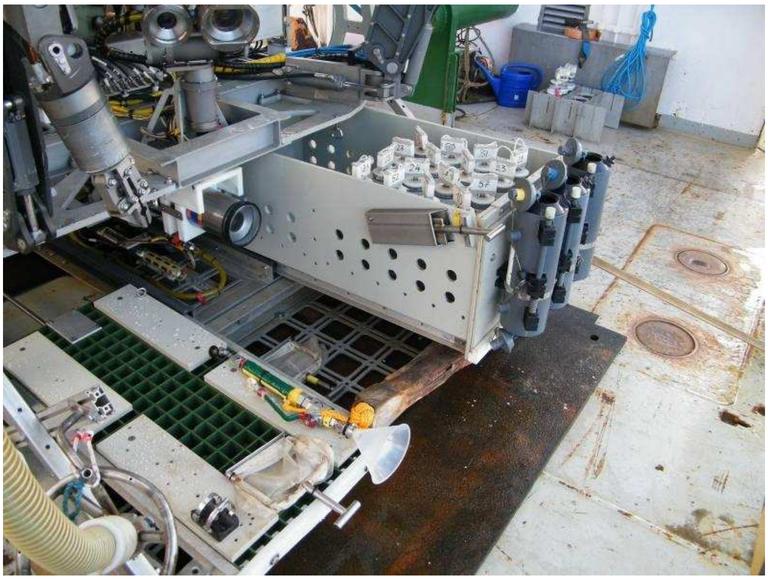

Fig. 4.4.2.2: ROV KIEL 6000 most common sampling set up with 16 push cores, 3 Niskin bottles, 2 nets and a gas-sampler on the front porch.

4.4.3 Preliminary Results

Including this cruise, ROV KIEL 6000 has accomplished 164 dives during 14 missions. During CE12010, 13 scientific dives (Tab. 4.4.3.1) were completed. Maximum diving depth was 120 m and maximum bottom time was 7:42 hours. In total, bottom time accumulated to approx. 56 hours (total dive time 61 hours).

Tab. 4.4.3.1: ROV station list CE12010 (all times in UTC).

Station No.	**Dive No.**	**Date**	**Time Start**	**At Bottom**	**Off Bottom**	**Time End (surface)**	**Location**	**Depth (m)**	**ROV Bottom Time**
	151	22.07.12	Harbour Test Bremerhaven						
01ROV01	152	24.07.12	06:45	07:03	09:35	09:45	Sleipner	82	02:32
04ROV02	153	25.07.12	06:54	07:10	14:52	15:07	Fracture 1	90	07:42
09ROV03	154	26.07.12	09:10	09:28	15:22	15:34	Fracture 2	90	05:54
12ROV04	155	27.07.12	10:47	10:57	14:52	15:05	Gas release 1	80	03:55
17ROV05	156	28.07.12	12:48	13:02	16:52	17:04	Fracture 3	92	03:50
20ROV06	157	29.07.12	09:22	09:48	12:43	12:53	Wellhead 16/7-02	80	02:55
24ROV07	158	30.07.12	10:25	10:37	15:18	15:37	Gas release 2	78	04:41
30ROV08	159	31.07.12	11:30	11:40	14:35	14:42	Recovery	80	02:55
32ROV09	160	01.08.12	07:16	07:33	13:50	13:57	Blowout	120	06:17
40ROV10	161	02.08.12	07:40	07:56	12:32	12:44	SE Crater	90	04:36
41ROV11	162	02.08.12	13:55	14:08	17:37	17:42	SE Creater real	110	03:29
44ROV12	163	03.08.12	06:20	06:30	12:52	13:01	Gas release 3	77	06:22
47ROV13	164	03.08.12	17:20	17:28	18:34	18:41	Recovery ADCP & Eddy	77	01:06
Total: 13 scientific dives									**56:14 h**

ROV KIEL 6000 was deployed at different stations in the Norwegian and the British Sector of the North Sea. One main goal was to explore the seafloor for gas seeps, indicated by bacterial mats. At selected bacterial mats, push cores (Fig. 4.4.3.1a) were taken for further microbiological and geo-chemical investigations.

A gastight gas sampler was deployed by the ROV on different occasions to collect samples for methane and/or CO_2 analyses (Fig. 4.4.3.1b).

Sensors for CH_4, CO_2 (both Contros) and pH were mounted on the ROV and partly integrated into the ROVs telemetry system, allowing on-line readings for real time control. A snorkel (Fig. 4.4.3.1c) enabled locally defined in-situ measurements.

The ROV was used for "bubble-watching" during a gas release experiment (Fig 4.4.3.1d) and at the same time for specific in-situ measurements of CO_2 contents by means of the Contros sensor mounted on the ROV.

Niskin bottles (Fig. 4.4.3.1e) mounted on one of the drawers of the ROV were used to collect samples of ambient water as well as methane and CO_2 enriched bottom water.

Carbonate crusts at a fracture zone, indicated by sonar images as well as large bacterial mats were sampled by means of nets and the ORION manipulator claw.

Fig. 4.4.3.1a: Push coring on bacterial mat at fracture zone.

Fig. 4.4.3.1b: Gas sampling at Sleipner.

Fig.4.4.3.1c: Fluid sampling on bacterial mat at fracture zone.

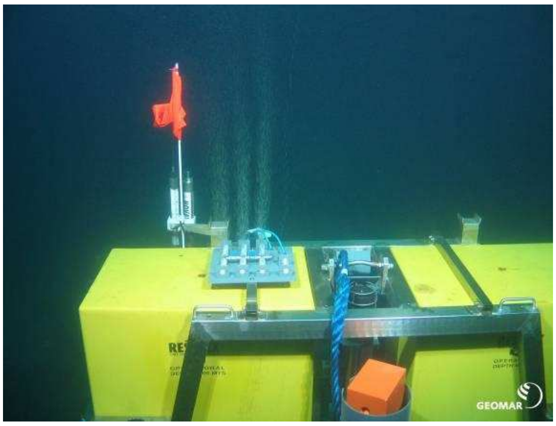

Fig. 4.4.3.1d: Observation of gas release experiment installed on GEOMAR Ocean Elevator (OCE).

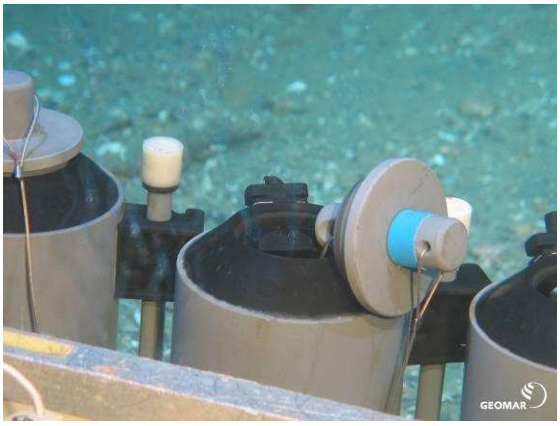

Fig. 4.4.3.1e: Niskin bottles on portside drawer.

Fig. 4.4.3.1f: Gas seep at Blowout site.

Fig. 4.4.3.1g: Push core sampling in near-vertical crater wall at blowout site.

Fig. 4.4.3.1h: Hook-wire-construction for recovering ADCP and anchor weights.

At the most southerly working station, the "Blow out", ROV KIEL 6000 went to the bottom of the crater and sampled gas (Fig. 4.4.3.1f), sediments (Fig. 4.4.3.1g), bottom water and alleged carbonate crusts. Two dives were conducted at another crater hole, southeast of the main crater. Here, gas, sediments and bacterial mats were sampled. Finally the ROV was used to recover weights and instruments from the seafloor using a hook-wire-construction (Fig. 4.3.3.1h). More details on individual dives and respective scientific results are given in the scientific chapters of this report. For more details on the ROV system please visit http://www.geomar /KIEL6000

Tools that were installed on and deployed by ROV KIEL 6000 during CE12010:

- CTD real-time probe (GEOMAR) (permanent)
- Cable cutting knife (GEOMAR) (permanent)
- Pushcores, 6 or 16 in portside drawer (GEOMAR) (optional)
- 5 litre Niskin bottles (GEOMAR) (optional)
- Hand-Nets (GEOMAR) (optional)
- Contros CH_4 and CO_2 sensors (GEOMAR/Contros) (optional / integrated)
- FSI / pH Sensor (GEOMAR) (optional/ autonomous)
- Gassampler (IOW) (optional)
- Additional sampling boxes (compartmented) (GEOMAR) (optional)
- Acoustic HOMER Beacon markers (GEOMAR) (optional)

4.5. Eddy Correlation Measurements

L. Bryant

4.5.1 Introduction and Overview of Data

O_2 is a primary constituent in aquatic ecosystem functions and variation in O_2 concentrations and corresponding biogeochemical fluxes are of particular interest in aquatic research (Lorrai et al. 2010, Bryant et al. 2011a,b). CO_2-stripping of O_2 in already-suboxic sediment environments paired with O_2 consumption via oxidation of enhanced levels of organic matter (due to CO_2-induced increases in mortality rates of marine organisms) can result in rapid depletion of O_2 and subsequent shifts in redox conditions which, in turn, lead to a cascade of detrimental effects for marine ecosystems (Ardelan and Steinnes 2009). Quantifying turbulent transport of dissolved substances (e.g., O_2) in aquatic environments is therefore critical for understanding physical and biogeochemical processes and how these processes are interrelated.

The eddy correlation method (ECM) has been used for over 50 years to measure constituent fluxes in the atmosphere (Lee et al. 2004) and is becoming a more routine and established measure of turbulent benthic fluxes at the sediment-water interface (SWI) in the bottom water of lakes and oceans (McGinnis et al. 2011). However, it is still a relatively new approach in aquatic systems, which was first implemented by Berg et al. (2003) to determine O_2 fluxes in coastal environments. Significant advantages of the ECM, as compared to more traditional flux-measurement techniques, are the capabilities to measure fluxes at high temporal resolution over a large (10-100 m^2) spatial footprint, to incorporate the influence of local hydrodynamics into flux characterization, and to obtain measurements at study sites where the terrain (e.g., rocky bottoms) makes it unfeasible to deploy traditional equipment (McGinnis et al. 2011). The ECM is thus ideally suited for obtaining flux measurements and capturing increased mixing effects associated with enhanced exchanges between acidified water and the surrounding environment at CO_2-seep sites (Caramanna et al. 2011); additionally, some of the key studies sites have been found to have relatively rocky terrain (McGinnis et al. 2011).

4.5.2 Methods

The eddy correlation system (ECS) used during the CE12010 expedition (Figure 4.5.2.1) was developed at GEOMAR and the temperature addition was developed within the context of a proposal to the cluster of excellence "Future Ocean". The ECS, following Berg et al. (2003), Lorrai et al. (2010), and McGinnis et al. (2011b), consists of a NORTEK Vector ADV (Acoustic Doppler Velocity meter), amplifier and housing, a fast-response O_2 sensor (response time < 0.3 s), a fast-response temperature sensor (response time < 0.01 s), and a deployment frame. In addition to the O_2 sensor required for characterizing variations in O_2 flux, equipping the ECS with a temperature sensor allows for characterization of bubble-induced water motion and heat fluxes by defining point velocities and temperature within bubble plumes. The frame is designed to be easily deployable using a remotely operated vehicle (ROV). CO_2 sensors compatible with the ECS have not yet been developed. As shown in Fig. 4.5.2.1, the ADV and sensors are mounted so that, upon deployment, measurements are obtained at 10-15 cm above the SWI. An O_2 optode was attached to the deployment frame at approximately 10 cm above the SWI to verify O_2 microsensor measurements for each ECS deployment.

The concept of the ECM is relatively straight-forward in that, by measuring and correlating vertical velocity fluctuations (v) with fluctuations of the constituent of interest (C; e.g., O_2), the instantaneous exchange flux can be estimated via the product (v × C) of these two parameters (Lorrai et al. 2010). The resulting net exchange flux characterizes flux directed towards (e.g., O_2 consumption, heat loss) or away from (e.g., O_2 production, heat gain) the sediment.

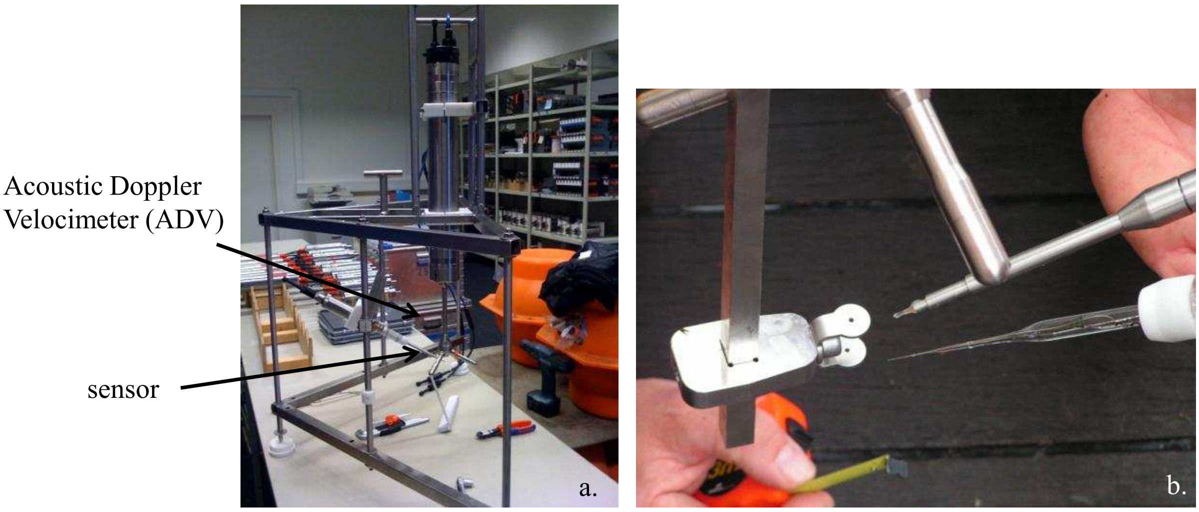

Fig. 4.5.2.1: Eddy correlation system (ECS) on deployment frame (a). A fast-response O_2 and temperature sensor are positioned below the ADV to define the measurement volume for flux estimates (b).

4.5.3 Preliminary Results

During the CE12010 cruise, an ECS was deployed via ROV during two of the CO_2-release experiments to measure variations in sediment O_2 consumption (flux) both during and following the periods of CO_2 release. To our knowledge, this was the first time the ECS was used in conjunction with a controlled CO_2-release experiment. The ECS was deployed on July 30 for ~24 hrs at ~10 m from the CO_2 release site. The ECS was deployed a second time on August 3 for ~12 hrs at ~20 m from the release site. The ECS was equipped with an O_2 and temperature sensor during both deployments. Unfortunately, the O_2 sensor did not work properly during the second deployment so O_2 flux estimates are not possible from these data.

Although conceptually the ECM is a simple technique, the process involved with accurately estimating fluxes is non-trivial. Flux calculation can become complicated due to the extremely large size of the resulting datasets and the need for linear detrending. However, preliminary O_2 flux estimates for the CO_2-release period during the first deployment are presented in Figure 4.5.3.1. While vertical flow velocities and O_2 fluxes remained relatively low during this period, there is good correlation between these two parameters with enhanced (more negative) O_2 flux typically occurring during periods of increased velocity. We suspect most of the O_2 consumption (i.e., negative flux) may be a result of the CO_2 bubbles stripping O_2 from the water column, O_2 demand from labile organic matter, and/or re-oxidation of highly reduced substances released from the sediment. Caution should be used, though, in interpreting these flux values as the results are preliminary and final sensor calibrations must still be performed.

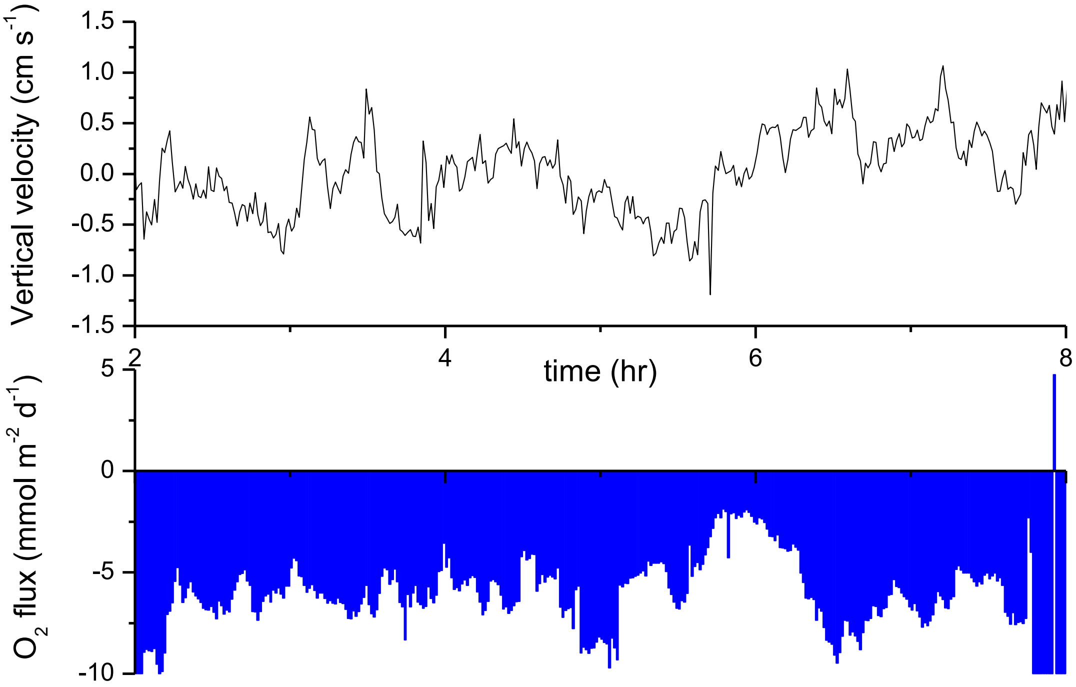

Fig. 4.5.3.1: Preliminary results showing variation in vertical velocity (top) and O_2 flux (bottom) at ~10 m away from a controlled-CO_2-release site during the CE12010 expedition.

4.6 Porewater and Sediment Geochemistry

M. Haeckel, M. Dibbern, D. Schroller, L. Vielstädte

4.6.1 Introduction

The geochemical analyses of the porewaters and sediments at the fracture north of Sleipner and the leaky wells and blowout sites aim to quantify methane fluxes and turnover rates of associated biogeochemical processes as well as the investigation of gas and fluid sources venting in these areas. At the fracture the main goal is to determine whether there is any connection to the CO_2 injection at Sleipner West into the Utsira formation. Therefore, a comprehensive geochemical dataset has been collected on this cruise.

Onboard, the collected samples were analysed for their content of NH_4^+, PO_4^{3-}, SiO_4^{4-}, H_2S, total alkalinity, and ex situ pH. In addition, sub-samples were taken for further shore-based analyses: DIC content and its $\delta^{13}C$ isotope ratio, dissolved metal cations, NO_3^-, SO_4^{2-}, Br^-, Cl^-, and I^- concentrations, dissolved hydrocarbon concentrations and their isotopic composition, isotopic ratios of Sr, Cl, Li, H, and O in the porewater, porosity and calcium carbonate, POC, PON, and total sulfur content of the solid phase (Tab. 4.5.1). 21 cores were taken at 14 stations and, in addition, water samples from two BIGO2 deployments (stations 8 + 27) and two CTD casts (stations 25/26 + 45) were analysed for total alkalinity and partly for ammonium and silicate. A total of 245 samples were collected. The sampling locations were primarily chosen based on SAS backscatter information from the Norwegian colleagues of University of Bergen and ROV observations of bacterial mats and black sediment spots that suggested potential fluid and gas seepage.

4.6.2 Materials and Methods

Sediment and porewater sampling

Surface sediment samples were retrieved using a ROV-operated push cores (PC) and a vibro corer system (VC). The Geo-Corer 6000 (provided by the Geological Survey of Ireland) is a high frequency, electrically driven, vibro corer system capable of fast penetration of all common seabed sediments, ranging from compact sands to stiff clays. It takes cores in PVC liners of 6 m length and 106 mm inner diameter. The sediments were extruded out of the PC plastic liners with a piston and cut into 2 cm thick slices, while the VC cores were cut in half and ~3 cm thick slices were taken in approximately 20-40 cm intervals. Subsequently, the porewater was extracted at ambient room temperature (~19 C) using a low pressure-squeezer (argon at 3-5 bar, sometimes up to 7 bar). While squeezing, the porewater was filtered through 0.45 µm regenerated cellulose Whatman filters and collected in recipient vessels. About 5 ml of wet sediment of each sediment slice was collected for porosity, carbonate and CNS element analyses at home. Aliquots of the extracted porewater were sub-sampled for various onboard and further shore-based analyses (Tab. 4.5.1). Subsamples for ICP-AES analysis were acidified with 30 µl of conc. suprapure HNO_3 per 3 ml of porewater sample (i.e., pH<1) and subsamples (~2 ml each) for $\delta^{13}C$ and DIC were treated with 10 µl of $HgCl_2$ to inhibit further microbial degradation. All of these samples for home-based analyses were stored refrigerated. An additional 3 ml of wet sediment were subsampled with a cut-off syringe from each sediment slice for headspace methane gas analyses (see section 4.1.2).

Porewater analyses

Analyses for the nutrients NH_4^+, PO_4^{3-}, SiO_4^{4-} as well as H_2S were completed onboard using a Hitachi UV/VIS spectrophotometer. The respective chemical analytics followed standard procedures (GRASSHOFF et al., 1999), i.e. ammonium was measured as indophenol blue, phosphate and silicate as molybdenum blue, and sulfide as methylene blue. The total alkalinity of the porewater was determined by titration with 0.02 N HCl using a mixture of methyl red and methylene blue as indicator. The titration vessel was bubbled with argon to strip any CO_2 and H_2S produced during the titration. The IAPSO seawater standard was used for the calibration of the method. The ex situ pH was measured with a glass electrode directly submersed into the wet sediment. The pH electrode was calibrated using the AMPY and BIS pH buffer solutions in artificial seawater according to Dickson (1993a; 1993b). The analytical precision and accuracy of each method are given in Table 4.6.3.2.

4.6.3 Preliminary Results

In all research areas (see chapter 1) sediment cores were collected and analyzed, however, the prime area of interest of the geochemistry group was the large fracture ~25 km north of the Sleipner CO_2 injection point where seepage of reduced fluids, methane and bacterial mats is abundant all along this structure. Surface sediments collected with PCs and VCs will allow calculating methane and fluid fluxes as well as rates of anaerobic oxidation of methane (AOM) and constraining the fluid and gas sources.

Fracture

At the fracture 5 sites with bacterial mats, 1 site with a carbonate rock on the seafloor and 1 reference site 50 m south of the fracture were cored (Fig. 4.6.3.1). The locations were chosen based on visual observations during the ROV dives and details of the coring are given in Figure 4.6.3.2. The sediments consisted of sand throughout the core. The upper 10-20 cm of the sediment below bacterial mats as well as of cores in the near vicinity of those mats were typically black, likely due to high FeS contents, and also smelled of H_2S. As larger vent fauna, plenty of polychaetes and their calcareous tubes were frequently found in the top 10-15 cm of the black sediments and among the bacterial mats. No living clams or tube worms were observed. The black sediments were covered by a very thin cover of brownish sediment, sometimes the black sediment was exposed directly on the seafloor, likely due to bioturbation from ubiquitous crabs and flat fish. The black sediment layer was usually followed by a 5-10 cm thick layer of shell hash from clams and sea urchins (in about 30-40 cmbsf in the vibrocores). From this shell layer downwards the sandy sediment was of gray colour. In the vibrocores, a second shell layer was found in about 60-70 cmbsf. Outside the fracture the greenish-brownish sand with little brown grains were found instead of the black sediment. The transition to gray sand was typically observed below the upper shell layer. These shell layers suggest that the area around the fracture has been a paleo-beach, likely during the last glaciations (e.g., Carr et al., 2006).

As expected, at the fracture total alkalinity (TA) is produced in considerable amounts (5-12 meq/l; Fig. 4.6.3.3) from anaerobic methane oxidation (AOM) and particularly below thicker bacterial mats higher TA concentrations as well as a pronounced maximum are observed 4-10 cm below the sediment surface (see Fig. 4.6.6, upper panel). The reference situation is characterized by a moderate TA increase from 2.3-2.5 meq/l to ~3.5 meq/l at around 40-50 cm depth (Fig. 4.6.3.4), indicating degradation of particulate organic carbon (POC) utilizing manganese(IV) and iron(III) oxy-hydroxides. Ammonium and phosphate concentrations, produced during POC degradation, generally stay relatively low around 20-30 µM and 5-25 µM (Figs. 4.5.5 and 4.5.6), respectively. Only at a few bacterial mats, the porewater carries higher NH_4 concentrations of up to 400 µM (Fig. 4.6.3.4; the bacterial ring and 2 bacterial mats, 4-ROV2-PC56 and 9-ROV3-PC27/56, Fig. 4.6.3.5). At the bacterial ring (4-ROV2-PC56) the salt concentrations increase slightly downcore (e.g., Cl of up to 600 mM; Fig. 4.6.3.6) indicating pore fluid advection from greater depths. In contrast, at the 2 easternmost bacterial mats (9-ROV3-PC27/56 & 17-ROV5-PC33) pore fluids are depleted in salts (e.g., Cl of 460 mM; Fig. 4.6.3.7) and the profiles show a clear downward curvature indicating pronounced upward fluid flow (not shown). The relative salt composition of the pore fluids stays around seawater Na/Cl ratio (~0.86) in both cases (Fig. 4.6.3.7). Potassium and lithium exhibit a stronger depletion in the deep fluid when compared to chloride (Fig. 4.5.7). Also Ca is strongly depleted in all pore fluids due to carbonate precipitation induced by the TA increase from AOM and Mg roughly follows this Ca trend (Fig. 4.6.7). The depletion in SO_4 from AOM also seems to induce some barite dissolution (Haeckel, 2006) as indicated by the release of Ba to the porewater (up to 5 µM; Fig. 4.5.7). Despite some scatter in the data the intrusion of seawater into the shallow surface of the sand (5-15 cm) by either bottom currents and or fluid convection from the fluid flow is obvious.

Abandoned Wells & Blowout Craters

In general similar porewater trends than at the fracture can be observed at the abandoned wells and the two blowout craters (Figs. 4.6.3.5 and 4.6.3.6). Background POC degradation seems to be a little more active at the blowout crater as more NH_4 and also more TA are released into the porewater within the upper 20 cm, up to 100 µM and 3 meq/l (Fig. 4.6.3.5), respectively. The most active bacterial mat, in terms of AOM, was also found at one of the wells, i.e. 16/7-2 (Fig. 4.6.3.6, red curve in top panel). No clear salt depletions or enrichments were observed in cores from the well and blowout sites (Fig. 4.6.3.7).

The surface sediments at these sites were sandy as well, but showed a higher clay content, which made push coring easier. In the blowout craters clayey sediments dominated by far.

Tab. 4.6.3.1: List of retrieved sediment cores and sub-samples collected for geochemical analyses.

Station Device	Area	Latitude (N)	Longitude (E)	Water depth / m	PW	NO_3^-	CH_4	Poros + CNS	IC	ICP-AES/MS	DIC $\delta^{13}C_{DIC}$	Iso	Length of core / cm	No. of samples
1-ROV1 PC9	Well 15/9-13	58°22.394'	01°55.950'	77.2	X	X	X	X	X	X	X	X	15.5	9
4-ROV2 PC33	Fracture	58°35.769'	02°04.990'	94.6	X	X	X	X	X	X	X	X	10.5	6
4-ROV2 PC51	Fracture	58°35.769'	02°04.990'	94.6	X	X	X	X	X	X	X	X	18.0	9
4-ROV2 PC56	Fracture	58°35.706'	02°04.480'	94.6	X	-	X	X	X	X	X	X	17.0	8
5-VC1	Fracture	58°35.765'	02°04.942'	87.4	X	X	X	X	X	X	X	X	79.0	5
6-VC2	Fracture	58°35.774'	02°04.992'	87.4	X	X	X	X	X	X	X	X	77.0	4
9-ROV3 PC27	Fracture	58°35.750'	02°05.310'	88.6	X	X	X	X	X	X	X	X	15.5	8
9-ROV3 PC56	Fracture	58°35.750'	02°05.310'	88.6	X	X	X	X	X	X	X	X	15.5	8
9-ROV3 PC49	Fracture	58°35.750'	02°05.310'	88.6	X	X	X	X	X	X	X	X	17.0	9
10-VC3	Fracture	58°35.740'	02°05.297'	92.5	X	X	X	X	X	X	X	X	98.0	6
15-VC4	Fracture	58°35.590'	02°04.121'	87.8	X	X	X	X	X	X	X	X	52.0	5
17-ROV5 PC33	Fracture	58°35.744'	02°05.335'	88.6	X	X	X	X	X	X	X	X	17.5	9
17-ROV5-PC47	Fracture reference	58°35.750'	02°05.175'	88.6	X	X	X	X	X	X	X	X	19.5	10
18-VC7	Fracture reference	58°35.740'	02°05.179'	88.6	X	X	X	X	X	X	X	X	100.0	11
20 ROV6 PC57	Well 16/7-02	58°28.401'	02°01.952'	80.0	X	X	X	X	X	X	X	X	19.0	10
22 VC8	Fracture	58°35.698'	02°04.481'	87.9	X	X	X	X	X	X	X	X	73.0	7
28 VC9	Fracture	58°35.732'	02°05.341'	88.0	X	X	X	X	X	X	X	X	98.0	10
32 ROV9 PC33	Blowout Well 22/4b-4	57°55.293'	01°37.859'	121.7	X	-	X	X	X	X	-	X	19.0	9
32 ROV9 PC28	Blowout Well 22/4b-4	57°55.291'	01°37.856'	120.9	X	-	X	X	X	X	-	X	17.0	10
32 ROV9 PC35	Blowout Well 22/4b-4 reference	57°55.270'	01°37.888'	99.4	X	X	X	X	X	X	-	X	20.0	11
41-ROV10/11 PC25	SE blowout crater	57°54.797‘	01°38.708‘	98.2	X	-	X	X	X	X	-	X	21.0	11

Locations of PCs are ROV-coordinates and those of VCs are ship coordinates, i.e. the exact VC position on the seafloor is not known.

PC = push core; VC = vibro core; PW = onboard porewater analyses of TA, H_2S, NH_4, PO_4, SiO_4, ex situ pH; CH_4 = dissolved hydrocarbons (CH_4, and higher alkanes) and $\delta^{13}C_{CH4}$, δD_{CH4}; Poros = sediment porosity; CNS = sediment $CaCO_3$ and C, N, S, element concentration; IC = ion chromatography (SO_4, Br, Cl, I); ICP-AES/MS = inductively-coupled atomic emission spectroscopy and mass spectrometry (for various dissolved cations); Iso = Isotope ratios of porewater O, H, Cl, Sr, Li.

Tab. 4.6.3.2: Analytical methods of onboard geochemical analyses.

Parameter	Method	Detection limit	Analytical precision/accuracy
H_2S	UV/VIS photometry	1 µmol/l	3 %
NH_4^+	UV/VIS photometry	2 µmol/l	5 %
PO_4^{3-}	UV/VIS photometry	1 µmol/l	5 %
SiO_4^{4-}	UV/VIS photometry	5 µmol/l	2 %
ex situ pH	Glass electrode	-	0.1
TA	HCl Titration	0.01 meq/l	2 %

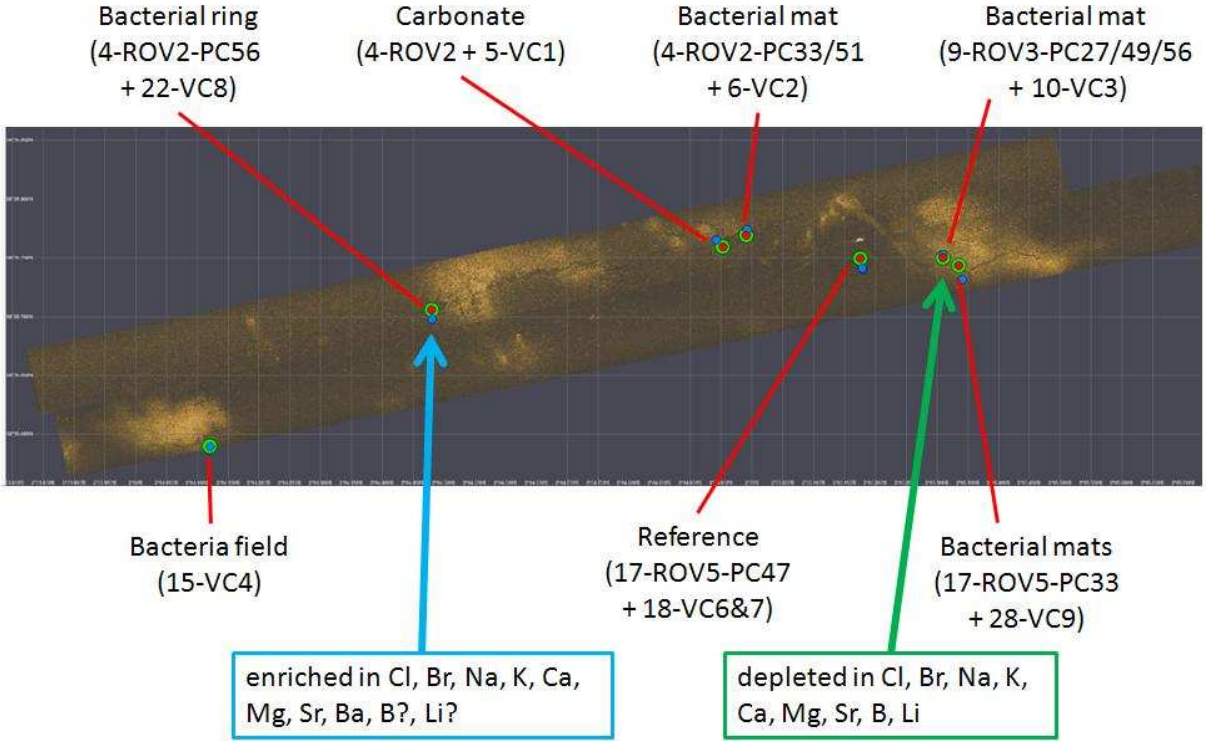

Fig. 4.6.3.1: PC (red) and VC (blue) coring locations at the fracture, ~25 km north of Sleipner.

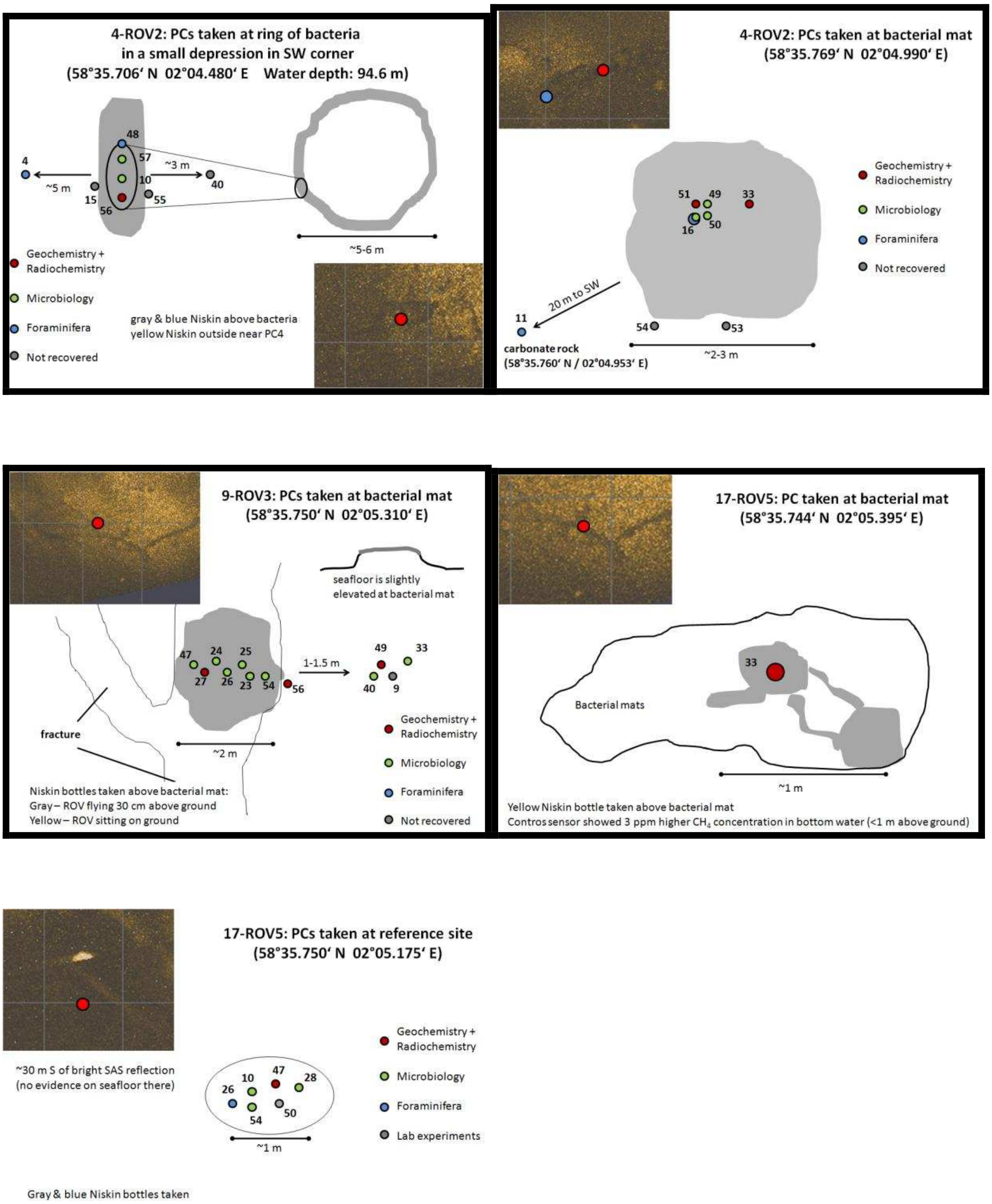

Fig. 4.6.3.2: Details of the push coring at the fracture north of Sleipner. The PCs used for geochemical analyses are indicated by red dots in the sketches.

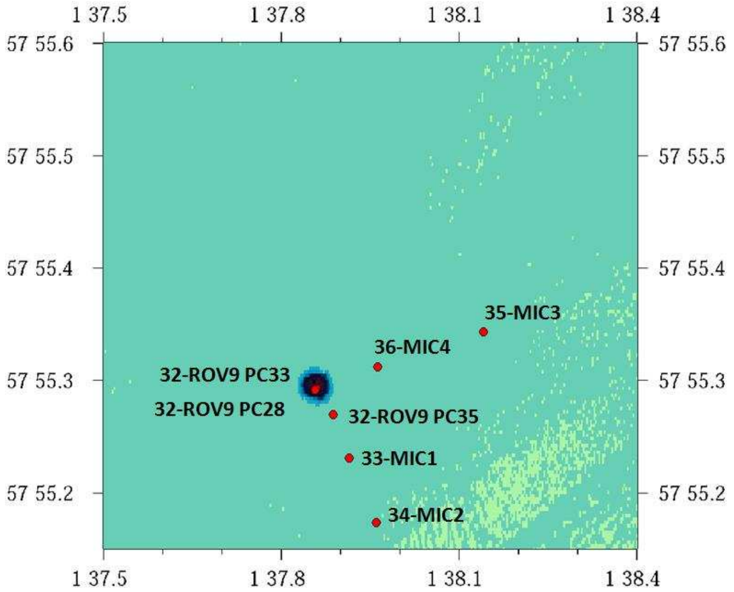

Fig. 4.6.3.3: Coring locations at the Blowout site, well 22/4b-4. The MICs were not collected for geochemical analyses.

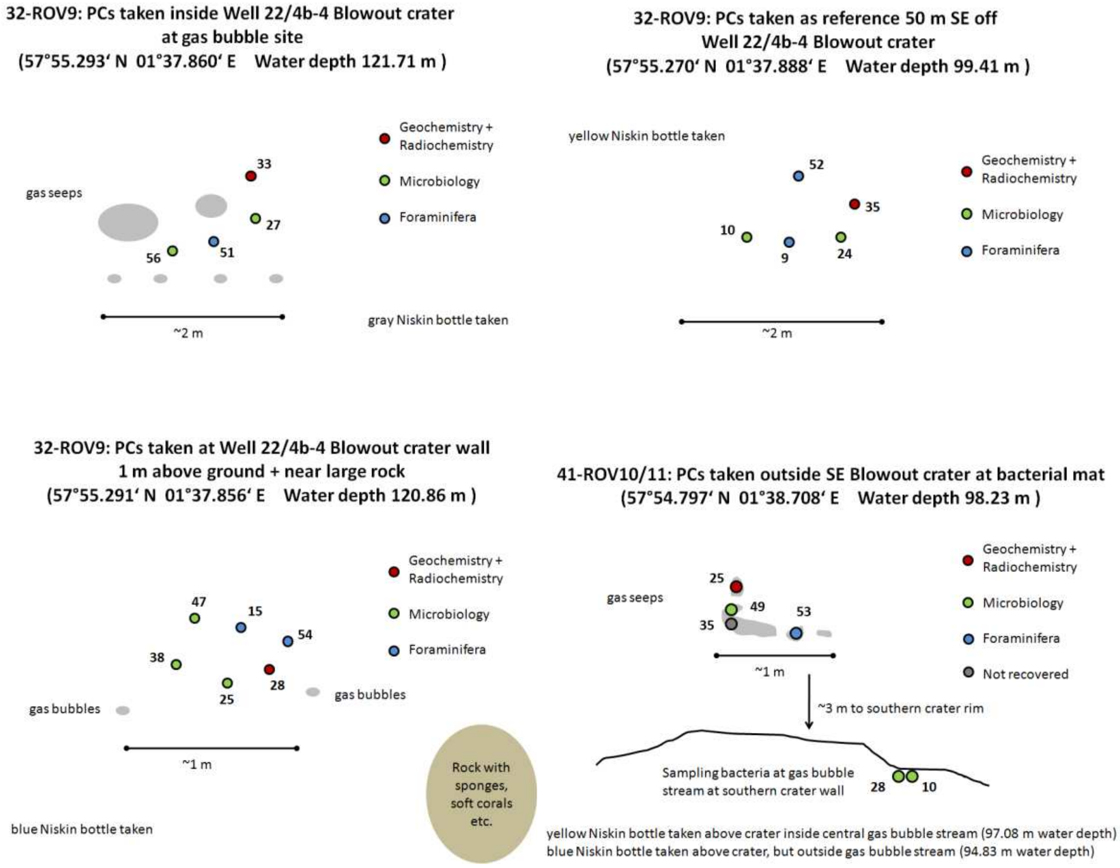

Fig. 4.6.3.4: Details of the push coring at the Blowout site Well 22/4b-4 and the 2nd crater ~1.2 km to the SE. The PCs used for geochemical analyses are indicated by red dots in the sketches.

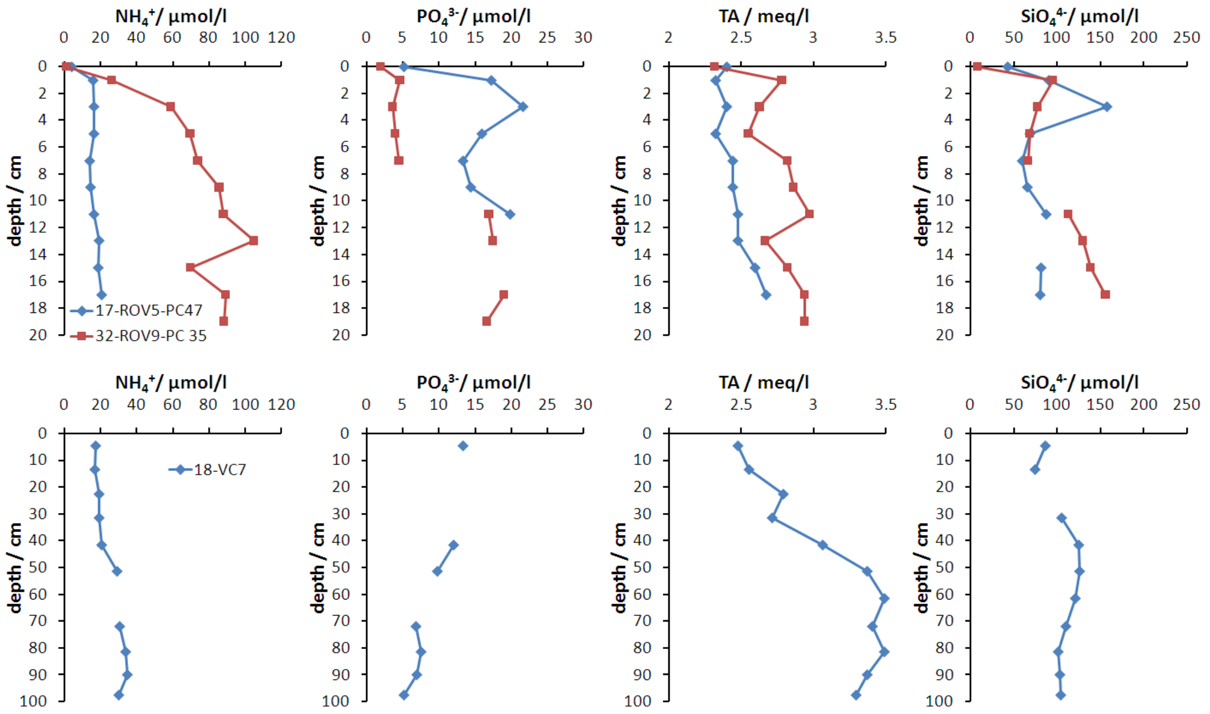

Fig. 4.6.3.5: Reference cores from the fracture north of Sleipner (blue) and the Blowout crater Well 24/4b-4 south of Sleipner (red). Depths are given with respect to the top of the recovered core and are not corrected for any sediment loss that has occurred.

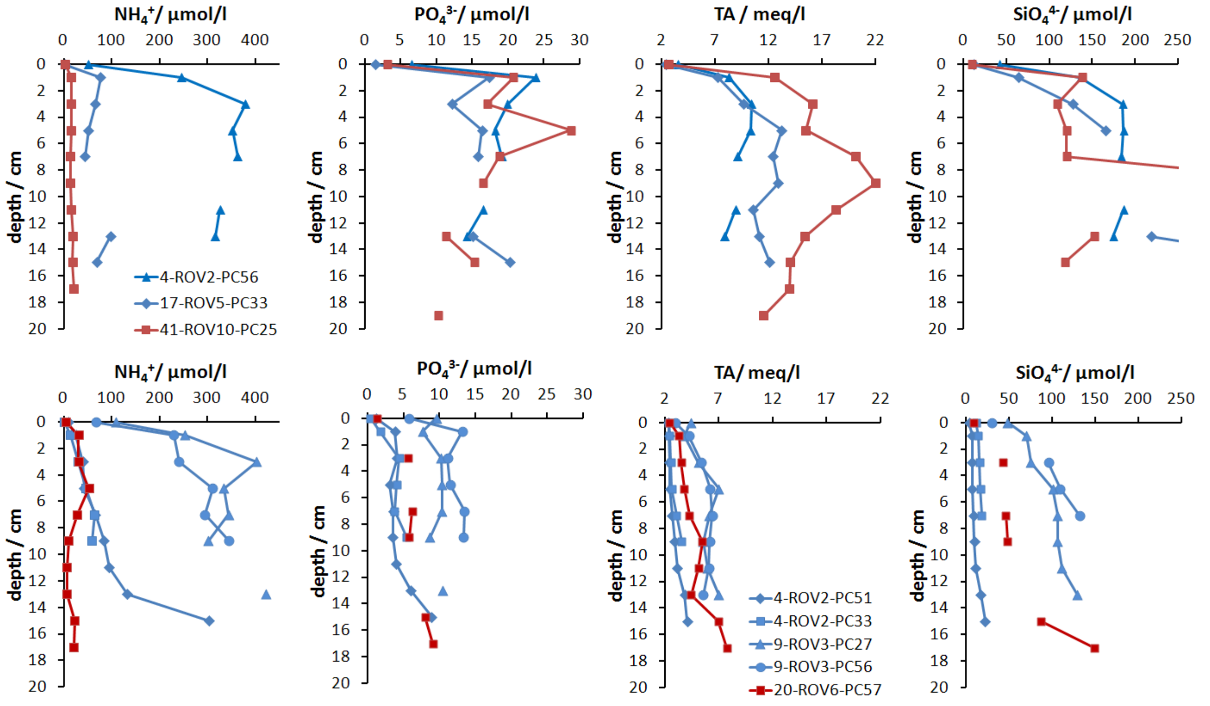

Fig. 4.6.3.6: Seep cores from the fracture north of Sleipner (blue, top and bottom) and the Blowout crater Well 24/4b-4 south of Sleipner (red, top) as well as the abandoned Well 16/7-02 above the Utsira formation (red, bottom). Depths are given with respect to the top of the recovered core and are not corrected for any sediment loss that has occurred.

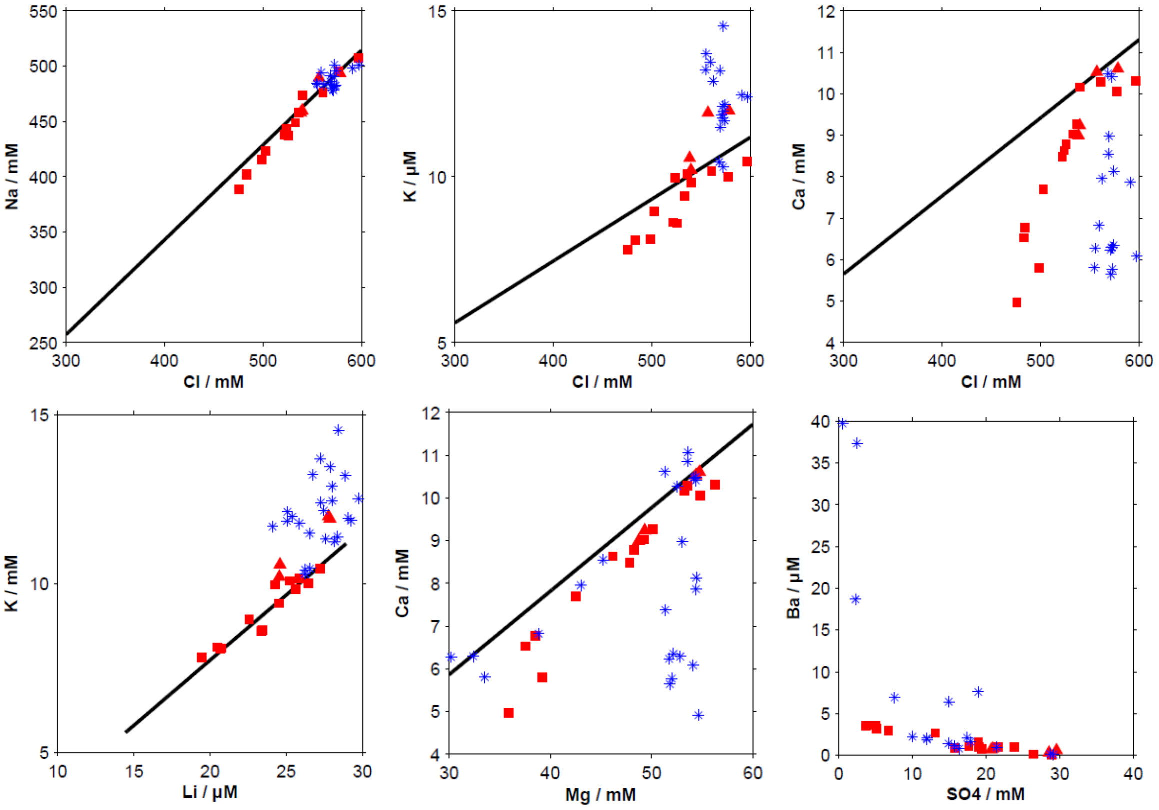

Fig. 4.6.3.7: Preliminary data of the pore fluid compositions from fracture sediments (red) and well sites (blue) based on onshore measurements by ion chromatography (Cl, SO_4) and atomic emission spectroscopy (Na, K, Li, Ca, Mg, Ba). The black lines indicate the mixing lines having IAPSO seawater concentration ratios.

4.7 Biogeochemistry and Microbial Ecology of Methane Seeps in the North Sea

L. Steinle

4.7.1 Introduction

Large quantities of the green house gas methane (CH_4) are stored in sediments of continental margins, most importantly in the form of clathrate hydrate, but also as free gas. At present, most methane is retained in anoxic ocean sediments because it is oxidised by specialised archaea in consortium with sulphate-reducing bacteria (Knittel and Boetius 2009). In addition, aerobic bacteria in the water column consume CH_4 that has bypassed the benthic, microbial filter (Reeburgh 2007). Nevertheless, at so-called cold seeps where large quantities of CH4 are transported into surface sediments, significant amounts of CH_4 may escape both, the sedimentary as well as the water column part of the microbial filter and are then released into the atmosphere. However methane cycling in (aerobic) marine waters is not well constrained. Typically, the identity and distribution of methanotrophic communities within the water column have not been investigated in depth. Similarly, further research is needed to understand key physical, chemical and biological factors controlling the magnitude of microbial activity and CH_4 transport to constrain CH_4 budgets at cold seeps. To close this knowledge gap, we were investigating microbial activity, abundance and identity at both natural and artificial seepage sites in the North Sea. Artificial sites were abandoned wells, one of them being the site 22/4-b, also referred to as "Blowout". The latter is especially interesting since it has been emitting larger quantities of gas than reported from any natural seep and has been intensively investigated on previous cruises with ALKOR (AL66, 259, 290).

4.7.2 Material and Methods

For our investigations of sediment and water samples, we applied a transdisciplinary approach using a suite of different biogeochemical, microbiological and molecular methods. Sediments for sampling were recovered with a vibro corer (VC) and the ROV KIEL 6000 (ROV). Water samples were recovered with a video-guided CTD rosette (CTD) or with the ROV.

Directly after sampling, samples were transferred into an incubator and maintained close to the *in situ* temperature (ca. 8 degrees).

Radiotracer experiments to assess methane oxidation and sulphate reduction were carried out in acrylic core liners and glass tubes (sediments), or in serum vials (water samples) incubated with ^{14}C-methane and $^{35}SO_4^{2-}$, respectively. The samples were incubated close to the *in situ* temperature in the dark for 24 h (sediment) to 2 days (water samples) and then fixed in NaOH (AOM, MOx) or ZnAc (SR). The rate is then calculated from the turnover of tracer:

$$\text{Rate} = \frac{{}^{*}\text{product}}{({}^{*}\text{product} + {}^{*}\text{substrate})} \times \frac{[\text{substrate}]}{t}$$

where *product and *substrate are the activities of the radioactive substrate ($^{14}CH_4$ or $^{35}SO_4^{2}$) and products ($^{14}CO_2$ or $H^{35}S^{-}$), [substrate] denotes the concentration of substrate (e.g. CH_4) and t the incubation time. Separation of the reactant and substrate pools will be carried out in the home laboratory.

Additionally, sediment samples for FISH analysis were fixed in formalin/seawater for 3-4 h at 8°C, subsequently washed in PBS and stored in PBS/ethanol. Complementary, sediment samples for DNA and lipid biomarker (LB) analysis were taken. Water samples for FISH analysis were fixed in formalin for 4 h at 8°C, and subsequently filtered. For LB and DNA analysis, water was filtered onto a glass-microfiber filter. All samples for FISH, DNA and LB analyses were then stored at -20°C and further analysis will be conducted in the home laboratories.

ROV KIEL 6000

Push cores were taken at sites with signs of active gas seeping i.e. the presence of chemotrophic communities or gas bubbling out of the sediment. Reference sites were chosen by the absence of such signs. Three 5-litre Niskin bottles fixed onto the ROV frame allowed us to take water samples at very precise locations. At each site we took push cores and also fired a Niskin bottle (ca. 30 cm above the seafloor). Additionally, we did targeted sampling of the water inside the bubble streams.

Furthermore, we also collected carbonate pieces and took samples of the macrofauna found around the seepage areas.

Vibro cores

In order to get a picture of the microbiological communities living further down below the seafloor, I took samples for lipid biomarker, DNA, and FISH analysis from selected vibro cores (maximum 1 m in length).

CTD Rosette

The CTD was combined with a rosette sampler (12 × 10 L), which was used to collect sea water samples from discrete water depth. In the Sleipner working area several single CTD casts were performed whereas we sampled three depths (80, 40 and 10 m) more extensively at the Blowout site.

4.7.3 Preliminary Results

All samples from the various sampling areas (Tab. 4.7.3.1) have to be processed in the home laboratory and, thus, we cannot present any preliminary results.

Tab. 4.7.3.1: List of stations, gear and samples obtained for microbiological analyses.

Station No	Station Name	Date	Lat. °N	Lon °E	Gear	Samples
CE 12010 1 ROV 1	Sleipner well 9/13	24.07.2012	58°22.382'	1°55.942'	ROV (Push Cores)	AOM, SR, LB, DNA, Acetate
					Niskin	MOx, FISH, PW
CE 12010 3 CTD cast 1	Seismic chimneys	25.07.2012	58°19.389'	1°52.027'	Video towed CTD	MOx, LB, FISH, PW
CE 12010 4 ROV 2	Sleipner, Fracture Middle	25.07.2012	58°35.584'	2°04.03'	ROV (Push Cores)	AOM, SR, LB, Acetate
					Niskin	MOx, FISH, PW
					Net	LB
CE 12010 7 CTD cast 2	Sleipner, Fracture	26.07.2012	58°32.2505'	2°03.9250'	Video towed CTD	MOx, LB, FISH, PW

Station No	Station Name	Date	Lat. °N	Lon °E	Gear	Samples
CE 12010 9 ROV 3	Sleipner, Fracture North	26.07.2012	58°35.745'	2°04.925'	ROV (Push Cores)	AOM, SR, LB, FISH, Acetate
					Niskin	MOx, FISH, PW
CE 12010 15 VC 4	Sleipner, Fracture South	28.07.2012	58°35.5930'	2°04.1204'	VC	LB, FISH, Acetate
CE 12010 17 ROV 5	Sleipner, Fracture South	28.07.2012	58°35.736'	2°05.330'	ROV (Push Cores)	AOM, SR, LB, FISH, DNA, Acetate
					Niskin	MOX, FISH, PW
CE 12010 18 VC 7	Sleipner, Fracture South	28.07.2012	58°35.7418'	2°05.1796'	VC	LB, FISH, DNA
CE 12010 20b ROV 6	Sleipner well 16/7-02	29.07.2012	58°28.402'	2°01.949'	ROV arms	LB, FISH
CE 12010 31 CTD 7	Sleipner well 15/9-13	31.07/1.08.2012	58°20.3915'	1°55.9486'	Video towed CTD	MOx, LB, FISH, PW
CE 12010 32 ROV 9	Blowout	01.08.2012	57°55.257'	1°37.8145'	ROV (Push Cores)	AOM, SR, LB, DNA, Acetate
					Niskin	MOx, FISH, PW
CE 12010 37 CTD 8	Blowout	01.08.2012	57°55.3692'	1°37.8797'	Video towed CTD	MOx, LB, FISH, PW
CE 12010 38 CTD 9	Blowout	01.08.2012	57°55.366'	1°37.877'	Video towed CTD	MOx, LB, FISH, PW
CE 12010 39 CTD 10	Blowout	01.08.2012	57°55.3627'	1°37.8781'	Video towed CTD	MOx, LB, FISH, PW
CE 12010 41 ROV 11	SE crater	02.08.2012	57°54.8075'	1°38.7207'	ROV (Push Cores)	AOM, SR, LB, DNA, Acetate
					Niskin	MOx, FISH, PW

4.8 Radon (^{222}Rn) Measurements

V. Liebetrau

4.8.1 Introduction

^{222}Rn is a member of the ^{238}U decay chain and directly produced by the decay of ^{226}Ra in the marine sediments. Because ^{238}U is enriched in sediments its production is depth dependent and increases as a function of the sedimentary height below the water column. Furthermore, the production of its parent isotope ^{226}Ra is supported by the decay of particle reactive ^{230}Th which is enriched in the sediments by the particle flux from the water column, where it is produced by the decay of dissolved ^{234}U, with ^{238}U as great-grandmother.

^{222}Rn is radioactive with a half-life of about 3.5 days (λ = 0.0001374 1/min) and chemically an inert gas. It tends to separate from the particle bound parent isotope into the pore and bottom water system where it may follow partially unsupported as ^{222}Rn$_{ex}$ (excess, enriched over the activity of dissolved ^{226}Ra) diffusive and/or advective flux processes. The amount of ^{222}Rn$_{ex}$ still reaching and escaping the sediment surface depends on ongoing primary production within the sediment, enrichment of the pore water and the transport velocity. Therefore, ^{222}Rn analyses potentially provide a sensitive, well detectable and suitable tracer in order to determine diffusion and advection rates. As direct tracer of submarine fresh water discharge ^{222}Rn may mark anomalies in the lowest bottom water column if the fresh water is enriched in radioactive decay products e.g. by prior passing through substrates enriched in U like granitoid basement rocks or glacial sediments.

The goal during CE-12010 was the monitoring of ^{222}Rn in the near bottom water at potential emanation sites of fluids originated in deeper geological formations with special respect to the radiochemical systematics and the determination of potential advection and diffusion rates.

4.8.2 Methods

Due to the short half-life of ^{222}Rn measurements must be performed on board, immediately after sampling. On cruise CE-12010 we applied a transportable liquid-scintillation-counter system (LSC, Hidex-Triathler) with alpha-beta-separation and equipment for the extraction of ^{222}Rn from water and pore water samples. Due to the expected low concentration a 6h measurement routine was conducted.

4.8.3 Preliminary Results

Accordingly to the ROV-station list on each site where niskin bottles of near bottom water were successfully recovered (ROV-1, -2, -5, -6, -9, -11) we performed ^{222}Rn extraction and measurement on final sample amounts around 1 l.

Additionally the first deployment of the BIGO2-Lander (BIGO2-1, 30h seafloor protocol) was accompanied by ^{222}Rn measurements on aliquots remaining after the lander specific subsampling protocol (K1-8, K1-1, K2-8, BW-8, BW-1, K1-6). The aim of this approach was to test time resolved the potential enrichment of ^{222}Rn from the sediment into the bottom water enclosed in the chambers of BIGO2 for 30 hours. Unfortunately, the sample size of this approach was limited on 10 ml from geochemistry syringe subsamples also for the latest stage due to the fact that the chambers could not be recovered in closed mode. The final closing step, potentially providing whole seafloor habitat with several liters of enriched bottom water on top, was skipped by purpose in order to avoid severe damage of the whole system by capture of blocking coarse grained residual sediments.

One set of pore water samples was extracted from soft sediment of vibro corer 9 (VC-9) remaining after core subsampling conducted by the pore water group. The purpose was to get information about the pore water ^{222}Rn$_{ex}$ and ^{226}Ra depth distribution. Unfortunately, the typically sandy sediment allowed only extractions of max. 2 ml samples of pore water from approximately 35 ml of sediment.

For all three general approaches final results depend on the time consuming back measurement of the original ^{222}Rn-extracted samples after the amount missing to equilibrium with ^{226}Ra is ingrown. For some sites even additional not extracted parallel samples could be recovered and have to wait until potential ^{222}Rn$_{ex}$ is decayed down to equilibrium with ^{226}Ra. This home-laboratory-procedure for ^{222}Rn$_{ex}$ determination is not finished and to date no precise final results are available.

However, in first approximation significantly elevated ^{222}Rn bulk concentrations, by factor >2 when compared to remote sea water samples, were observed in Niskin near bottom water samples of ROV-1 and -6 taken directly in bubble streams.

4.9 Carbonate Sampling Program and Sedimentation Rates

V. Liebetrau

4.9.1 Introduction

Often fluid and gas emanation from marine sediments is accompanied by increased methane (CH_4) fluxes of thermogenic and/or biogenic origin and related microbiological processes within the sediment column. The latter may enhance the precipitation of authigenic carbonates which are providing a stationary archive of chemical changes of their environment of formation through time.

The precipitation of calcium carbonate ($CaCO_3$) polymorphs (aragonite and calcite) is one the major chemical side effects of increased alkalinity, e.g. due to AOM (Anaerobe Oxidation of Methane) activity. The more or less formation of $CaCO_3$ directly reflects the stoechiometric amount of CH_4 and SO_4^{2-}consumption at vent sites. In general terms, the higher the abundance of cold seep carbonates the higher the related AOM activity.

The vent site carbonates are excellent archives for the reconstruction of past AOM activity and CH_4-fluxes. Furthermore, vent site carbonates preserve proxy information on vent site fluid and pore water composition, pore water temperature and the microbiological composition of the AOM consortia.

In order to reconstruct the evolution of the very different potential seep sites investigated during cruise CE12010 we sampled with the ROV consolidated sediments, coated hard-substrates and precise positioned short sediment push cores (PC) aside and within bacterial mats.

From sediments remaining from push corer taken for the pore water group and in some cases from parallel recovered PCs a selection will be made for the application of ^{210}Pb and ^{137}Cs profiles for the reconstruction of potentially varying sedimentation rates across the “fracture” zone and as comparison between the different sampling sites of cruise CE12010.

4.9.2 Methods

No on-board analytics were performed but selected samples are already under investigation with the following laboratory based methods:

- XRD (X-ray diffractometry) for mineralogical identification and relative abundances
- SIRMS (stable isotope ratio mass spectrometry) for $\delta^{18}O$ (here T and diagenesis sensitive marker for verification between exposed allochthonus old carbonates and authigenic formation) and $\delta^{13}C$ signatures as tracer of carbon sources
- TIMS (thermal ionization mass spectrometry) in first phase for radiogenic Sr isotope signatures of pore water and carbonates as tracer of fluids originated in deeper lithologies and influencing the formation of authigenic minerals (fingerprint of potentially ascending formation water), dependent on results additional application for $\delta^{44/40}Ca$ and $\delta^{88/86}Sr$ isotope ratios as proxy for conditions of authigenic carbonate formation.
- MC-ICP-MS (multi collector – inductively coupled plasma – mass spectrometry) for precise U-Th isotope systematics and geochronology on smallest sample amounts
- ICP-QMS (inductively coupled plasma – quadrupole mass spectrometry) for element ratios as proxy for conditions of authigenic carbonate formation
- Gamma counting for ^{210}Pb and ^{137}Cs down-core profiles for determination of sedimentation rates.

4.9.3 Preliminary Results

Main findings of potentially authigenic mineral formation recovered during cruise CE12010 are shown in the following (Figs. 4.9.3.1-3). The difficult recovery of these rare samples represents a preliminary and result by itself.

Fig. 4.9.3.1: One spot found in the "fracture" zone with exposed consolidated sediment close to a bacterial mat implying earlier formation of authigenic carbonates. Several cm thick plates are recovered successfully during ROV-2 (lower left, Niskin bottle closed for near bottom water sampling).

Fig. 4.9.3.2: Dark sediments underneath broken and turned platy carbonates exposed due to ROV-2 sampling.

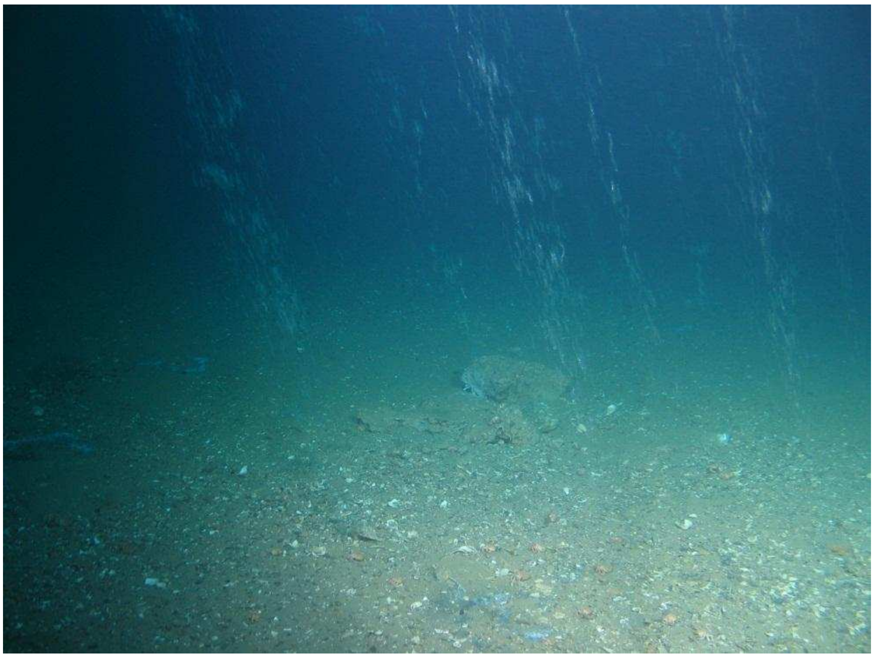

Fig. 4.9.3.3: Exposed hard ground at abandoned well 16/7-02 at Sleipner sampled during ROV-6.

5 Student Participation

EUROFLEETS encourages the training of students (pre-PhD level) and also provides vessel access to institutes which lack such ocean-going infrastructure, or those who normally conduct science on land. We were pleased that one student trainee from the University of Basel participated in the cruise with her own scientific objectives which added value to the outcome of the cruise – we are very grateful for this. The following is a summary of her activity and impressions aboard R/V Celtic Explorer.

Student trainee Lea Steinle

Past education: BSc in Biology at the University of Lausanne (CH), MSc in Plant Science at the University of Basel (CH).

Current studies: PhD in Environmental Biogeosciences at the University of Basel (CH).

Cruise activities: I was mainly involved in assessing methane oxidation and sulphate reduction rates in the water column and the sediment. Additionally, I collected water and sediment samples to carry out molecular and microbiological analyses in my home laboratory. The results from this cruise will be part of my PhD thesis about methane oxidation in different marine environments.

Impressions: Due to EUROFLEETS, I had the opportunity to participate in my second seagoing research expedition. Coming from a country without sea access or research fleet, it was an invaluable experience to be part of the CE12010 cruise and learn from senior scientists from GEOMAR, a renowned institute for ocean research. In particular, I learnt a lot about the sampling acquisition by using the ROV KIEL 6000 and the vibro corer. I had to decide where to take samples and how many replicates I would need and was kindly supported by the senior scientists on board. Moreover, I was able to carry out a water sampling campaign above the abandoned well 22/4b that I previously planned, again with the help of senior scientists. I also took an interest in the porewater sampling and the analysis of the samples, e.g. assessing the alkalinity by titration or how to determine the hydrogen sulfide concentration by means of photometrical analysis.

My take-home message from this cruise was that the skill of planning the sampling and deciding what might be interesting scientifically is a very important part of a successful expedition and that experience is invaluable. My thanks go to all the scientists who supported me and helped me grow in this regard, especially to the principal investigator, Peter Linke.

6 Data and Sample Storage / Availability

A dedicated data management strategy is installed within the ECO2 project. In brief, a separate work package together with the Kiel Data Management Team (KDMT) collects and manages all ECO2 related data in an information and data archival system where metadata are collected and publicly available 2 weeks after the cruise (portal.geomar.de/osis). This Ocean Science Information System (OSIS-Kiel) is accessible for all project participants and can be used to share and edit information and to provide scientific data, as they become available 6 months after the cruise (portal.geomar.de/osis). OSIS is providing information on granted ship time with information on the scientific program and the general details down to the availability of data files from already concluded cruises. The transparency on the research activities is regarded as an invitation to external scientists to start communication on collaboration on behalf of the newly available data.

The KDMT take care as data curators to transfer the data in a World Data Center (e.g. PANGAEA) 3 years after the cruise which will then provide long-term archival and access to the data. The data publication process will be based on the available files in OSIS and is therefore transparent to all reviewers and scientists. This cooperation with a world data center makes the data globally searchable, and links to the data owners provide points of contact to project-external scientists. This will guarantee the availability of the data to the scientific community beyond the life time of the proposed project. Data published within PANGAEA are provided through harvesting techniques for global distribution. The Cruise Summary Report (CSR) including the station list, cruise track and list of Principal Investigators (PIs) in charge of the different measurements and data has been send to the German Oceanographic Data Centre.

Samples of the gas geochemistry of the water column and sediment are analysed by Mark Schmidt; data of the membrane inlet mass spectrometer and the lander deployments are processed by Stefan Sommer, both at GEOMAR. Samples of the porewater and sediment geochemistry are analysed by Matthias Haeckel; archive cores from vibro corer deployments are archived at the Lithothek Core Repository, GEOMAR. Data on short-lived isotopes and carbonates are processed by Volker Liebetrau, GEOMAR. Samples of the microbial activity are processed by Lea Steinle, University Basel, Switzerland. ROV pictures and video footage are stored on a server at GEOMAR and are available on request to the communication and media group at GEOMAR.

7 Participants

No.	Name	Gender	Affiliation	On-board tasks
1	Peter Linke	M	GEOMAR	Chief scientist, lander & ROV deployments
2	Mark Schmidt	M	GEOMAR	CTD deployments, sensors, GIS
3	Stefan Sommer	M	GEOMAR	MIMS, lander deployments
4	Lee Bryant	F	GEOMAR	CTD watch, ECM deployments
5	Sergiy Cherednichenko	M	GEOMAR	Lander electronics and programming
6	Sonja Kriwanek	F	GEOMAR	pCO2 measurements
7	Andrea Bodenbinder	F	GEOMAR	Methane and Oxygen analysis
8	Matthias Haeckel	M	GEOMAR	Sediment sampling, pore water analysis
9	Dirk Schroller	M	GEOMAR	Sediment sampling, pore water analysis
10	Lisa Vielstädte	F	GEOMAR	Sediment sampling, CO2 release experiment
11	Maike Dibbern	F	GEOMAR	Sediment sampling, pore water analysis
12	Lea Steinle	F	UniBas	AOM/SR rate measurements
13	Volker Liebetrau	M	GEOMAR	Carbonate sampling
14	Friedrich Abegg	M	GEOMAR	ROV coordinator/Pilot
15	Martin Pieper	M	GEOMAR	ROV-Mechanics/Pilot
16	Inken Suck	F	GEOMAR	ROV-Pilot
17	Patrik Cuno	M	GEOMAR	ROV-Programming/Pilot
18	Jan Hennke	M	GEOMAR	ROV-Mechanics/Pilot
19	Matthias Bodendorfer	M	GEOMAR	ROV-Mechatronic/Pilot

GEOMAR	Helmholtz Centre for Ocean Sciences Kiel, Germany
UniBas	University of Basel, Switzerland

8 Station List

Station No.	**Date 2012**	**Time [UTC]**	**Latitude [°N]**	**Longitude [°E]**	**Water Depth[m]**	**Gear**	**Remarks/Recovery**
01	24.07	06:53	58°22.382'	1°55.942'	78.2	ROV	HISEM, 6 push cores, 1 gas sampler
02	24.07	14:41	58°22.374'	1°55.955'	78.3	BIGO	
03	24/25.07	18:49	58°19.389'	1°52.027'	81	CTD	completed transect of 1st chimney. Not much observed. 9 bottles fired
04	25.07	07:06	58°35.584'	2°04.03'	87.6	ROV	HISEM, HydroC, 3 Niskins
05	26.07	17:20	58°35.76'	2°04.9'	87.4	VC	carbonates and shells; ~0.5 m long
06	27.07	18:30	58°35.7'	2°05.005'	87.5	VC	
07	25/26.07	19:51	58°32.2505'	2°03.9250'	87.6	CTD	arrived at end of transect 00:40. Moved north and repeated transect in reverse. Lots of microbial mats but no change in CH4, CO2, or pH. 12 bottles fired.
08	26.07	06:50	58°22.356'	1°55.915'	77.3	BIGO	BIGO recovery
09	26.07	08:56	58°35.745'	2°04.925'	87.2	ROV	HISEM, HydroC (CO2), ph sensor, Niskins, push cores
10	27.07	17:50	58°35.7403'	2°05.2974'	87.2	VC	
11	27.07	09:18	58°24.365'	2°01.421'	76.9	OCE	gas release experiment (CO2/Krypton)
12	27.07	10:35	58°24.364'	2°01.412'	76	ROV	HISEM, HydroC, pH sensor, 3 Niskins, push cores, ADCP (300 kHz)
13	27.07	16:58	58°24.362'	2°01.420'	76	CTD	HISEM, HydroC, pH sensor, MIMS pump. 3 bottles fired.
14	28.07	06:33	58°24.342'	2°01.473'	76.9	OCE	OCE recovery
15	28.07	08:25	58°35.5930'	2°04.1204'	88.2	VC	
16	28.07	09:18	58°35.7090'	2°04.4927'	87.6	VC	almost empty; problems with power supply of VC. Repeat station
17	28.07	12:35	58°35.736'	2°05.330'	86	ROV	
18-1	28.07	17:30	58°35.7418'	2°05.1796'	88.1	VC	1 m long
18-2	28.07	18:00	58°35.7414'	2°05.1791'	88.4	VC	
19	28/29.07	20:25	58°19.187'	1°54.029'	78	CTD	6 bottles fired.
20-1	29.07	07:18	58°28.404'	2°01.957'	80.4	ROV	ground fault problems; repeat station
20-2	29.07	09:16	58°28.402'	2°01.949'	80	ROV	HISEM, HydroC, Niskins, push cores, gas sampler. Still had issues during deployment
21	29.07	15:05	58°35.733'	2°05.341'	88.3	BIGO	deployed on top of microbial mat
22	29.07	17:31	58°35.7006'	2°04.4852'	87.3	VC	
23	30.07	08:45	58°24.360'	2°01.424'	77	OCE	gas release experiment (CO2/Krypton)
24	30.07	10:05	58°24.357'	2°01.4247'	77.1	ROV	HISEM, HydroC, ph sensor, ECM 1
25/26	30/31.07	16:03	58°24.3542'	2°01.4234'	75.2	CTD	8 bottles fired.
27	31.07	06:05	58°35.698'	2°05.296'	88	BIGO	BIGO recovery
28	31.07	06:45	58°35.8338'	2°05.3365'	88.2	VC	
29	31.07	08:42	58°24.326'	2°01.326'	77	OCE	OCE recovery
30	31.07	11:10	58°24.3366'	2°01.4206'	76.9	ROV	HISEM, HydroC, pH, ECM and ADCP recovery

Station No.	**Date 2012**	**Time [UTC]**	**Latitude [°N]**	**Longitude [°E]**	**Water Depth[m]**	**Gear**	**Remarks/Recovery**
31	31.07/01.08	17:10	58°20.3915'	1°55.9486'	77.2	CTD	12 bottles fired.
32	01.08	07:05	57°55.257'	1°37.8145'	91	ROV	HISEM, HydroC, Niskins, push cores
33	01.08	14:13	57°55.2311'	1°37.9168'	91.5	MC	2 failures, 3rd dployment 1 core
34	01.08	15:05	57°55.1746'	1°37.5397'	91.4	MC	2 deployments, 1 core each
35	01.08	15:40	57°55.3410'	1°38.1412'	91.1	MC	2nd try good
36	01.08	16:05	57°55.3135'	1°37.9612'	91	MC	2 failures, 1 good
37	01.08	16:58	57°55.3692'	1°37.8797'	90.9	CTD	85-m depth transect; 12 bottles fired
38	01.08	19:30	57°55.366'	1°37.877'	92	CTD	40-m depth transect; 12 bottles fired
39	01.08	22:22	57°55.3627'	1°37.8781'	91.2	CTD	10-m depth transect; 12 bottles fired
40	02.08	07:35	57°54.9217'	1°38.9086'	90.4	ROV	
41	02.08	13:54	57°54.8075'	1°38.7207'	91.7	ROV	
42	02.08	18:20	57°56.4079'	1°38.6203'	90.6	CTD	Background 6 bottles (2 per depth) in single cast
43	03.08	05:04	58°24.3626'	2°01.4250'	76.4	OCE	gas release experiment (CO2/Krypton)
44	03.08	06:12	58°24.358'	2°01.4246'	76	ROV	HISEM, HydroC, pH sensor, niskins, push cores, deploy ADCP and ECM
45	03.08	13:20	58°24.3717'	2°01.4199'	77.1	CTD	12 bottles fired.
46	03.08	16:41	58°24.3244'	2°01.4370'	76.3	OCE	OCE recovery
47	03.08	17:12	58°24.3603'	2°01.4501'	76.6	ROV	ADCP and ECM recovery
49	04.08	06:30	56°30.1273'	3°00.1444'	69	MC	3 cores

Gear abbreviations:
BIGO Lander (BIGO)
Mini Corer (MC)
Ocean Elevator Lander (OCE)
ROV KIEL 6000 (ROV)
Vibro Corer (VC)
Video-guided CTD-Rosette (CTD)

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No.	Title
1	FS POSEIDON Fahrtbericht / Cruise Report POS421, 08. – 18.11.2011, Kiel - Las Palmas, Ed.: T.J. Müller, 26 pp, DOI: 10.3289/GEOMAR_REP_NS_1_2012
2	Nitrous Oxide Time Series Measurements off Peru – A Collaboration between SFB 754 and IMARPE –, Annual Report 2011, Eds.: Baustian, T., M. Graco, H.W. Bange, G. Flores, J. Ledesma, M. Sarmiento, V. Leon, C. Robles, O. Moron, 20 pp, DOI: 10.3289/GEOMAR_REP_NS_2_2012
3	FS POSEIDON Fahrtbericht / Cruise Report POS427 – Fluid emissions from mud volcanoes, cold seeps and fluid circulation at the Don-_Kuban deep sea fan (Kerch peninsula, Crimea, Black Sea) – 23.02. – 19.03.2012, Burgas, Bulgaria - Heraklion, Greece, Ed.: J. Bialas, 32 pp, DOI: 10.3289/GEOMAR_REP_NS_3_2012
4	RV CELTIC EXPLORER EUROFLEETS Cruise Report, CE12010 – ECO2@NorthSea, 20.07. – 06.08.2012, Bremerhaven – Hamburg, Eds.: P. Linke et al., 65 pp, DOI: 10.3289/GEOMAR_REP_NS_4_2012

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