



Maria S. Merian Cruise 1 leg 3

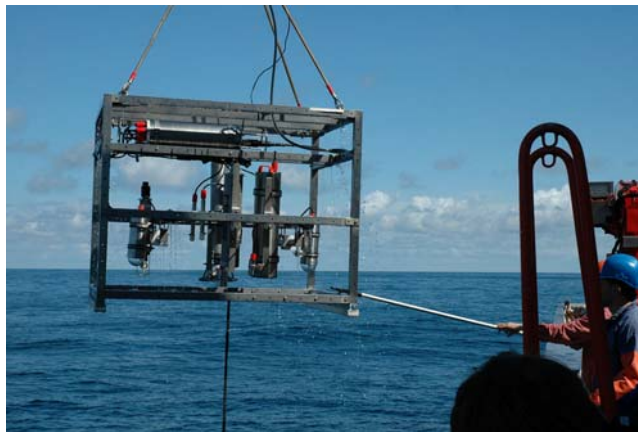
First weekly report: 12. - 18. 04. 2006

MARIA S. MERIAN cast off at Bollhörn Kai in Kiel at 10:12h on 12. 04. starting the third leg of expedition No. 1. On board were a party of 23 scientists and a group of distinguished guests and journalists. The visitor group left the ship after entering the Kiel Kanal locks at Holtenau and was replaced by a second visitor group which joined us for the 99km passage through the Kiel Kanal. The passage through the canal took 9 hours to reach the locks at Brunsbüttel where the second visitor group was disembarked. We continued our journey down the Elbe estuary into the North Sea. During the night we passed through the German Bight and continued our journey along the Dutch and Belgian coast during Thursday.

We passed the Channel during the next night and steamed along the English south shore under moderate weather conditions. In the afternoon we changed our course to approach Brest to take over two technicians from IXSEA for the still outstanding calibration of the Posidonia USBL system.

We progressed towards Brest during Friday night and reached Brest roadstead at mid day for the rendezvous with the pilot boat. We then proceeded towards Brest Harbour where we took over the technicians from a pilot boat. Maria S. Merian left immediately and headed for Cape Finistere. In the late evening we started to calibrate the Posidonia system at the continental slope (ca. 1600m depth). Unfortunately the system was not working when attached to the deck unit. Since the reason for the malfunction could not be located we decided to dismantle the whole Posidonia system for an inspection at IXSEA in France. We agreed to disembark the technician and the Posidonia parts in Vigo on Monday morning.

During Sunday we crossed the Bay of Biscay. At 12:30h we stopped the ship to test the LWL-cable in combination with the OFOS System at a sounding depth of 4830m. We paid out 4900m of LWL cable to get a sea floor view and towed the OFOS system with a speed of 1kt 1,5m above the sea bed for about 10min. The colour TV-transmission was very good and all systems triggered by the telemetry unit functioned well. The spooling of the deep sea winch went smoothly. Afterwards we continued our progress to Vigo.



Test deployment of the Ocean Floor Observation System (OFOS) on the LWL cable at 4830m depth in the Bay of Biscay.

We reached the anchorage outside Vigo on Monday morning where we dropped anchor. After a boat took ashore the IXSEA technicians and the Posidonia equipment we continued our journey along the Lusitanian coast towards the Gulf of Cadiz.

We reached our first station the Bonjardim Mud Volcano in the western Gulf of Cadiz on Tuesday afternoon (18. 04.) at 17:30 h, where we started station work with a CTD/Rosette water sampler cast at 3100m depth. During the night we mapped the Bonjardim MV area with the multi beam and run several OFOS transect across the mud volcano.

An Bord sind alle wohlauf.

Es grüssen.

O. Pfannkuche und alle Fahrtteilnehmer



Maria S. Merian Cruise 1 leg 3

Second weekly report: 18. - 25. 04. 2006

Station work of the entire last week was dedicated to the investigation of the deep mud volcanoes in the western Gulf of Cadiz (Fig. 1). We surveyed three MVs: Carlos Ribeiro MV (2200m), Bonjardim MV (3150m) and Porto MV (3850m).

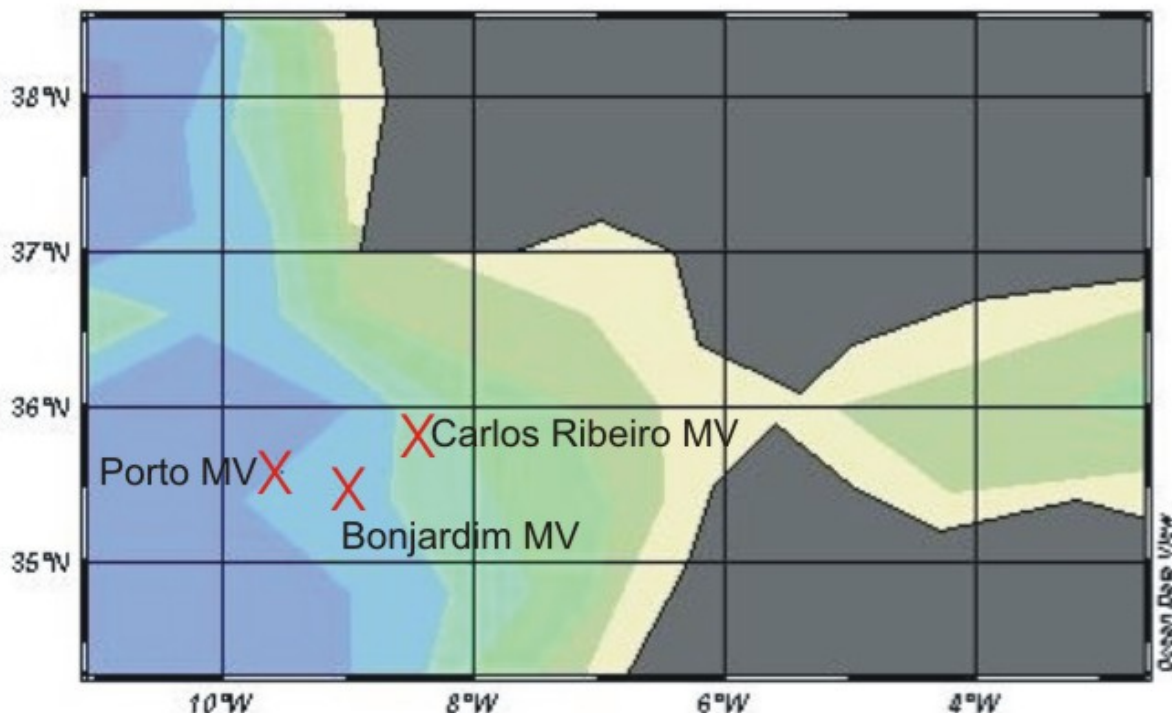


Fig. 1: Working area with positions of the three investigated mud volcanoes

All three MVs were mapped with multi-beam. Based on the multi-beam maps we set out OFOS profiles to identify sediment patterns and megafauna biocoenoses with special attention to organisms indicating chemosynthetic activity driven by geosphere-surface sediment coupling. Sediments were sampled at all three MVs with the TV-MUC, gravity corer and box grab for geochemical, biogeochemical, microbiological and benthos biological investigations. The Fluid Flux Observatory Lander (FLUFO) and the Deep Sea Observatory Lander (DOS) were deployed at Bonjardim MV and Porto MV. CTD/Ro casts for physical oceanographic and water chemical investigations were performed at all three MVs.

Megafauna exhibits a quite distinct zonation at Bonjardim MV. The lower flanks show low density of animals and are characterised mainly by enteropneust burrows and feeding marks. The upper flanks are dominated by hexactinellid sponges and holothurians accompanied by a rather high density of worm burrows. The top of Bonjardim MV is asymmetrical with an elevation at the south-eastern side where some patches of Pogonophora occurred among areas of disturbed sediment with exposed breccia and some bivalve shells. This area is surrounded by coarser

sediments populated mostly by Ophiuroida and Holothuria, the latter forming dense aggregations at the rather flat north-western area of the top. The box grab sample from Bonjardim MV contained a mollusc fauna of at least 17 species in a well oxygenated environment. A high amount of species were of planktonic origin. The sediment was also very rich in Foraminifera, most of them planktonic species.

At the rim of Porto MV megafauna is scarce but the seafloor is highly bioturbated with Enteropneust burrows and feeding marks and different kinds of Lebensspuren. Siboglinids (Pogonophera) were first recorded when approaching the north-western area of the MV and appear to be covering the entire top of the MV (Fig. 2) where some *Acharax* shells were also spotted. Living specimens of *Acharax* and Siboglinidae were recovered with a box core. The latter belong to a species different from the others previously recorded in the Gulf of Cadiz. The siboglinids are accompanied mainly by hexactinellid sponges (tubular and stalked) and ophiuroids as well as a few galatheid crabs.

The box grab samples proofed the existence of a relatively small oxygenated surface zone and the occurrence of H₂S in deeper strata. Characteristic for this environment is the presence of the solenomyid bivalve *Acharax* sp., a deep burrowing species living in endosymbiosis with sulphide oxydizing bacteria. The finding of shells of the epifaunal carnivorous gastropod species *Mohnia abyssorum* in the deeper part of the core shows that the ancient surfaces were previously oxydized.

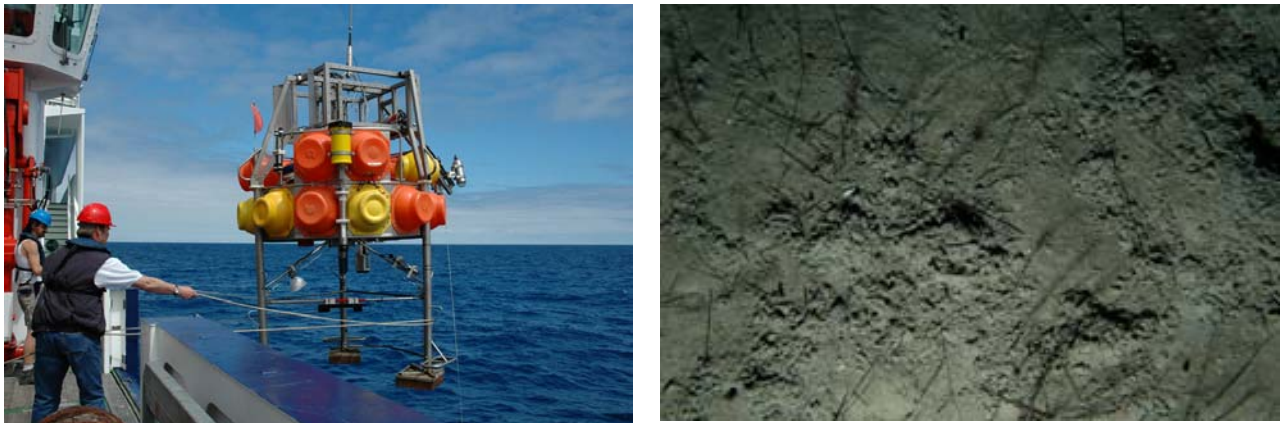


Fig. 2: Deployment of the Deep Sea Observatory (DOS Lander) at Porto MV. The time lapse camera confirmed the placement of the DOS on a Pogonophora assemblage.

At Carlos Ribeiro MV the megafauna assemblage is dominated by echinoderms, mainly Ophiuroida accompanied by stalked Crinoida at the flanks and some aggregations of Holothuria. There are numerous burrows of different shapes and sizes, sometimes arranged in clusters. Hexactinellid sponges are also frequent and there is a rather high diversity of Cnidaria especially at the north-eastern flank. The top of the MV is almost devoid of megafauna with the exception of a few borrows and scattered ophiuroids and thyasirid shells at the surface of the sediment. The presence of living Thyasiridae was confirmed by a box-core sample retrieved from the MV top.

A second box core from the flank of the Carlos Ribeiro MV consisted of well oxygenated pelagic mud and clay. The abundance of different pteropod species and other planktonic gastropods was striking. The impoverished endobenthic community

comprised of *Bentharca* sp. and some other mollusc species. Planktonic foraminifers were abundant. Only a few clasts originating from the mud volcano were observed.

Pandalid shrimps and fishes were frequently sighted at all MVs but without a clear pattern in their distributions.

Geochemical analyses of pore waters were conducted at a number of cores from the three MVs in order to determine their present state of activity and decipher the origin of the fluids. The results indicate the advection of strongly methane enriched fluids, which causes an upward shift of the zone of anaerobic-oxidation of methane (AOM) to less than one meter below the sediment surface (indicated by the depletion of sulphate and the simultaneous increase in alkalinity and hydrogen sulphide (Fig. 3). At all sites the advecting fluids are significantly depleted in chloride with respect to normal seawater. This chloride depletion is already known from earlier studies at Bonjardim MV and is most likely caused by mineral dehydration processes at a few kilometres depth. In addition, the fluids are characterized by elevated levels of ammonium, accompanied by low concentrations of other nutrients (phosphate and silicate). Ongoing activities aim at a deeper understanding of fluid mobilization processes and their specific control mechanisms in this tectonically active region.

Gas hydrates were sampled at Porto MV with the gravity corer and preserved in liquid nitrogen. Traces of gas hydrates destabilized during the sampling procedure were found at Bonjardim (gravity corer sample) and Carlos Ribeiro (box grab and gravity corer sample).

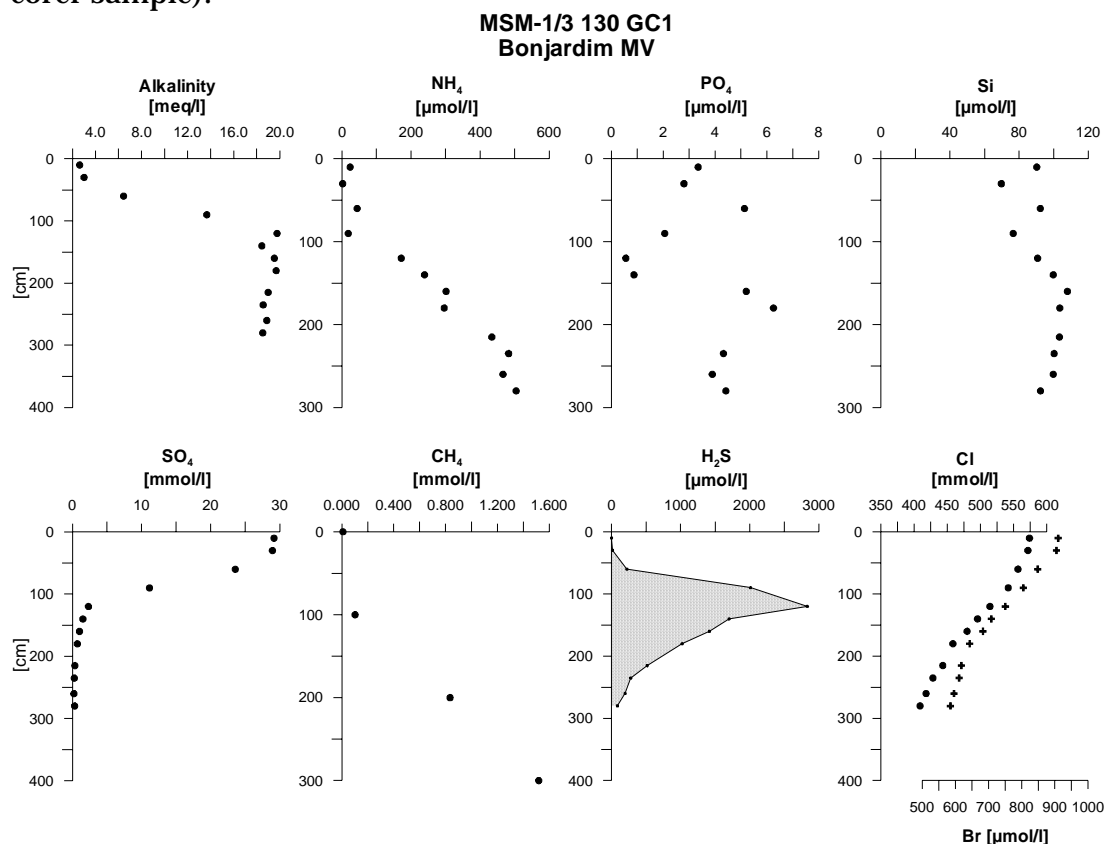


Fig 3: Pore water profiles of a gravity core at Bonjardim MV.

CTD measurements (SBE 9 *plus* - SBE 11*plus* V2 deck unit) in the Porto MV area show the expected water mass characteristics, including the typical occurrence of an upper and lower core of the Mediterranean Outflow Water (MOW, Fig. 4). The site

was visited twice, on April 22 and April 24. The measurements indicate variation of the MOW between 750m and 1250m. During our first visit the typical two tongues of high saline MOW, ~ 36.10 for the upper portion and ~ 36.30 for the lower portion were encountered. However, during the second CTD cast a different pattern emerged. Between 750m and 1250m the upper and lower core were less defined. Instead we detected one single core between 800m-1200m with varying salinities between 36.00 and 36.20.

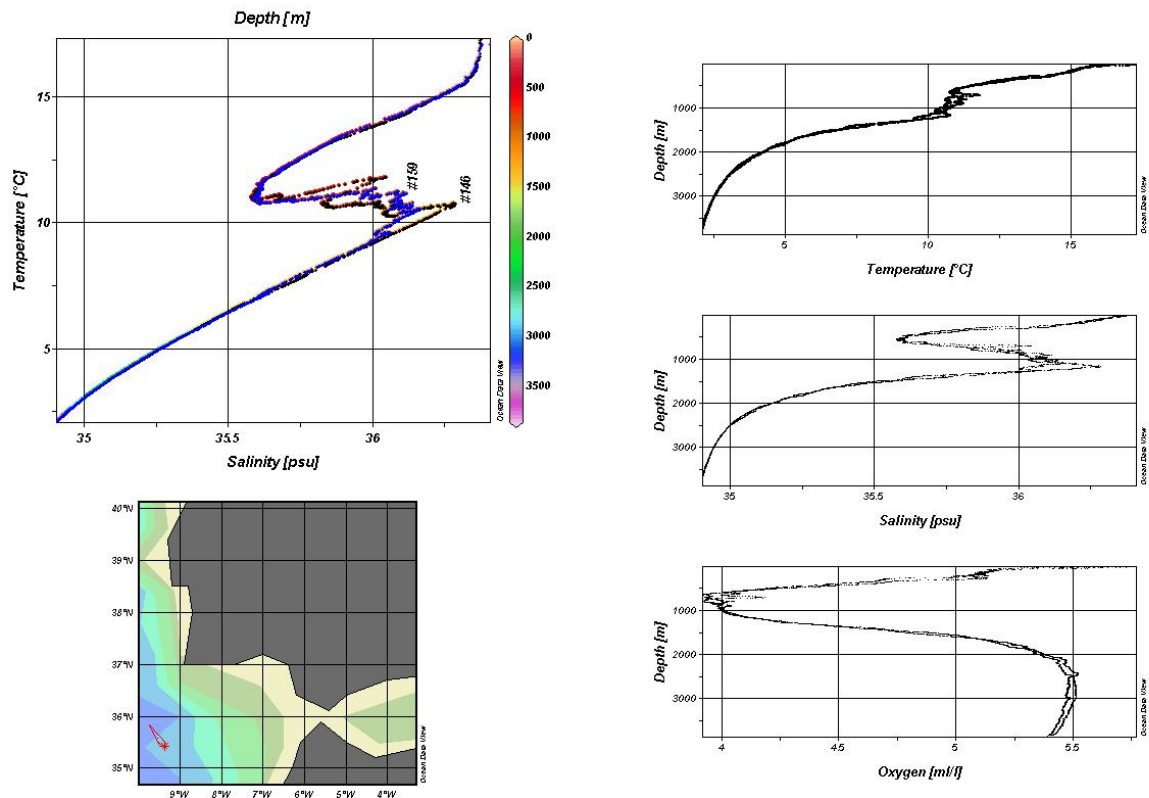


Fig. 4: CTD profiles and T/S plot from Porto MV.

An Bord sind alle wohlauf.
Es grüssen.

O. Pfannkuche und alle Fahrtteilnehmer



Maria S. Merian Cruise 1 leg 3

Third weekly report: 26. 04. - 02. 04. 2006

Station work of the entire last week was transferred to the realm of the mud volcanoes occupying the depth range 1300m to 1000m. Our activities focused on a detailed sampling at Captain Arutyunov MV (CAMV, Fig. 1). This MV located in 1320m depth has been previously known for intense subsurface biogeochemical activity and the occurrence of gas hydrates.

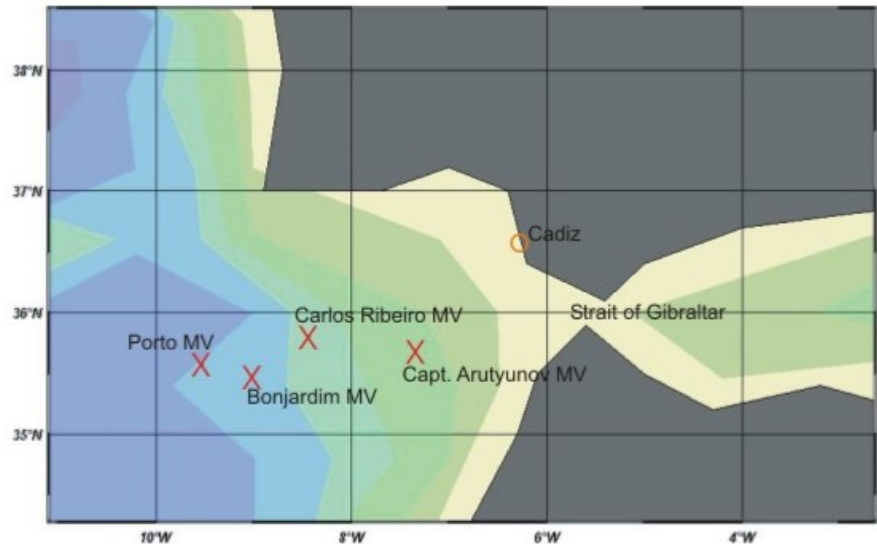


Fig. 1: Working area with positions of the mud volcanoes so far investigated.

A highlight of our CAMV survey was the finding of hand sized gas hydrates, which were sampled with a box corer from quite shallow sediment depth of 10-20cm. In contrast to other sites with surficial gas hydrates such as in the Gulf of Mexico or at Hydrate Ridge no bacterial mats (*Beggiatoa*) indicated the presence of the hydrates. Only dense occurrence of *Thyasira* shells and a peculiar grooved sediment surface morphology covered with a network of brownish polychaete aggregations pointed to the presence of enhanced biological activity. Thus the sampling of substantial gas hydrate deposits in such shallow depth came as a surprise to us although it was already indicated by the large gas bubbles escaping from the box grab when it came to the water surface. Due to the rapid destabilization of the hydrates the water in the sampling box seemed to boil when opened (Fig. 2). We could recover a quantity of gas hydrates which were stored in liquid nitrogen for further analysis at home.



Fig. 2: "Boiling" water indicating the presence of gas hydrates in a box corer sample. Ten minutes after taken on board gas hydrates of substantial size were picked from the mud.

Steep geochemical gradients close to the sediment-water interface could be detected at CAMV, indicating strong fluid advection rates at this site (Fig. 3). In comparison to the deep-water mud volcanoes investigated earlier on this cruise the fluids are obviously more enriched in ammonium and depleted in bromine. The strong exponential decrease in bromine, which can be regarded as a conservative tracer within the sampled depth interval, can be used as a measure for the upward advection of deeply mobilized fluids. Another major difference is that chloride concentrations slightly increase with depth and indicate the dissolution of halite in the subsurface. High-resolution geochemical analyses of surface sediments (retrieved from multicorer and lander deployments) indicate a high efficiency of the benthic filter, which is responsible for generally low rates of fluid expulsion into the bottom water in the vicinity of the whole mound structure. At some places, active pumping of seawater and H₂S consumption by dense populations of Pogonophora maintain almost zero H₂S-levels in the pore water even within the zone of anaerobic methane oxidation.

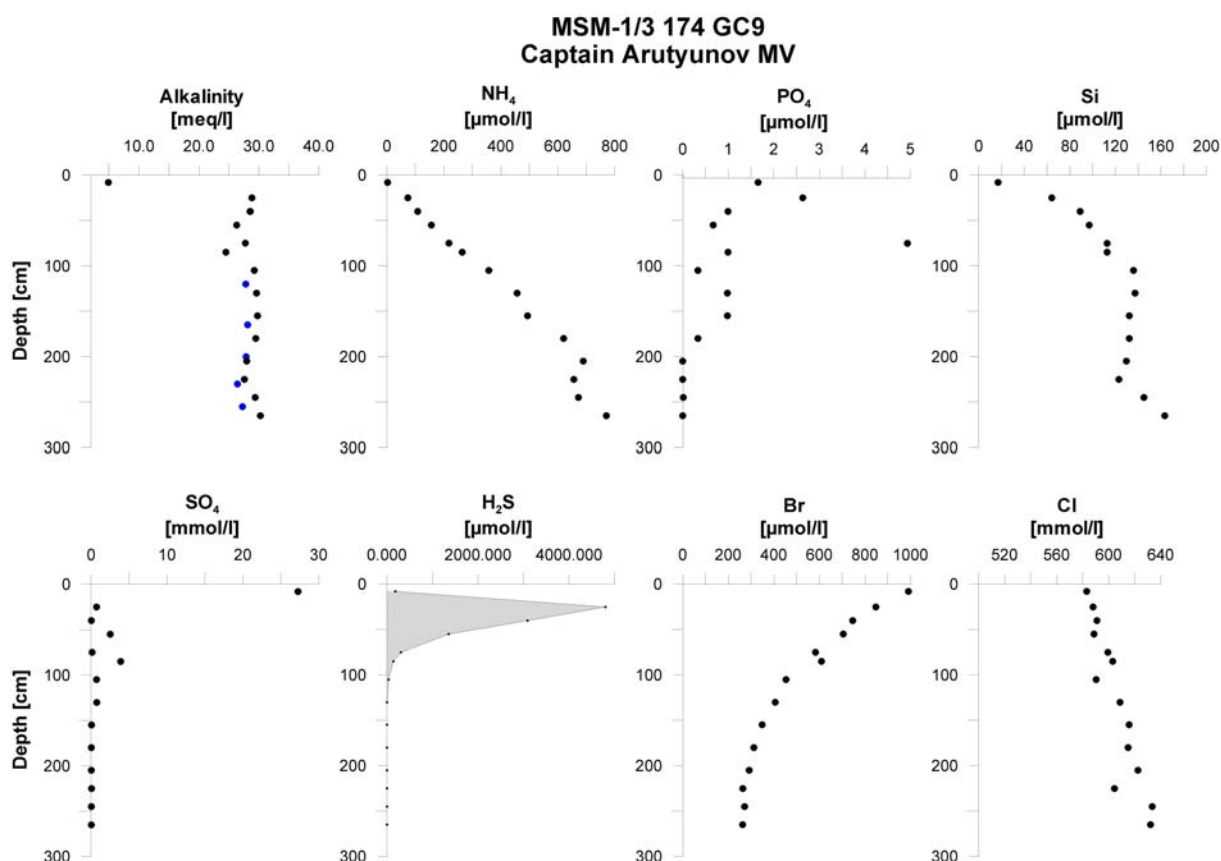


Fig 3: Pore water profiles of a gravity core at Captain Arutyunov MV.

Outflow breccias from the investigated mud volcanoes contained a varying proportion of erratic clasts. They are enriched in layers forming indurated breccias as revealed by sediment cores. On the sea bed, the clasts may be enriched in stripes probably depicting the margins of different mudflows. These stripes are moulded by the lower Mediterranean Outflow Water to starved ripples of subangular gravel on the top plateau of Captain Arutyunov mud volcano. Every mud volcano is characterised by a unique lithological composition of the xenolithic clasts. Outflow breccias from Bonjardim mud volcano contained green clay pebbles and a substantial proportion of dark, indurated claystone. Porto mud volcano yielded pebbles of green clay, chalk, and tectonised yellowish sandstones with vein fillings. Sediments from Carlos Ribera mud volcano contained dark green claystones. They showed evidences for brittle and ductile deformation, in particular cleavage faces and slickensides. The claystones were of Eocene age as revealed by numuliths while the clay matrix contained *Globorotalia inflata* and *G. tumida* indicating that Pliocene or Pleistocene sediments were liquified and thus contributed to the mud flow formation. Captain Arutyunov yielded tectonised grey marls and green claystones, sandy siltstones and quartz sandstones. In particular the siltstones showed vein fillings of sparry calcite, and open cracks filled with mud breccia probably formed during fluidisation. Pelagic sediments in the vicinity of the mud volcanoes were yellowish to dark grey clays with a prominent contouritic fine sand layer of approximately 10 cm thickness at 154 cm depth in core MD01/3-183. This bed is widely distributed in the Gulf of Cadiz

and was formed by an extraordinary strong Mediterranean Outflow activity at depths during Heinrich E.

The finding of living reef building cold water corals at CAMV was another highlight of the last week. Patches of corals were observed around the 1400m depth contour at the base of CAMV in several OFOS surveys. Many of them were partly buried or nearly covered with sediment, but we still found living specimens on larger reef structures. Due to the extraordinary manoeuvrability of M. S. MERIAN we were able to sample such a structure with the large TV grab and prove for the first time the existence of living coral patches in such water depth in the Gulf of Cadiz (Fig. 4).



Fig. 4: Coral reefs at the base of Captain Arutyunov MV; sampling with the large volume TV-grab; close up of a living stone coral (*Caryiophyllia* sp.).

The three OFOS Surveys at CAMV showed a diverse range of microhabitats. At the flanks the fauna is scarce but there are numerous burrows arranged in clusters at the lower flanks and forming small mounds of bioturbated sediment (mud breccia) up slope. Patches of semi-buried corals were observed especially around the depths of 1400m. The larger structures of coral, mainly occurring at the southern flank, show abundant epifauna (eg., Octocorallia, Ophiuroidea, Arcidae, Cirolanidae) and are often accompanied by a higher density of shrimps (*Pandalidae* and others) and fish. The top of the MV appears highly active with a rim of disturbed sediment and numerous *Buccinidae* shells and clasts. A few living specimens of *Neptunea contaria* were sighted in this area. Towards the centre the seafloor is rippled, covered by numerous clasts and shells and has a patchy appearance. The most conspicuous animals were *Cidaridae* echinoids clustered at the centre of the MV. Several samples taken at the top showed that some areas are densely covered by *Siboglinum* aggregates while other areas have fewer *Siboglinidae* but a high abundance of other *Polychaeta*. In the most active areas these *Polychaeta* are accompanied by *Thyasiridae* bivalves.

The molluscan thanatocoenoses of the CAMV was studied from van Veen grab, box core and a TV-grab sample, taken in areas representative for the variety of different sediment facies as seen from the OFOS investigations. Samples from muddy areas showed the lowest mollusc diversity. They were almost completely built by bivalves (e.g. *Limopsis minuta*, *Yoldiella* sp., *Katadesmia* sp. and *Cuspidaria cuspidata*).

Pebbly habitats, as the detected fields on the top and the north-western part of the Captain Arutyunov MV were dominated by *Limopsis minuta* and *Bathyarca pectunculoides*. Gastropods settling on stones as *Emarginula* sp. and small carnivorous gastropods of the family Turridae or *Amphissa acuticostata* were present.

A biodiversity hotspot was sampled at the coral built ups. Although the corals were mainly dead a very rich reef-associated fauna was found. From a representative sample a highly diverse mollusc fauna was extracted with more than 100 species. Highest diversity with at least 15 species was found within the family Turridae (e.g., *Spirotropis modiola*, *Gymnobela* spp., *Mangelia* spp.), furthermore many Trochidae (e.g., *Calliostoma* sp., *Putzeysia wiseri*, *Solariella* sp.). Other families included were Turbinidae, Rissoidae, Epitonidae, Eulimidae, Architectonicidae, Bullidae. The gastropod fauna is dominated by *Amphissa acuticostata*. It includes all feeding types as grazers, deposit feeders and carnivores.

The bivalve fauna is clearly dominated by *Asperarca nodulosa*, a suspension-feeding species attached to the corals by byssus. Other suspension feeders as pectinids are also common, dominated by species also attached by byssus. It is worthwhile to mention that even bivalve families adapted to a life in unfavourable deep-sea conditions show a much higher diversity here than in other habitats investigated. The carnivorous Cuspidariidae are represented by at least 6 species in the reef association, while only 2 species (*Cuspidaria cuspidata* and *C. inflata*) were found in the other samples.

On Monday evening we stopped our station work at CAMV, leaving the DOS- and BIGO-Lander deployed and steamed to Cadiz where we docked on Tuesday morning. At Cadiz a part of the scientific crew is changed and a multitude of repairs and guarantee works are undertaken by various contractors.

An Bord sind alle wohlauf.
Es grüssen.

O. Pfannkuche und alle Fahrtteilnehmer



Maria S. Merian Cruise 1 leg 3

Fourth weekly report: 03. 05. - 09. 05. 2006

We left Cadiz on Wednesday (03.05) at 19:50h and headed back to Captain Arutyunov MV (CAMV) with a service technician from IXSEA on board. We stopped our transit to CAMV some miles off the MV where we deployed a POSIDONIA transponder on a short mooring at 1160m depth in order to calibrate the newly installed POSIDONIA System. The calibration proceeded routinely. However, when we tried to retrieve the mooring with the POSIDONIA transponder the mooring did not swim up although the acoustic releases had confirmed the release from the anchor weight. We decided to postpone any salvage operation and steamed to CAMV where we successfully retrieved the BIGO lander deployed on Monday (01.05). We headed back to the mooring side and decided to salvage the mooring with the OFOS equipped with some short draglines and hooks. Another POSIDONIA beacon on the OFOS enabled a precise navigation of the OFOS and concurrently turned out as an excellent test for the functioning of the POSIDONIA system. In consequence we could spot the anchor weight with the first deployment of OFOS and with the help of the outstanding manoeuvrability of the ship we were able to push OFOS against the mooring next to the release transponders and thus to set free the entangled acoustic releases. The mooring swam up immediately after the first impact and could be retrieved safely. We then headed back to the pilot station to disembark the IXSEA service technician and to take in a journalist from a pilot boat who will report about our activities from Leg 3b. A web log about MSM 1-3b is installed on the home page of the Deutsche Welle : www.dw-world.de (search under: dw tv / „was gibt´s“ / Sendungen / Projekt Zukunft or Tomorrow Today)

We steamed back to CAMV and continued station work. The FLUFO Lander was deployed “right within a crater of mud flow” and for the first time the PWPL Lander (Pore Water Pressure Lance) only 6m apart from FLUFO (Fig. 1b). The PWPL carries a pore water lance of two metres length which is driven by a motor into the sediment. With this deployment we finished our station work at CAMV and steamed east towards the region of the shallow Moroccan mud volcanoes. Our first target was the Mercator MV where we started with a comprehensive OFOS survey in order to identify areas of enhanced biological activity triggered by methane flow. We could visualize methane bubbles near the top of the MV. We also enlarged our investigation box to the adjacent Renard Ridge and performed an OFOS survey at the Pen Duick escarpment to detect coral occurrences on a transect perpendicular to the ridge. We left the area again to revisit CAMV where we deployed the BIGO Lander at the gas hydrate site and retrieved three landers from the top of CAMV: DOS Lander, FLUFO Lander and PWPL Lander. Afterwards we steamed back to Renard Ridge and started an intensive OFOS survey on the western crest of the ridge where massive occurrence of dead Lophelia reefs were detected. On Monday night we headed further south to the Mekenese MV near 35°N and mapped the area with multi beam.

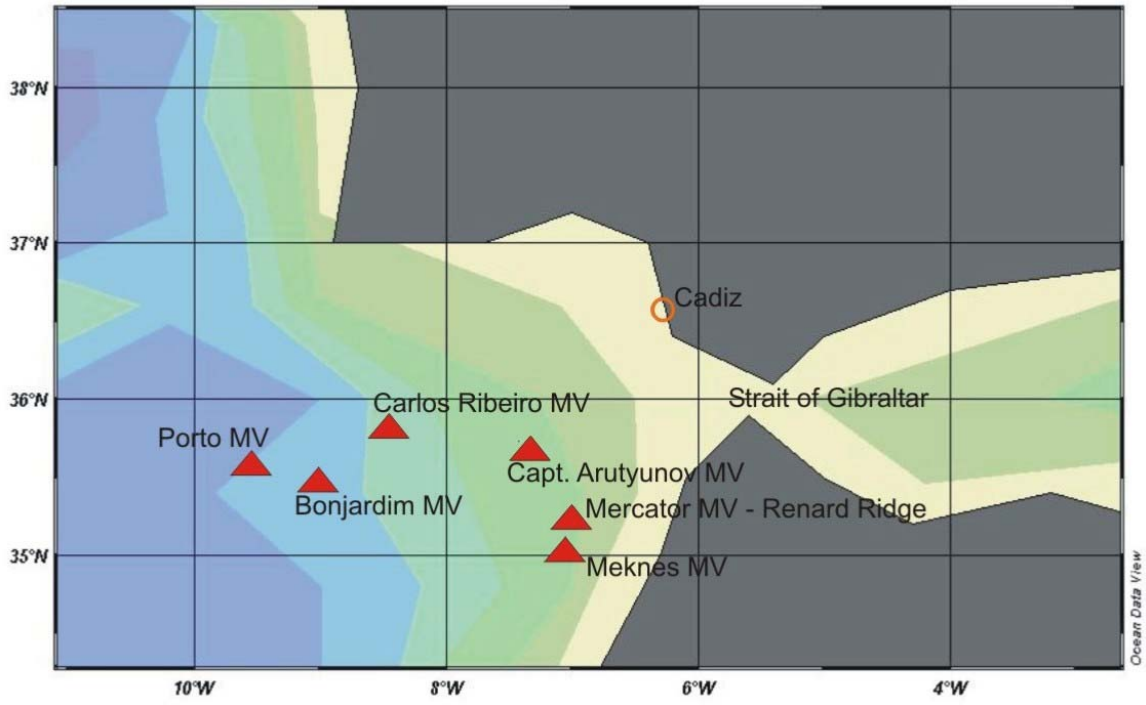


Fig. 1a: Working area with positions of the surveyed mud volcanoes.

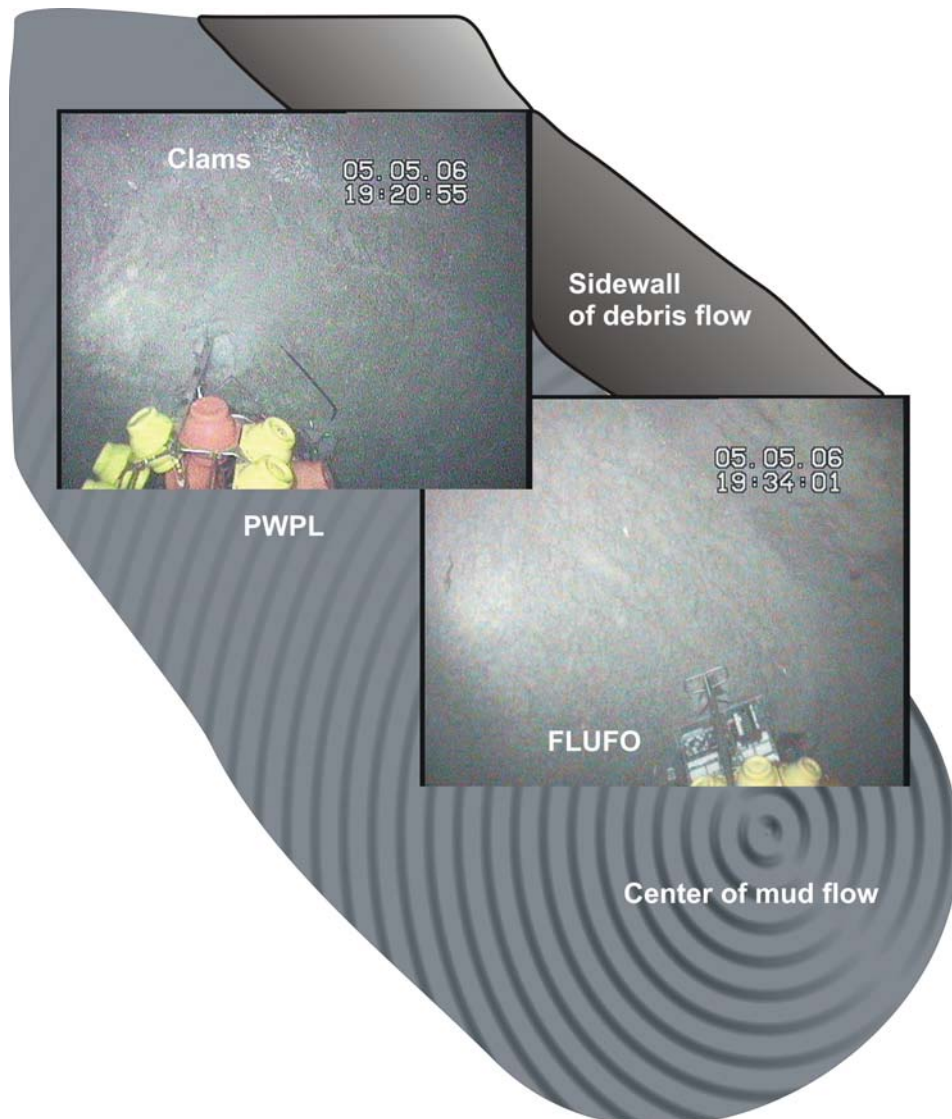


Fig. 1b: Illustration of the CAMV site

The hydrographic regime at CAMV was studied in detail and can be described as follows: Situated at a water depth between 1420 and 1312m, the top of the mound lies well below the lower tongue of the Mediterranean Outflow Water (MOW). The aim of the CTD casts was to investigate possible relations between physical properties and spatial variability of water masses and the occurrence of cold water corals at the mound which were sampled with the TV-Grab.

High-resolution CTD measurements (potential temperature, salinity, density, and dissolved oxygen) in the working area allowed the identification of the main water masses present in the study area. The potential temperature versus salinity multiplots of the CTD casts show the following hydrological structure (see Figure 2): (a) the upper surface layer (0- ~170m); (b) the permanent thermo-halocline, corresponding to the North Atlantic Central Water (NACW) between ~170-700m; (c) the two layers of warm and salty MOW at ~780 and 1200m; and the (d) the presence of North Atlantic Deep Water (NADW) associated with depth-decreasing thermocline properties.

A total of 13 CTD/Ro casts have been carried out in 5 days which spanned over two full tidal cycles covering ~ 24 hours. The measurements indicate strong variation of water masses between 250 and 1250 meters. The greatest changes occur within the upper and lower core of the MOW suggesting either tidal influence or varying outflow from the Strait of Gibraltar. Closer analysis of weather patterns in the study area and the Alboran Sea will be used to investigate these two options. Changing pressure systems have already been identified to influence Mediterranean outflow (W. Zenk; pers. comm.). Analysis of the distribution of potential temperature and salinity indicate variable water masses. The greatest variation occurs within the two cores of the high saline and warm MOW. In the upper core salinity varies between 35.85 and 36.09, whereas salinity in the lower core ranges from 35.99-36.10. At the same time the depth of the salinity maxima varies between 761 and 816m for the upper core and 1128 and 1209m for the lower core. For the analysed parameters such as potential temperature, salinity, density, and oxygen content no variation within the bottom waters surrounding the few living corals has been observed. Bottom waters show only minimal variation of the physical parameters across tidal cycles in the vicinity of the CAMV.

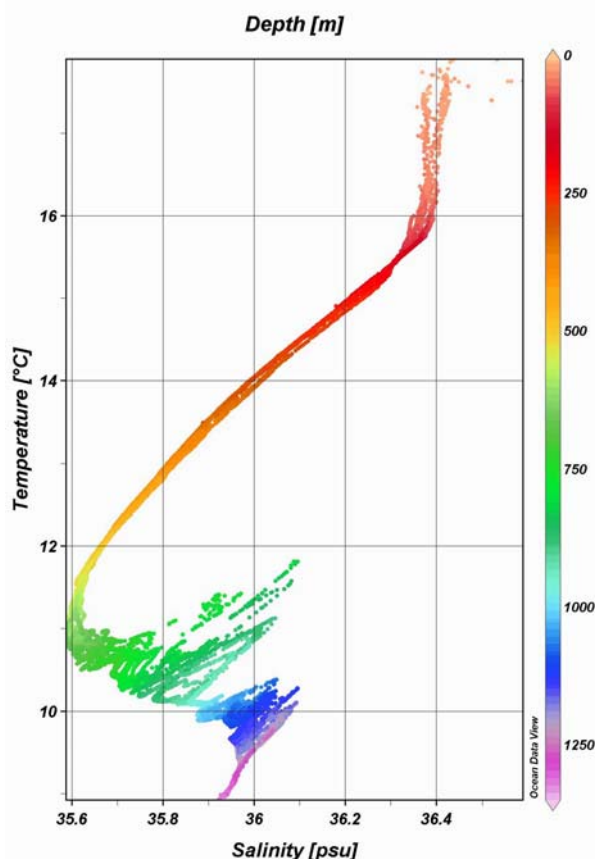


Fig. 2: T/S plot from Captain Arutyunov MV.

At the Mercator MV, sediment was sampled at the only gas bubble site reported so far in the area of the Gulf of Cadiz. The occurrence of gas bubbles could be confirmed by our OFOS observations. The pore water showed an extreme enrichment of Cl^- and SO_4^{2-} (Fig. 3) which are amongst the highest reported for mud volcanoes. Bottom water concentrations start at values only slightly higher than normal seawater, but rapidly increase below the surface to more than 8000 mM of chloride at a sediment depth of 200 cmbsf. Sulphate concentrations at the Mercator MV show a sulphate maximum at about 100 cmbsf and are about 2-3 times higher than sea water concentrations throughout the gravity core. These elevated SO_4^{2-} levels coincide with findings of gypsum in the core. The distinctive curvature in the Cl^- profile is indicative for quite rapid fluid ascent compared to the other mud volcanoes investigated in the previous weeks. The advection rate was preliminarily estimated to be in the order of 2 cm/a using simple transport-reaction modelling (see solid line in the Cl^- plot in Fig. 3). Potential sources for the chloride and sulphate are halite and gypsum dissolution, respectively.

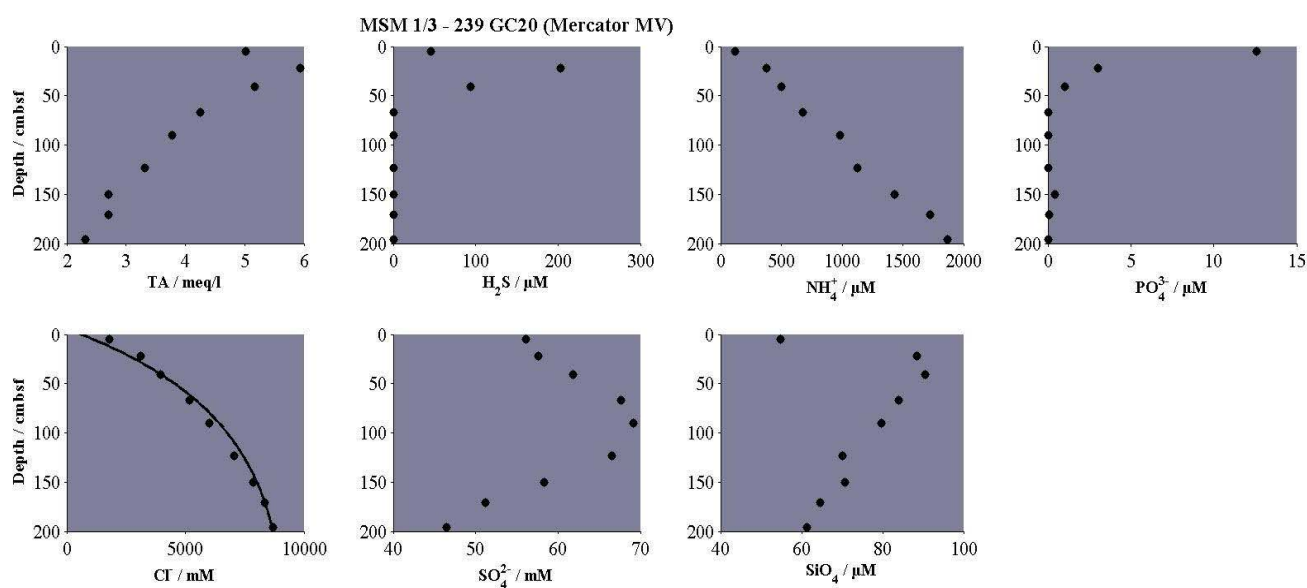


Fig. 3: Porewater profiles of a gravity core at a gas bubble site of the Mercator MV.

Mud volcanism represents an important pathway for fluids and gases from deeper reservoirs. Although several studies about the geochemistry and biology of mud volcanoes in the Gulf of Cadiz have been conducted, their activity in terms of methane emission into the water column and associated biogeochemistry has been only very poorly constrained.

Seabed methane emission, turnover and flux rates of oxygen, sulfate, sulfide, nitrate and ammonium are measured in situ using the Biogeochemical Observatory, BIGO, and the Fluid Flux Observatory, FLUFO. Parallel investigations are conducted using the TV-Multicorer, DOS (Deep Sea Observation Lander) BWS (Bottom Water Sampler Lander) and OFOS. BIGO and FLUFO are equipped with two benthic chambers each, which are driven into the sediment also enclosing a certain volume of overlying water from which at defined time intervals water samples are taken during the measurements. At the end of the measurements the sediment is retrieved by the observatories for later pore water analyses (Fig. 4).

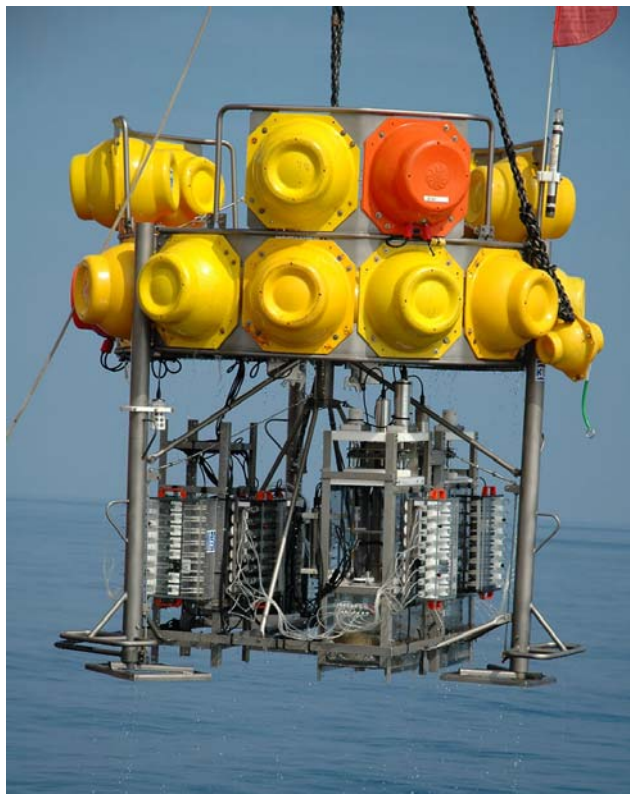


Fig: 4: Retrieval of the BIGO Lander with two mesocosms containing sediments.

From the water samples the time course of the concentration of methane, oxygen, sulfate, sulfide, nitrate, ammonia, pH and total alkalinity is deduced allowing the calculation of interfacial fluxes. Although the chambers are driven very slowly into the sediment instantaneous release of methane and other solutes into the overlying water column can occur. Thus, briefly after the chambers of BIGO have been driven into the sediment the chamber water is exchanged with ambient sea water to establish natural conditions for the start of the measurement. During the deployment the so called “Control” (CO) chamber of BIGO is flushed with ambient seawater at several time periods. By this means it is possible to measure seabed methane emission and other fluxes with a defined temporal resolution inside the same chamber. The second chamber of BIGO, further referred to as “Exchange” (EX) chamber is equipped with a gas exchange system (“Kieme”). This system maintains the oxygen level inside the Exchange chamber at the out-side level or it can be set to a defined oxygen concentration. Since the release of many solutes from the sediment is redox-sensitive, this system allows to measure fluxes at stable natural conditions or to conduct experiments under different oxygen tensions.

During the past weeks the mud volcanoes Bonjardim, Porto, Carlos Ribeiro, Captain Arutyunov and Mercator have been investigated. The biogeochemistry group focused their activity on CAMV where we found gas hydrates near the sediment surface. At all mud volcanoes distinct biological chemotrophic communities of bivalve molluscs and different species of tube worms are present. With respect to the occurrence of methane in the upper 30 cm layer of the sediment a wide range of methane concentrations were found (Fig. 5). Lowest concentrations were measured at Bonjardim MV and Porto MV, whereas highest concentrations were found at Carlos Ribeiro MV and CAMV. Within site variability is very high thus methane concentrations vary considerably. At almost all studied mud volcanoes elevated methane concentrations were not found at the surface of the sediment, except at CAMV in BIGO 2 CO_PL_1 (Fig. 5), where methane concentrations of up to $40 \mu\text{mol.l}^{-1}$ sed. were detected in the uppermost sediment layer. At this site we also detected high methane concentrations in the benthic boundary layer with a maximum of 687 nmol.l^{-1} at about 7cm above the sea floor (BWS #4, Fig. 6, indicating seabed methane emission. CTD casts at this site revealed maximum methane concentrations of 16 nmol.l^{-1} about 4 m above the sediment surface (Fig. 7). The background methane concentration in this area is 2.5 nmol.l^{-1} .

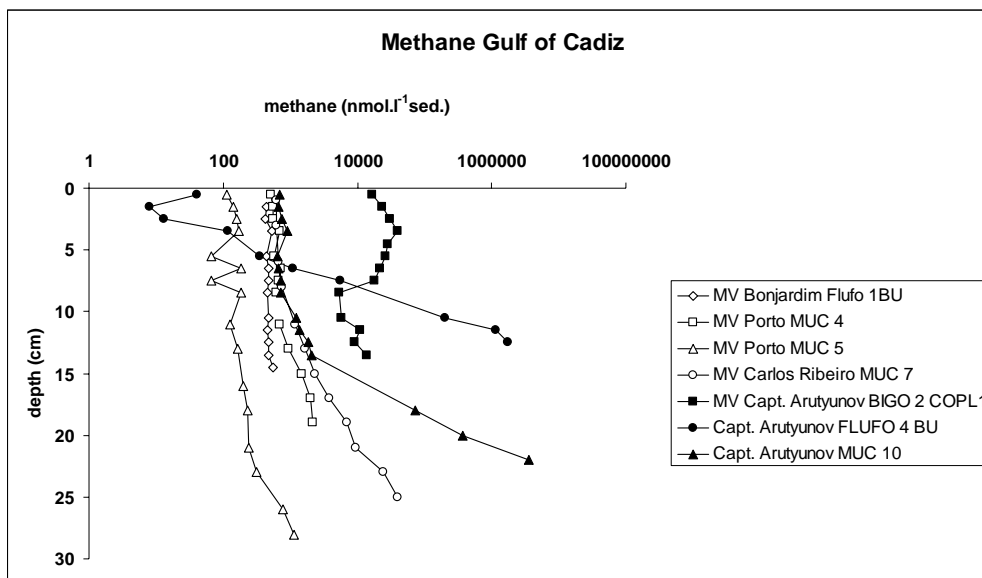


Fig. 5: Methane concentrations (log scale) in the uppermost 30 cm of the sediment at different mud volcanos in the Gulf of Cadiz.

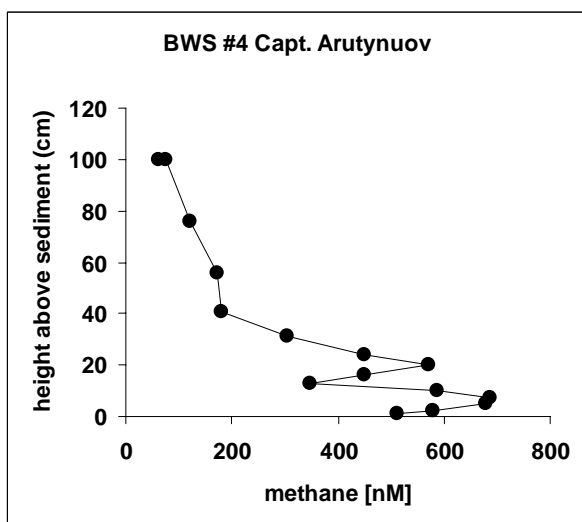


Fig. 6: Vertical methane concentration profile in the benthic boundary layer at the mud volcano Captain Arutyunov.

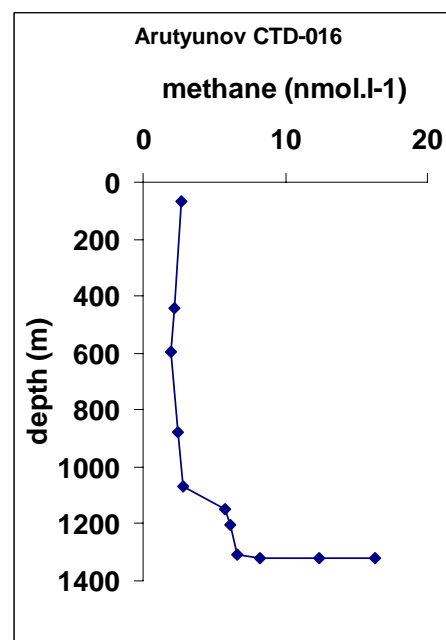


Fig. 7: Methane concentration in the water column above Arutyunov mud volcano.

At CAMV two BIGO (BIGO #1/#2) and one FLUFO (FLUFO #4) deployments were conducted for about 50 – 69 hours. Operation of the observatories was perfect. The gas exchange system deployed in BIGO to compensate oxygen consumption inside the benthic chamber (EX chamber) worked perfect and maintained the oxygen level inside the chamber at the defined level of $160 \mu\text{mol.l}^{-1}$ over the entire time period of the measurement (Fig 8). At defined time intervals the water enclosed by Control chamber was exchanged with the ambient sea water to re-establish ambient natural conditions. By these means interfacial fluxes at different time intervals can be measured inside the same chamber. Oxygen consumption inside the control chamber is similar during the different time intervals. The noisy oxygen signal during the 3rd and fourth time interval is due to a failure of the stirring mechanism. During these measurements water samples for the later determination of methane, oxygen and other solutes

were taken at defined time intervals from inside the chambers (Fig 9). Additional samples were taken from the bottom water to monitor ambient conditions. From these water samples and the sediments retrieved by the benthic chambers Radon measurements were conducted, which will allow to reconstruct fluid flow rates.

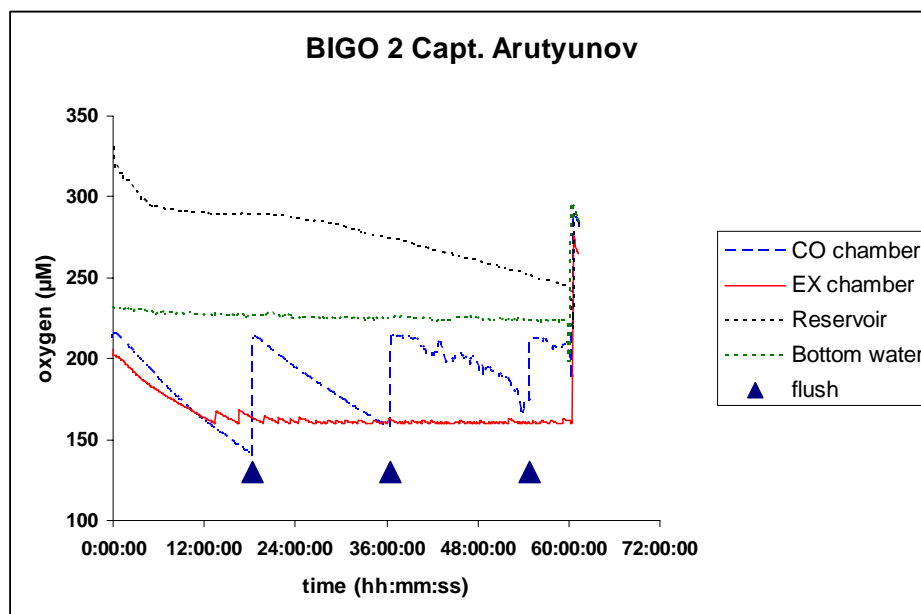


Fig. 8: Time course of the oxygen concentration inside the benthic chambers (EX and CO), the reservoir and the bottom water during deployment BIGO #2. The EX chamber is equipped with a gas exchange system. Oxygen is provided to this chamber from a reservoir containing filtered oxygen saturated sea water. At several time intervals (see triangles) the water inside the CO chamber was exchanged with the ambient bottom water.

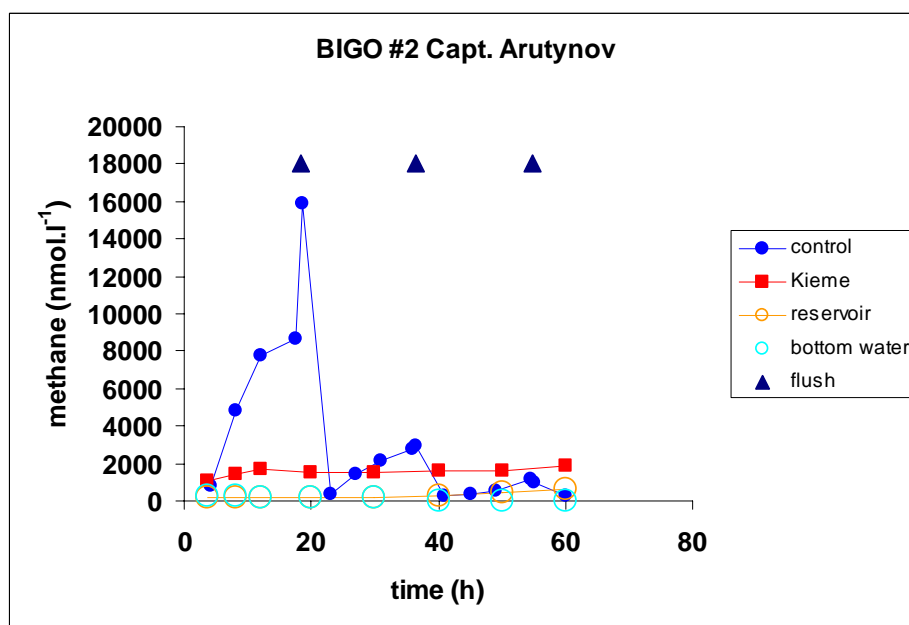


Fig. 9: Time course of the methane concentration inside the benthic chambers, the reservoir and the ambient bottom water during deployment of BIGO #2. Time periods, where the water inside the CO chamber was exchanged with ambient bottom water are indicated by triangles.

The diverse, presence of subsurface methane at CAMV appears to be correlated with the occurrence of extremely high abundances of pogonophores, probably of the genus *Siboglinum*, (Fig. 10), bivalve mollusks of the genus *Thyasira* and clasts (Fig. 11a-d).



Fig. 10: Bundles of pogonophorans (red bundles) sticking out at the base of the benthic chamber of FLUFO #4. They form dense forests on the surface of the sediments (see also Fig. 11)



Fig. 11: a. Bundles of tubes of *Siboglinum* sp.; b. living bivalve mollusk of the genus *Thyasira*; c. sparite (Kalkspat); d. clast, the stripes on clast shown in plate d might be caused from pogonophoran tubes. Samples are taken from different gears at MV Capt. Arutyunov.

Pogonophorans of the genus *Siboglinum* have been also described from methane seepage sites in the central Skagerrak (*S. poseidoni*) or from organically highly enriched sediments in fjords of Norway and Sweden (*S. ekmani*, *S. fjordicum*). They live in long tubes. They do not possess a mouth and gut openings. Instead of the presence of the digestive tract, the interior of *Siboglinum* carries a long sac like trophosome filled with chemosynthetic endosymbiotic sulfide- (*S. ekmani*, *S. fjordicum*) or methane- oxidizing bacteria (*S. poseidoni*). The posterior ends of the pogonophores extend out from the sediment into the oxygenated bottom water (Fig.12).

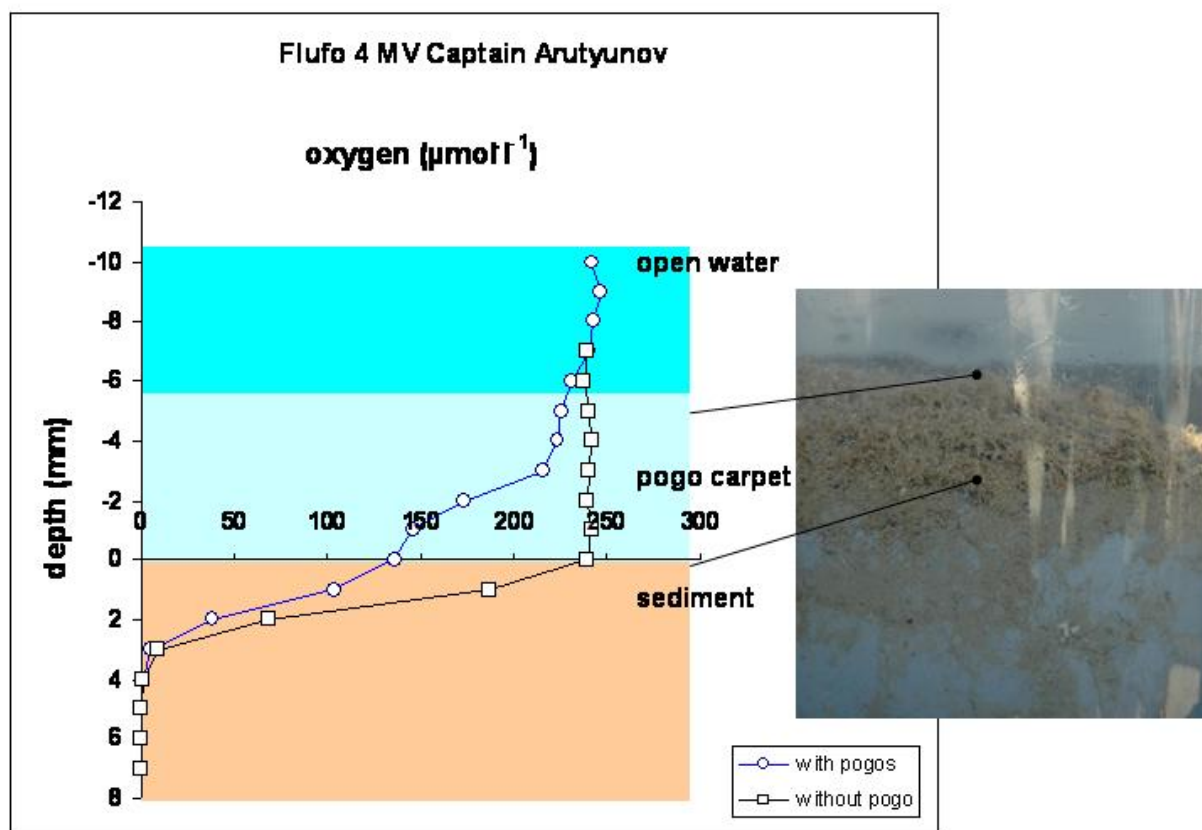


Fig. 12: Oxygen micro-profiles in sediments densely covered with pogonophorans (circles) in comparison to a location a few centimeters away with bare sediment (quadrats) (FLUFO #4). Photo insert shows vertical view of the benthic chamber of FLUFO #4.

The anterior end of the pogonophoran tubes penetrates deep down into the sediment. There the tube might be connected to sediment horizons with increased methane and sulfide concentrations, which are needed by the pogonophorans for their chemotrophic endosymbionts. During slicing the sediment cores from CAMV (FLUFO 3 Flux, MUC #9, MUC #10, BIGO 2 EX/CO) a smell of sulfide was detected in deeper sediment layers. Although dissolved sulfide was not detected in the upper 13 cm of the sediment core in FLUFO #4, elevated methane concentrations of $>200 \mu\text{mol.l}^{-1}$ sed. were measured at a depth of 10 cm. We can only speculate whether the chemotrophic endosymbionts of these pogonophorans depend on the supply of methane or sulfide. Anaerobic oxidation of methane which represents a major process in the methane turnover in seep sediments of the Gulf of Mexico and Hydrate Ridge releasing high levels of sulfide into the pore water apparently is not active at the seep sediments of CAMV, but there is a strong need for further microbiological investigations.

The tubes of the pogonophorans might represent ideal escape pathways for methane from deeper sediment layers into the water column. However, only very little methane has been released from this sediment into the overlying water column during FLUFO #4 deployment. In contrast to the methane measurements Radon show the highest concentrations ever measured

in this sea area. This points to the likelihood that Uranium is enriched in the anoxic sediment associated with the pogonophores. It is likely that the pogonophorans, their endosymbionts but also microbes attached to their integument control methane flux through these tubes. The high abundances of pogonophorans create a dense "forest" extending about 5 to 7mm into the water column. In this zone we measured lower oxygen concentrations than in the upper water column (Fig. 12). Probably this forest creates its own micro-climate which might further affect flux of methane and other solutes.

Our findings demonstrated that the Gulf of Cadiz mud volcanoes are highly different in comparison to the seep environments of the Hydrate Ridge or the Gulf of Mexico. We had to learn to think on different scales and concentration ranges, but we observe fascinating methane driven environments with distinct biological communities.

An Bord sind alle wohlauf.

Es grüssen.

O. Pfannkuche und alle Fahrtteilnehmer



Maria S. Merian Cruise 1 leg 3

Last report: 10. 05. - 18. 05. 2006

In the last week our activities were split geographically between Captain Arutyunov MV (CAMV) in the north, Meknes MV in the south and Mercator MV with the adjacent Vernadski Ridge and Renard Ridge/Pen Duick Escarpment in between. Geochemical work focussed on Meknes MV and Mercator MV whereas coral mound investigation was more concentrated to the ridges. The biogeochemistry group further focussed on CAMV with additional lander deployments, BBL water sampling and multiple corer sampling. We retrieved more gas hydrates from about 20cm sediment depth and found substantial gas flares with the 12kHz echo sounder extending up to 400m above the sea floor on top of CAMV. We deployed the Pore Water Pressure Lance Lander (PWPL) for long-term observation at the gas hydrate field on top of CAMV and the Deep Sea Observatory Lander (DOS) on a coral mound at Renard Ridge. Both long-term observatories will be retrieved with FS Meteor in August this year. At 02:00h on Thursday (18.05.) we finished station work and started our voyage to Lisbon where we will arrive on Friday morning (19. 05).

The geochemistry group investigated six mud volcanoes, Bonjardim, Porto, Carlos Ribeiro, Captain Arutyunov, Mercator, and Meknes, with a total of 48 cores. These structures cover the range from 3800 m to 360 m water depths. The objective was to determine the origin of the fluids expelled into the overlying water column and to quantify the present day activity of the mud volcanoes.

At all mud volcanoes, the geochemical concentration-depth profiles are influenced by anaerobic methane oxidation. The depth of this reaction front strongly depends on the upward advection rate of deep-sourced fluids pushing the AOM zone close to the sediment surface (< 1m). In many places, data from the top few centimetres of the sediment show the effectiveness of the benthic filter at the sediment surface, e.g. pogonophora, in changing the composition of these fluids and thus preventing H₂S- and CH₄-rich fluids to escape into the water column. A good example is given by the data of a multi corer from CAMV (Fig. 1). The sediments contained finely dispersed gas hydrates below a sediment depth of 20 cm. Upon core retrieval the decomposition of the hydrates could be followed with the camera mounted to the MUC. No solid hydrate pieces survived until the gear was secured on deck. The respective pore water profiles show the irrigation of bottom water into a sediment depth of 10 cm, most likely due to pogonophorans and polychaetes. This sulphate-rich pore water then reacts with the upward advecting methane-rich fluid from below. As a consequence, a very narrow AOM zone was observed around 1 cmbsf, accompanied also by steep gradients in sulphide and total alkalinity.

The fluid regime of the six MVs can be divided into 2 general groups according to their salinity. The deep fluids from Bonjardim, Porto, Carlos Ribeiro and Meknes carry a low chloride signature with concentrations as low as 200 mM, whereas the fluids of CAMV and Mercator are enriched in Cl⁻ with extreme values (> 8700 mM) at Mercator MV. Low chlorinities are usually due to mineral dehydration processes in several kilometres depth. High chloride contents, on the contrary, are often related to dissolution of salt deposits. Further studies of the pore water composition will provide the respective answers.

Overall, highly active sites appear to be of small size and are often indicated by gray patches with clam shells or pogonophora colonies at the sea floor. A quite good correlation of the fluid flow activity and temperature and salinity anomalies can be measured with CTD mounted to the OFOS, suggesting that the OFOS-CTD data might be suitable for a

spatial quantification of the activity on these mud volcanoes. Preliminary estimates of fluid flow rates applying numerical transport-reaction models at a couple of sites suggest moderate to low advection rates at the investigated mud volcanoes.

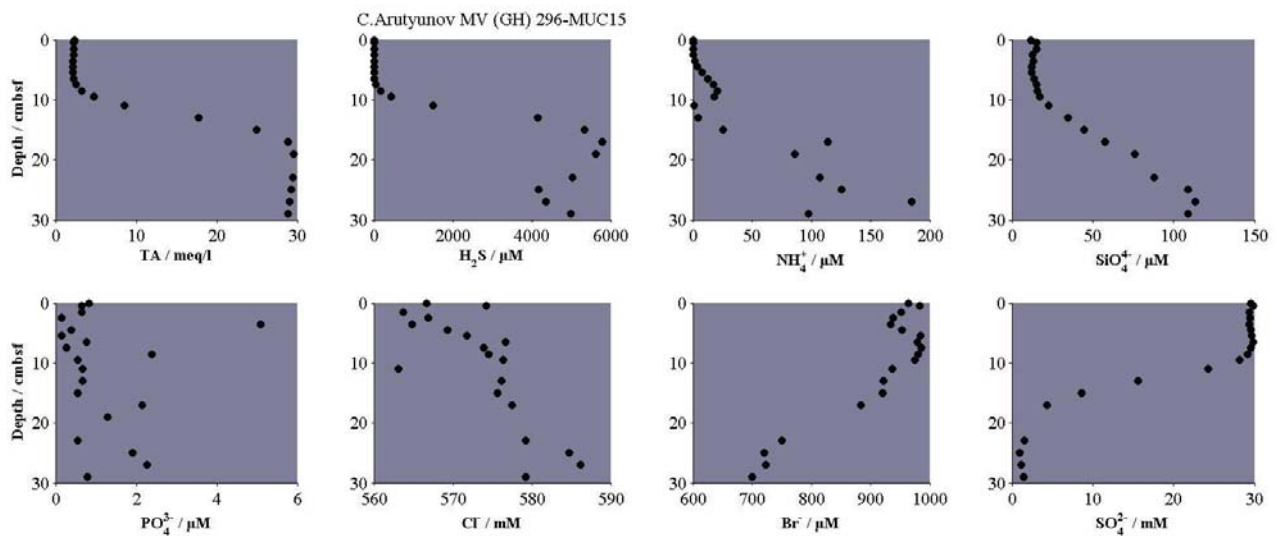


Fig. 1: Porewater profiles of a multicore at Captain Arutyunov MV with near surface gas.

The presence of numerous carbonate mounds, in the close vicinity of mud volcanoes (Gemini MV, Fiuza MV, Don Quichote MV, etc), and overlaying large faults (Pen Duick escarpment, Renard Ridge), suggests a possible relationship between carbonate mound distribution and fluid migration through the sea floor. A previous coring of a carbonate mound in this area (Privilege cruise- R/V Marion Dufresne) showed that mounds were indeed the place of an enhanced flux of methane, bearing a sulphate to methane transition zone at 3.5 m below the mound surface. At this depth, ^{13}C depleted carbonate as well as sulfide are released in the sediment column, suggesting an active zone of anoxic methane oxidation. Hence, a possible relationship between focused fluid flow and the carbonate mound distribution at Renard Ridge has been hypothesized.

One aim of this cruise was to confirm or infirm this hypothesis, by sampling several other carbonate mounds along the Renard Ridge, including the Pen Duick Escarpment and examine if they all show the same trend. We cored in total seven carbonate mounds, and measured on-board several geochemical parameters such as methane, sulphate, sulphide and alkalinity. We determined the sampling position according to the numerous topographic elevations in the form of knolls, present all along the ridge. In each case, we could recover long cores (around 5m) containing coral rubbles from bottom to top. It is therefore most likely that every single knoll on the Renard ridge is a coral carbonate mound, and that the entire ridge has been massively colonized by cold water coral over a long period.

Similar to the previous results, every carbonate mound sampled during this cruise shows a decrease of sulphate with depth, suggesting the presence of a methane oxidation zone in the deeper sediment. However, the penetration of the traditional gravity core was insufficient to reach the sulphate to methane transition zone.

According to the first measurements, methane migration seems to be of greater importance in the carbonate mounds at the south-eastern part of the ridge (Pen Duick II and Pen Duick III mounds), whereas the sulphate gradient becomes weaker toward the center of the ridge. Furthermore, the “no-name structure”, a carbonate mound sampled during the SONNE cruise 175, and located at the north-western part of the ridge was the place of a significant methane flux. Measures of bacterial activity showed a zone of anoxic oxidation of methane at 2.5 mbsf. Hence, this part of the ridge is again subject to fluid flux.

In the context of carbonate mound studies, the Renard ridge is of particular interest, and constitutes the first case of co-occurrence of fluid flow, microbially mediated oxidation of methane, and cold-water corals. However, further studies on these mounds would require the use of alternative coring or drilling facilities, to be able to reach the methane zone and the base of the mounds to determine the eventual role of fluid flux in the initiation stage of carbonate mounds.

The intense sampling of CAMV by the biogeochemistry group with different gears revealed a highly diverse environment with a distinct fauna of pogonophoran tube worms and bivalves of the genus *Thyasira* both harbouring chemosynthetic endosymbionts, thus indicating an active mud volcano. We retrieved sediment samples which obtained gas hydrates, buried about 20cm below the sediment surface with a multiple corer (MUC 15). During the heaving of the gear back through the water column, gas bubbles were observed escaping at the base of the corer liners. A single beam echo sounding record (12khz), revealed that bubble development in the sediment cores of MUC 15 coincided with the limit of the gas hydrate stability zone. Although gas release from gas hydrates created a big void in the sediment column (Fig. 2) the surface of the sediment overlying the gas void remained surprisingly intact and remained apparently relatively gas tight. This observation is completely different to sediment cores retrieved at Hydrate Ridge, where gas release from gas hydrates completely disturbed the surface sediments in multi corer tubes. Hydrate Ridge sediments appear to be more permeable enabling sulphide to diffuse up the sediment surface, inducing the formation of dense bacterial mats of *Beggiatoa*.



Fig. 2: Gas void in a sediment core retrieved by MUC deployment 15.

The sediment retrieved by MUC#15 was densely populated by pogonophoran tubeworms, furthermore empty shells of thyasirid bivalves and living polychaete worms were found. Methane concentrations in the uppermost 6 cm were below $2\mu\text{mol l}^{-1}$ sediment. As hypothesized in the fourth weekly report the pogonophoran tubeworms are apparently perfectly adapted to “bridge” the gap between well oxygenated zones at the surface of the sediment and deeper sediment strata with higher methane and sulphide concentrations to nourish its endosymbionts. Figure 3 impressively shows that these massive occurrence of pogonophorans which are able to exploit the methane derived energy (Fig. 4) for their metabolism and growth.



Fig. 3: Dense populations of pogonophoran tubeworms (red tubes) in sediments above shallow gas hydrates.



Fig. 4: After gas samples have been taken for isotope analyses the remaining gas was enlightened.

A major scientific objectives of leg MSM 1/3b was related to the investigation of framework-constructing cold-water corals in terms of distribution patterns, community analysis, physical environment and geology in the southern Gulf of Cadiz off Morocco. Special attention was paid to the interaction of active fluid flow and mud volcanoes with the spatial occurrence of scleractinian corals. This thematic priority links the objectives of the COMET project with the aims of the HERMES project and the recently launched ESF-MICROSYSTEMS project.

The areas surveyed for cold-water corals with the OFOS were Mercator MV and its adjacent ridge structure, the Vernadski Ridge, the Pen Duick Escarpment, the Renard Ridge and the Meknes MV with its surroundings. In addition, corals were mapped and collected along the deep slopes of CAMV which is the only site being affected by the Mediterranean Outflow Water.

We could confirm observations from previous cruises that framework-building coral communities were almost dead. We could not find any live *Lophelia pertusa*, *Madrepora oculata* or *Dendrophyllia cornigera*, *D. cornucopia*, *D. alternata* (Fig. 5). Careful analysis of box corer collected coral sites yield evidence of living *Stenocyathus vermiformis* that use the fossil framework as substrate. Presumably the „freshest“ *Lophelia pertusa*

frameworks were collected on the CAMV at 1400 m water depth. The morphotype of *Lophelia* is a dwarfed form with thin calcified, slender corallites as they characteristically occur elsewhere in the NE Atlantic in areas where this species comes close to its ecological limits. This is in contrast to the growth form of the fossil *Lophelia* remains from the sites in the southern Gulf of Cadiz, where thick calcified morphotypes are dominating. However, their preservation is poor due to bioerosion and chemical dissolution.

Box-coring from coral sites in the southern Gulf of Cadiz reveals a similar down core alternation of framework-constructing corals. The surface sedimentary units are dominated by *Dendrophyllia* spp. and *Stenocyathus vermiformis* with the clam *Spondylus gussoni* attached to the coral skeleton. Further down core, this assemblage becomes replaced by *Madrepora oculata* and increasingly by *Lophelia pertusa*. The latter is associated with *Desmophyllum cristagalli* and *Caryophyllia sarsiae* or *C. calveri*.

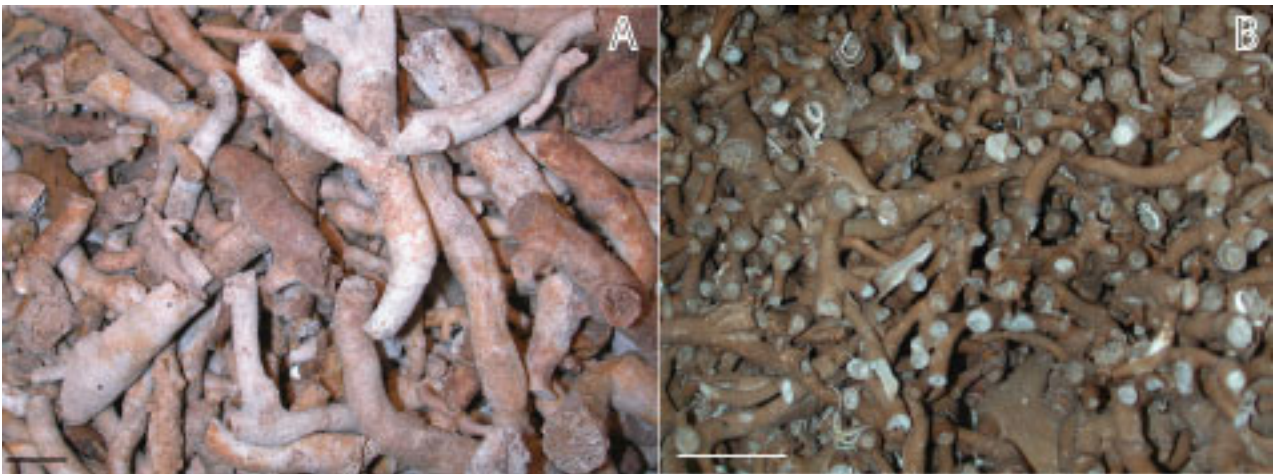


Fig. 5A: *Dendrophyllia cornigera* represents the youngest framework-producing coral community in the area studied. **B** Thin-calcified and tubular morphotype of *Lophelia pertusa* sampled at 1400 m depth from Captain Arytunov MV. Scale bars = 1cm.

The richest coral grounds were found on the Renard Ridge and Pen Duick Escarpment. This prominent structure is characterised by a series of elongated up to 40m-high elevations and knolls measuring about a half a kilometre in length. OFOS surveys, box- and gravity-coring confirms their nature as carbonate mounds. The life in and between the dead but exposed coral framework is very rich. Gorgonians and redbrown isidid colonies form important constituents of the megafauna. Current rich mound areas are indicated by masses of unstalked crinoids. The macrofauna and microfauna consists of bryozoans, serpulids, brachiopods, molluscs, hydroids, foraminifers and komokiaceans. Further down slope of the individual carbonate mounds, fine-grained deposits increasingly bury the fossil coral framework and the fauna changes to a soft-bottom community dominated by current aligned *Isidella elongata* (Fig. 6), whip corals, rare in antipatharians but rich in Lebensspuren and burrows. The surface sediment is a silty clay and it has to be analysed in the lab, how much of aeolian contribution has been accumulated in the recent past. Stochastically in the *Isidella* Facies but much more common in the coral mounds, boulder fields and outcropping rocks are a prominent feature. Especially the carbonate rocks are colonised by large sponges (Fig. 7).

Concerning the question about the interaction of scleractinians with active fluid flow it becomes clear that the framework-generating stone corals were not found in close vicinity to fluid flow sites. For instance, one of the most actively gas emitting mud volcanos, the CAMV, shows a clear spatial separation between chemosymbiotic communities on its top

and oxygen-demanding coral communities along the lower slopes. However, we find several lines of evidence for a scleractinian coral with affinities to gas seeping - the solitary coral *Caryophyllia* sp. that lives in between the pogonophoran forests on CAMV and on Mercator MV.

The overall question remains: What caused the widespread decline of framework-building cold-water corals in the southern Gulf of Cadiz? Viewing along the NW European continental margin and the Mediterranean slopes, the most vivid zones of coral reef growth are confined to the higher latitudes from the Porcupine Seabight to the southern Barents Sea. On the contrary, coral ecosystems in the Mediterranean and off Mauretania were in decline since the beginning of the postglacial period. The wide occurrence of dead cold-water corals in the wider Gulf of Cadiz calls for more suitable environmental conditions allowing even coral mound formation in the recent geological past. We have to check with a couple of datings of coral skeletons when this decline happened and what does the change of framework-building coral species means. We were quite sure that the regional extinction of the coral reefs is not related to the emission of methane by the abundant mud volcanoes. Instead, the fertility of the surface waters must have been much more productive to sustain rich coral life fuelled by benthic-pelagic coupling. Can we relate the vanishing savanna condition of the Sahel zone with the increasing desertification and surplus of aeolian transport with the decline of the coral ecosystem in the southern Gulf of Cadiz? Fascinating new scientific questions arise on the screen. This cruise is going to fill an important biogeographic gap to better understand the (paleo)-ecology of cold-water coral ecosystems as a mirror of climate change.



Fig. 6: OFOS images from the *Isidella* Facies on Renard Ridge. The octocoral colonies are oriented perpendicular to the current.



Fig. 7: Slabs of isolated boulders which are intensely colonised by sponges, hydroids and other sessile organisms, Renard Ridge.

Merian ends her maiden voyage with her arrival at Lisbon on May 19th. Her first expedition lead from the ice covered Bothnian Bay to the deep sea of the Gulf of Cadiz. Leg 3 encompassed all major oceanographic disciplines and had very ambitious goals with respect to sea floor sampling on decimetres scales under video control. Besides the A-frame we used all winches, cranes and pushing beams intensively at 233 working stations from 3800m to 360m water depth. Like with all major building sites we had to fight with initial technical difficulties which still need adjustment and fine tuning. However, we regard our achievements as excellent and are impressed by the technical potential of the ship. Maria S. Merian represents a major step towards the development of a new generation of multi purpose research vessels fit for multidisciplinary marine earth system research. The construction, propulsion system and technical installations appear to be trend setting for future constructions of German research vessels e.g. R/V SONNE replacement.

The success of this expedition was not possible without the dedicated and professional performance of captain von Staa and his crew which is acknowledged gratefully by us.

An Bord sind alle wohlauf.
Es grüssen.

O. Pfannkuche und alle Fahrtteilnehmer