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Mud volcanoes and gas hydrates in the Black Sea: new data from Dvurechenskii and Odessa mud volcanoes

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Abstract *Meteor* cruise M52/1 documented the presence of gas hydrates in sediments from mud volcanoes in the Sorokin Trough of the Black Sea. In a mud flow on the Odessa mud volcano, a carbonate crust currently forms in association with anaerobic methane oxidation. Dvurechenskii mud volcano (DMV), a flat-topped “mud pie”-type structure, appeared to be very active. Pore water in sediments of DMV is enriched in several constituents, such as ammonium and chloride, which seem to originate at depth. High sediment temperatures of up to 16.5 °C in close contact to the ambient bottom water of 9 °C also suggest strong advective transport of material from greater depth. Steep temperature gradients indicate a high fluid and/or mud flux within DMV, which is confirmed by the shape of the pore water pro-

files. Active fluid expulsion sites are evidenced by direct seafloor observation, and a potential flux of methane from the sediment to the bottom water is indicated by water-column methane measurements.

Introduction

Mud volcanoes are geological features from which mud and fluids emanate or erupt (Kopf 2002). Although they occur worldwide, their geographic distribution shows that mud volcanoes are clustered in areas of active plate boundaries where compressional tectonic regimes cause the flow of fluids, gases, and mud. More than 1,000 mud volcanoes are known to exist onshore and most of them seem to be concentrated along the Alpine–Himalaya Active Mountain Belt (Dimitrov 2002). The number of submarine mud volcanoes is unknown and may exceed the number of onshore features by far. Mud volcanoes are important as they transport water, dissolved elements, gas and oil and may act as special pathways for methane to the atmosphere and into the ocean (Kopf 2002; Milkov et al. 2003). There are uncertainties concerning the global material flux from mud volcanoes because the number and distribution of submarine mud volcanoes are poorly known, their activity, quiescent or eruptive is largely unconstrained and flux measurements from their environments are absent (Milkov et al. 2003). However, in recent years interest in the investigation of submarine mud volcanoes has increased in several areas such as the Caspian Sea, the Mediterranean, the Black Sea and in active subduction zones (e.g. Kopf et al. 2002; Bohrmann et al. 2002; Delisle et al. 2002). Within the Black Sea, mud volcanoes were investigated in the central abyssal plain and the Sorokin Trough area (e.g. Woodside et al. 1997; Bouriak and Akhmetjanov 1998; Ivanov et al. 1998; Kenyon et al. 2002).

During *Meteor* cruise M52/1 (MARGASCH) we studied mud volcanoes from the central part of the

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Black Sea and the Sorokin Trough (Bohrmann and Schenck 2002). In both areas, mud volcanoes were known from previous investigations and from multidisciplinary cruises within the framework of the UNESCO program Training-Through-Research (e.g. Woodside et al. 1997; Bouriak and Akhmetjanov 1998; Ivanov et al. 1998; Kenyon et al. 2002). During cruise M52/1 (January 2002), we carried out interdisciplinary investigations on the distribution, composition and structure of gas hydrate occurrences, as well as their relationship to fluid migration through sediments and venting of gases to the seafloor. Because gas discharge and seepage in the deeper parts of the Black Sea are in most cases related to the presence of mud volcanoes, our investigations have been focused on such geological features. In this paper, we summarize various results from the Dvurechenskii and Odessa mud volcanoes (Fig. 1) using water-column measurements and seafloor and subseafloor data obtained during the cruise. Both mud volcanoes differ in morphology, sediment and fluid composition as well as activity. Seismic and sidescan-sonar data of the mud volcanoes and their relation to deeper structures are presented by Krastel et al. (2003, this volume). Detailed data on the hydrocarbon composition of gases and gas

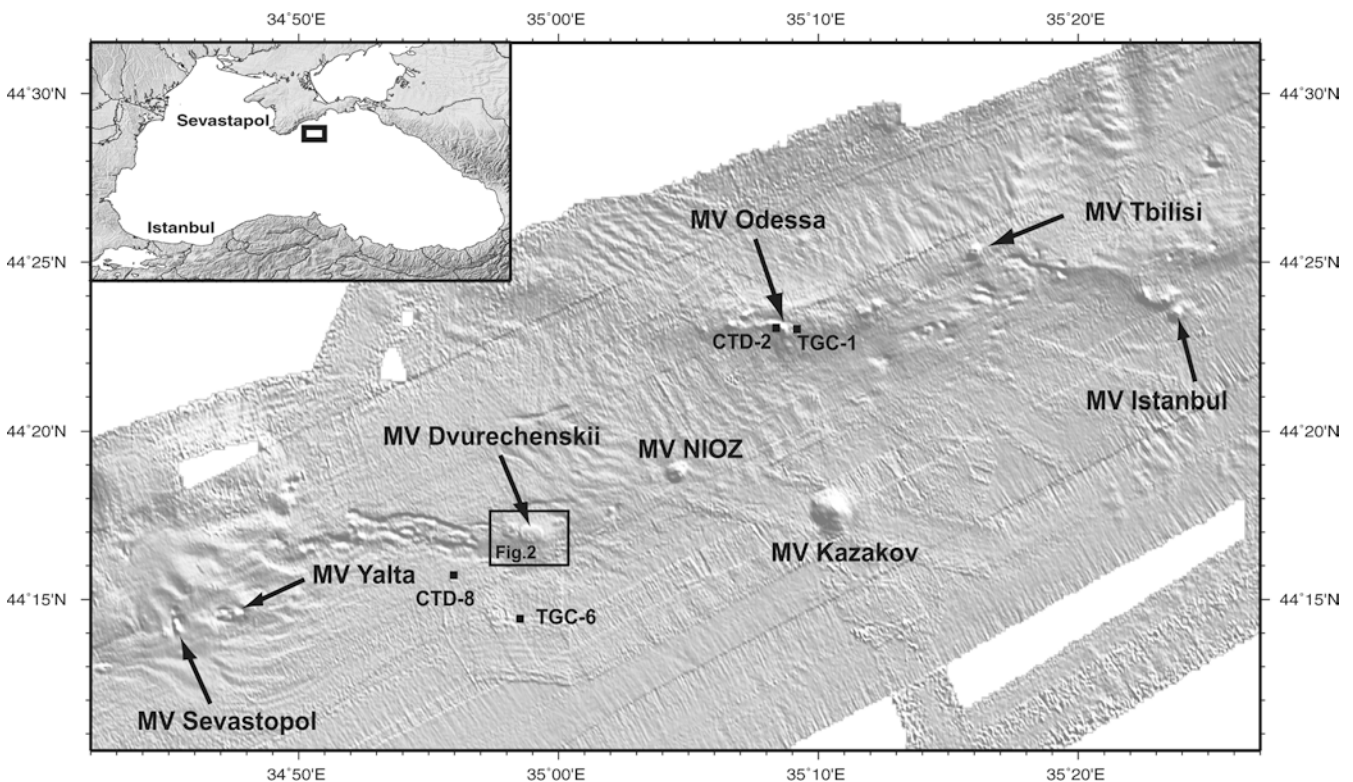
hydrates from the mud volcanic deposits are presented by Blinova et al. (2003, this volume).

Geological background

The Black Sea is a marginal ocean with a water depth of 2–2.2 km. It is surrounded by Cenozoic mountain belts such as the Great Caucasus, the Pontides and the Balkanides (Robinson 1997). Two deep basins, the western and eastern Black Sea basins, are underlain by oceanic or thinned continental crust with a sediment cover of 10–19 km thickness (Tugolesov et al. 1985). The basins are separated by the Andrusov Ridge, which consists of continental crust and is overlain by only 5–6 km of sediment. The Black Sea presumably originated as a back-arc basin during late Cretaceous times (Nishishin et al. 2003). Subsequently, the area changed to a compressional regime during the Eocene and the further tectonic evolution of the basin is characterized by subsidence that resulted in a separation of the two basins (Nishishin et al. 2003). Modern stress field observations from structural data, earthquake foci, stress field measurements onshore in the Crimean and Caucasus regions and GPS data show that the Black Sea region is still in a dominantly compressional environment (Reilinger et al. 1997; Nishishin et al. 2003).

The Sorokin Trough, as a foredeep of the Crimean Mountains, belongs to the eastern basin of the Black Sea and forms a large depression of 150 km in length and 50 km in width south-east of the Crimean Peninsula (Tugolesov et al. 1985). A large number of mud volcanoes

Fig. 1 Bathymetry of the central Sorokin Trough area of the Black Sea south-east of the Crimean Peninsula. Locations of major mud volcanoes and some stations are shown. *Box* marks the area of Dvurechenskii mud volcano (DMV) that is shown in Fig. 2. Swath bathymetry data used in this figure were collected by a SIMRAD EM-12 multibeam system during the TTR-6 cruise of RV *Gelendzhik* in summer 1996 (Woodside et al. 1997) and by HYDROSWEEP during *Meteor* cruise M52/1 (Bohrmann and Schenck 2002)



in this area evolved from diapiric zones in a compressional regime between the Cretaceous to Eocene blocks of the Tetyaev Rise and the Shatskiy Ridge (Tugolev et al. 1985). The sediments extruded from the mud volcanoes are clay-rich deposits from the Maikopian Formation that forms an Oligocene–Lower Miocene sequence of 4–5 km thickness. The Maikopian Formation is overlain by at least 2–3-km-thick Pliocene to Quaternary sediments.

Methods

A deep-towed ocean floor observation system (OFOS) was used for optical seafloor mapping and to locate individual seep sites. OFOS is equipped with a black-and-white video camera and a still camera providing high-quality color slides. The instrument was towed behind the ship at approximately 0.8 knots at a distance of 0–4 m above the seafloor. A memory CTD (Seabird SBE 19) was mounted onto the system to record depth as well as the temperature in the near-bottom water. For water samples, hydrocasts with a conventional CTD (Seabird 911) and rosette sampler equipped with twelve 12-l-Niskin bottles were used. Methane concentrations were measured by a gas chromatograph (CARLO ERBA GC 6000; for details see cruise report Bohrmann and Schenck 2002). Surface sediments were sampled by a minicorer (MIC; Table 1), which recovered four 50-cm-long cores from the seawater/sediment interface with minimum disturbance. Deeper sediments were sampled by a conventional gravity corer (Table 1). Four IFR-EMER/Micrel thermistor temperature sensors were attached to the coring pipe at a 1-m spacing at distances of 0.45, 1.45, 2.45 and 3.45 m from the cutting edge of the corer. The corer was kept in the sediment for a period of 6–10 min at each station, during which time the temperature was recorded at a lateral distance of 6 cm from

the corer. Each sensor took temperature measurements in 10-s intervals. Equilibrium temperature values in the sediment were extrapolated from the transient temperature curves with an accuracy of a few milli-degrees. For sediment sampling we used special liners made of polythene sheeting instead of normal PVC liners, which allowed fast access to the sediment after retrieval of the cores. This allowed gas hydrate sampling before dissociation of the hydrates. Pore water was squeezed from the sediment through 0.2- μ m cellulose acetate membrane filters using argon gas in a mechanical polypropylene press and analyzed for its chemical constituents (for details see cruise report; Bohrmann and Schenck 2002).

Results

Seafloor observation and water column work

We conducted more station work in the area of Dvurechenskii mud volcano (DMV) than at Odessa mud volcano (OMV), especially gravity cores (Table 1), because DMV seemed to have more active seepage. Because the Black Sea water is anoxic at \sim 100 m below sea level, seep sites below that water depth show no colonization by chemosynthetic clams or tube worms because of the lack of oxygen, which these organisms need for their symbiotic metabolism with bacteria. The absence of macroscopic chemosynthetic life in the deeper Black Sea makes seepage hard to identify. Other seep manifestations that help to identify active venting are bacterial mats and, to a certain extent, carbonate build-ups, which form at seep sites because of increased rates of anaerobic methane oxidation (Michaelis et al. 2002). Gas bubbles emanating from the seafloor were not observed by visual observation of the seafloor, and acoustic plumes in the water column detected by echosounders were only observed north-east of the Sorokin

Table 1 Stations taken during RV *Meteor* cruise M52/1: CTD/hydrocast stations, gravity corer with temperature sensors (TGC), minicorer (MIC) and TV-sled (OFOS) profiles. *OMV* Odessa mud volcano; *DMV* Dvurechenskii mud volcano

Station	Instrument	Latitude	Longitude	Water depth (m)	Location
M52/1-4	CTD-2	44°23.05'N	35°08.44'E	1,785	West of OMV
M52/1-18	TGC-1	44°23.01'N	35°09.28'E	1,836	Eastern flank of OMV
M52/1-33-2	CTD-8	44°15.03'N	34°55.96'E	2,112	Sorokin Trough, reference
M52/1-34-1	TGC-2	44°16.96'N	34°58.95'E	2,074	Centre of DMV
M52/1-36-1	TGC-3	44°17.00'N	34°58.86'E	2,071	Centre of DMV
M52/1-37	TGC-4	44°17.13'N	34°58.99'E	2,073	DMV
M52/1-38	TGC-5	44°17.00'N	34°59.18'E	2,075	DMV
M52/1-39	TGC-6	44°14.03'N	34°58.85'E	2,161	Sorokin Trough, reference
M52/1-40-2	CTD-9	44°17.01'N	34°59.00'E	2,030	Centre of DMV
M52/1-47-2	CTD-11	44°16.96'N	34°58.62'E	2,039	DMV
M52/1-48-1	TGC-7	44°16.85'N	34°58.80'E	2,087	DMV
M52/1-48-2	MIC-4	44°16.97'N	34°58.61'E	2,089	DMV
M52/1-49-1	TGC-8	44°16.95'N	34°58.63'E	2,087	DMV
M52/1-62-1	OFOS-8 start	44°16.35'N	34°57.96'E	2,147	DMV
M52/1-62-1	OFOS-8 end	44°17.41'N	34°59.37'E	2,094	DMV
M52/1-62-2	OFOS-9 start	44°17.24'N	34°57'99"E	2,100	DMV
M52/1-62-2	OFOS-9 end	44°16.79'N	34°59.85'E	2,116	DMV
M52/1-64	CTD-15	44°17.36'N	35°00.02'E	2,102	Northeast of DMV

Fig. 2 Detailed bathymetric map of the Dvurechenskii mud volcano (DMV) showing CTD and gravity core stations as well as the OFOS track lines crossing major features of the mud volcano

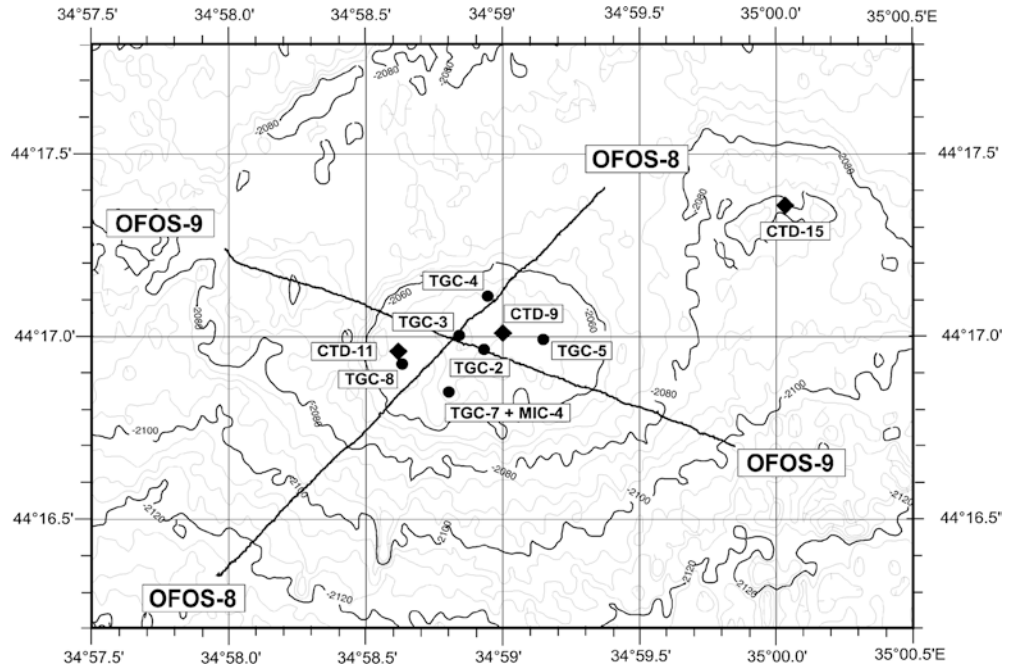
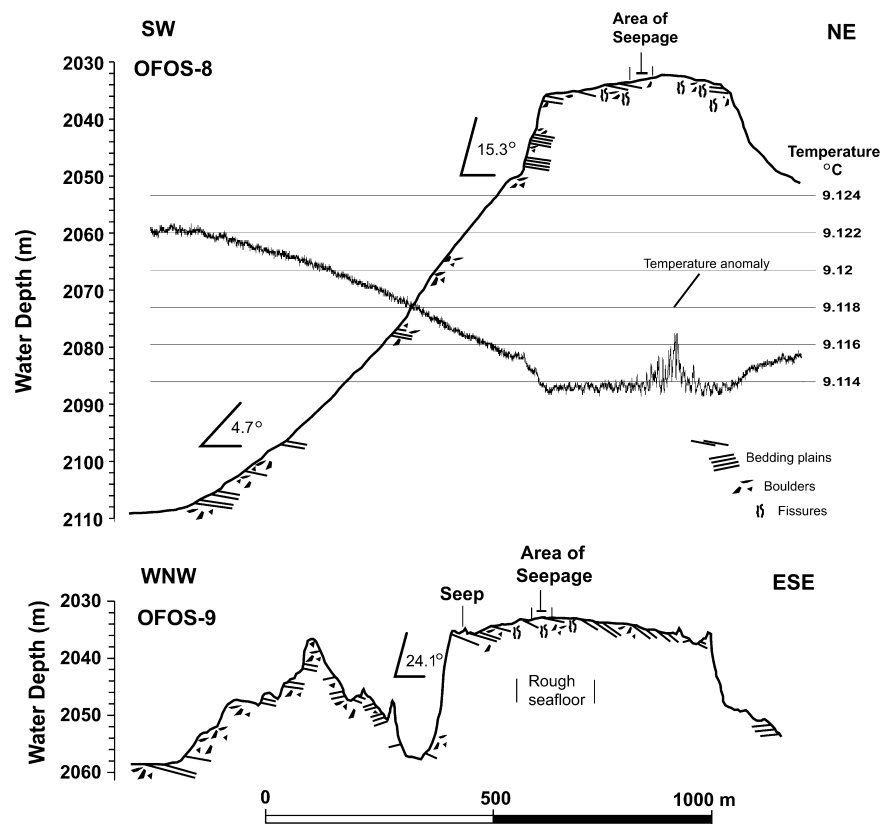


Fig. 3 OFOS observation along tracks crossing DMV (coordinates of the tracks are shown in Fig. 2). Depth and temperature data are from the memory CTD, mounted on the TV-sled



Trough in an area of less than 700 m water depth. In contrast to DMV, no clear evidence for active seepage was found in the OMV area.

OFOS lines 8 and 9 (Figs. 2 and 3) crossed DMV from WNW to ESE (OFOS-8; Fig. 3) and SW to NE (OFOS 9; Fig. 2). The lines show the flat-topped mor-

phology of DMV and several indications for mud flow activity. Recent mud flows were observed on video images and color slides by distinct color changes that are probably caused by the higher water content in fresh mud compared with older mud, or by differences in the bacterial activity of several mud layers. Recent mud

flows have been observed close to the western rim of the mud volcano, where mud outflow on the seafloor was detected along fissures (Fig. 4A). Clear seepage activity was identified close to the south-western rim of DMV by a bright bacterial mat that occurred in a patch related to fractures on the seafloor (Fig. 4C). This area of higher seepage activity was located in the central part of the mud volcano in a small area of approximately 50–70 m in diameter. Seep activity was indicated by several round spots of 10 to 30 cm in diameter showing a light gray to white colour with darker inner spots that were interpreted to indicate bacterial mats (Fig. 4B). These round spots were not covered by the dense flocculating pelagic material from the upper water column, which covers the seafloor outside the spots nearly everywhere. We interpret these small spots as active sites where gas or fluids emanate from the sediments. During OFOS track-8, the temperature sensor of the CTD read a higher bottom water temperature in an area on top of the mud volcano (Fig. 3). Even if the temperature change was only small (0.003 °C), this temperature anomaly fits well with the idea that warm fluids emanate from the sediment at the seep sites. The water temperature anomaly does not exactly coincide with the area where seepage was observed by our OFOS surveys. However, this offset may have been caused by bottom water currents.

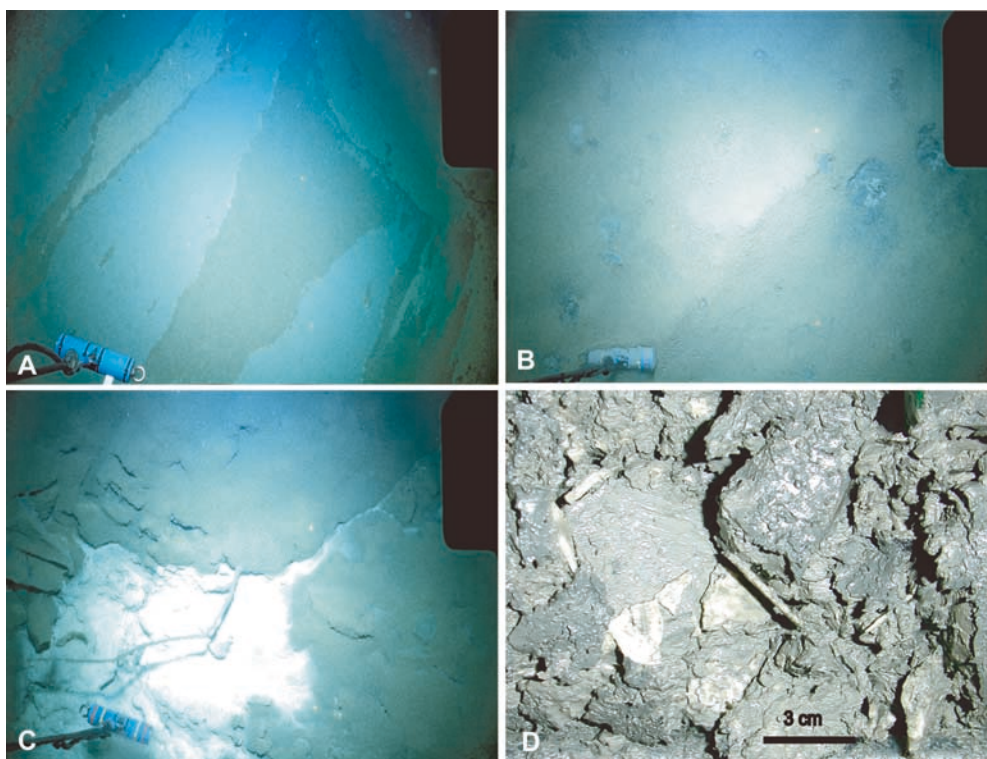
Methane concentrations in the water column of the Sorokin Trough were measured during several CTD runs (Fig. 5). Surface water values of $0.03 \mu\text{mol l}^{-1}$ are well above the atmospheric equilibrium and remain at this level or increase only very slightly down to the oxic/anoxic transition zone (Fig. 5A) at a depth of about

100 m below sea level (m b.s.l.). From the transition zone down to approximately 500 m b.s.l. methane concentrations increase to values of $14 \mu\text{mol l}^{-1}$. Below 500 m b.s.l. no further strong variations in methane concentrations are observed (Fig. 5A). However, methane concentrations at stations CTD-9 and -11 show slightly increasing values near the seafloor (Fig. 5B). Both stations are located directly above DMV, whereas station CTD-15 is located outside DMV and shows a more constant methane level in the lowermost 120 m above the seafloor. Increasing concentrations of methane in the bottom water of DMV may indicate methane flux from the sediment into the bottom water. However, other effects, such as bottom water currents and methane consumption by anaerobic oxidation, may also be important for modulating the methane concentration profile.

Seafloor temperature measurements

Seafloor temperature measurements were performed, together with gravity cores, at eight sites. TGC-6 was a reference site taken in an area of smooth topography and uniform sediments, about 5 km south of DMV. The measurements at TGC-6 revealed a temperature of 9.09–9.25 °C at 1–4 m below the seafloor (Fig. 6). Using the downcore temperature increase, a mean temperature gradient of 29 °C km^{-1} was calculated. A total of six temperature profiles were taken at DMV (Fig. 7). Stations TGC-2 to -5, TGC-7 and TGC-8 consistently show the presence of warm mud in the upper meter below the

Fig. 4 Seafloor and sediment images from DMV (4A-C): **A** recent mud flow sheets from a seafloor fissure; **B** small vent sites from an area of seepage on DMV; **C** white bacterial mat in a seafloor crack on DMV; **D** fractured gas hydrate slabs in sediments from Odessa mudflow core M52/1-18



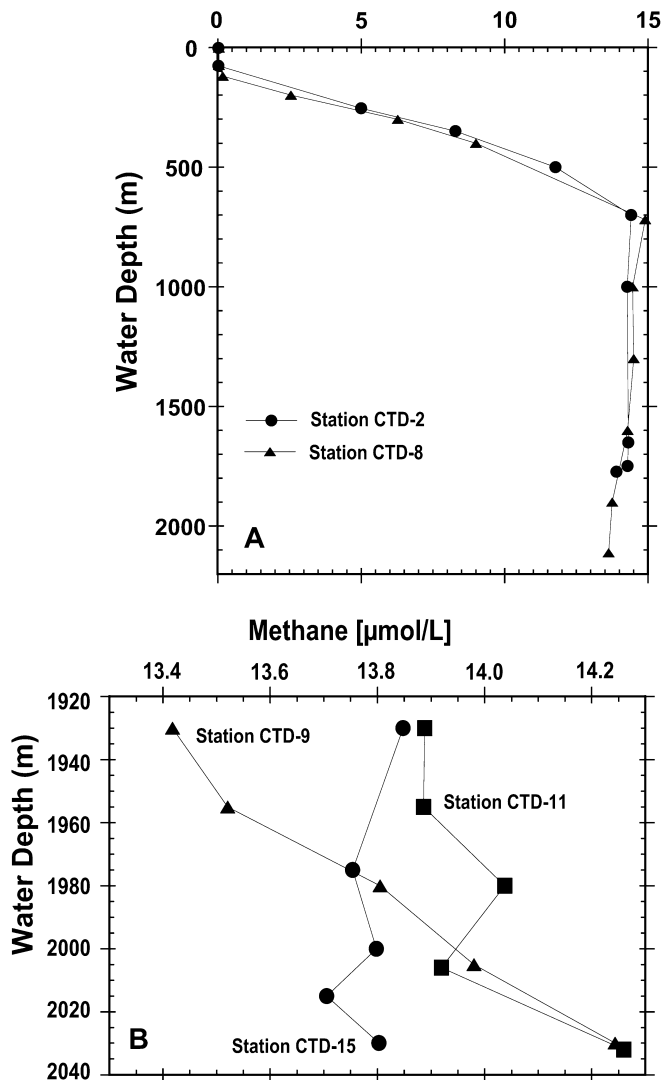


Fig. 5 A, B Concentrations of dissolved methane detected in five CTD casts. **A** Methane concentrations from CTD stations 2 and 8 document the general pattern through the water column of the Black Sea (for location see Fig. 1). **B** Methane concentrations from the bottom water measured in the DMV area (for locations see Fig. 2)

surface of Dvurechenskii mud volcano (Figs. 6 and 7). Temperatures reach up to 16.5 °C in the axial and southern parts of the summit of the mud volcano (TGC-2, TGC-3 and TGC-7; Figs. 6 and 7), with no apparent temperature gradient with depth. Instead, a constant to near constant temperature value was measured (Fig. 6). Mud temperatures in the more distal part of the summit are intermediate between 16.5 °C and the bottom water temperature of 9 °C. These differences result in high gradients between 0.177 and 0.310 °C m⁻¹ (Fig. 6).

Sediment cores and pore water

During M52/1, sediment cores were taken using various coring tools (Bohrmann and Schenck 2002) and gas hydrates were sampled from DMV, OMV, Yalta MV

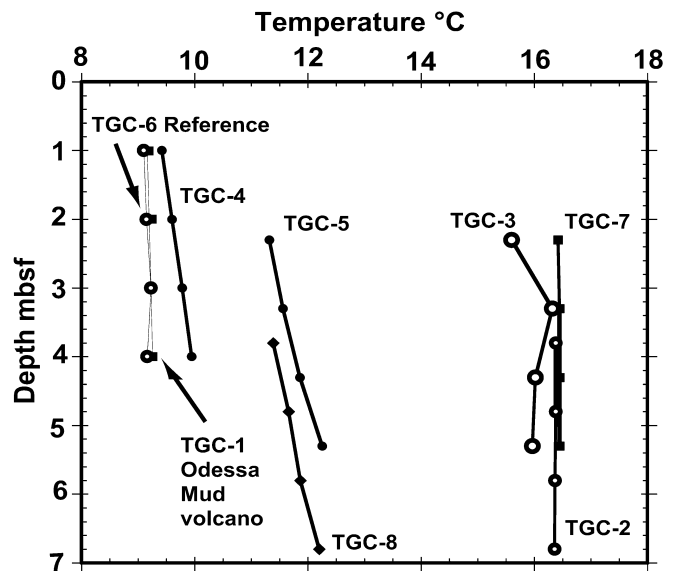


Fig. 6 Downcore temperature gradients from in-situ temperature measurements (TGC-2, -3, -5, -7 and -8 stations are from Dvurechenskii MV)

and an unnamed mud volcano (Bohrmann and Schenck 2002). In this paper, we only present data from two cores that may serve as examples for DMV and OMV (Fig. 8). Thermistor gravity core-1 (TGC-1; station 18) from a mud flow of OMV recovered 410 cm of gray to dark gray hemipelagic mud (Fig. 8). The carbonate content of the sediment is in most cases below 10%. A higher carbonate content close to the surface is attributed to coccoliths, which sometimes form a laminated coccolith ooze as a minor lithology. A 2-cm-thick authigenic carbonate crust is present at 23 cm b.s.f. at a very sharp color boundary between light grey mud (above the crust) and a black sapropel layer, which extends from below the crust to 60 cm b.s.f. Yellowish, submillimeter-sized bacterial colonies fill small pores on the surface of the crust and are abundant inside the crust as well. Another

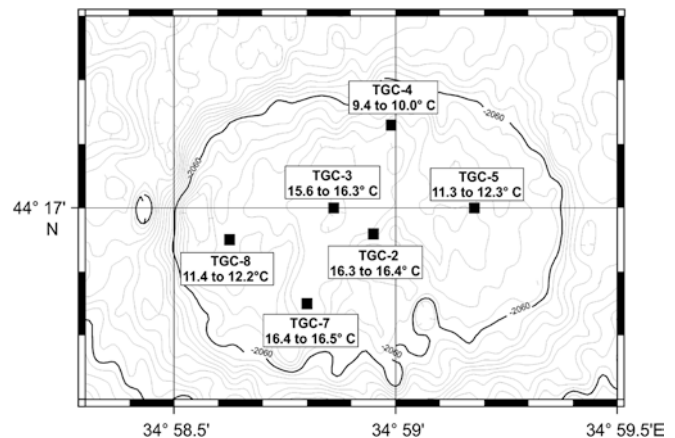
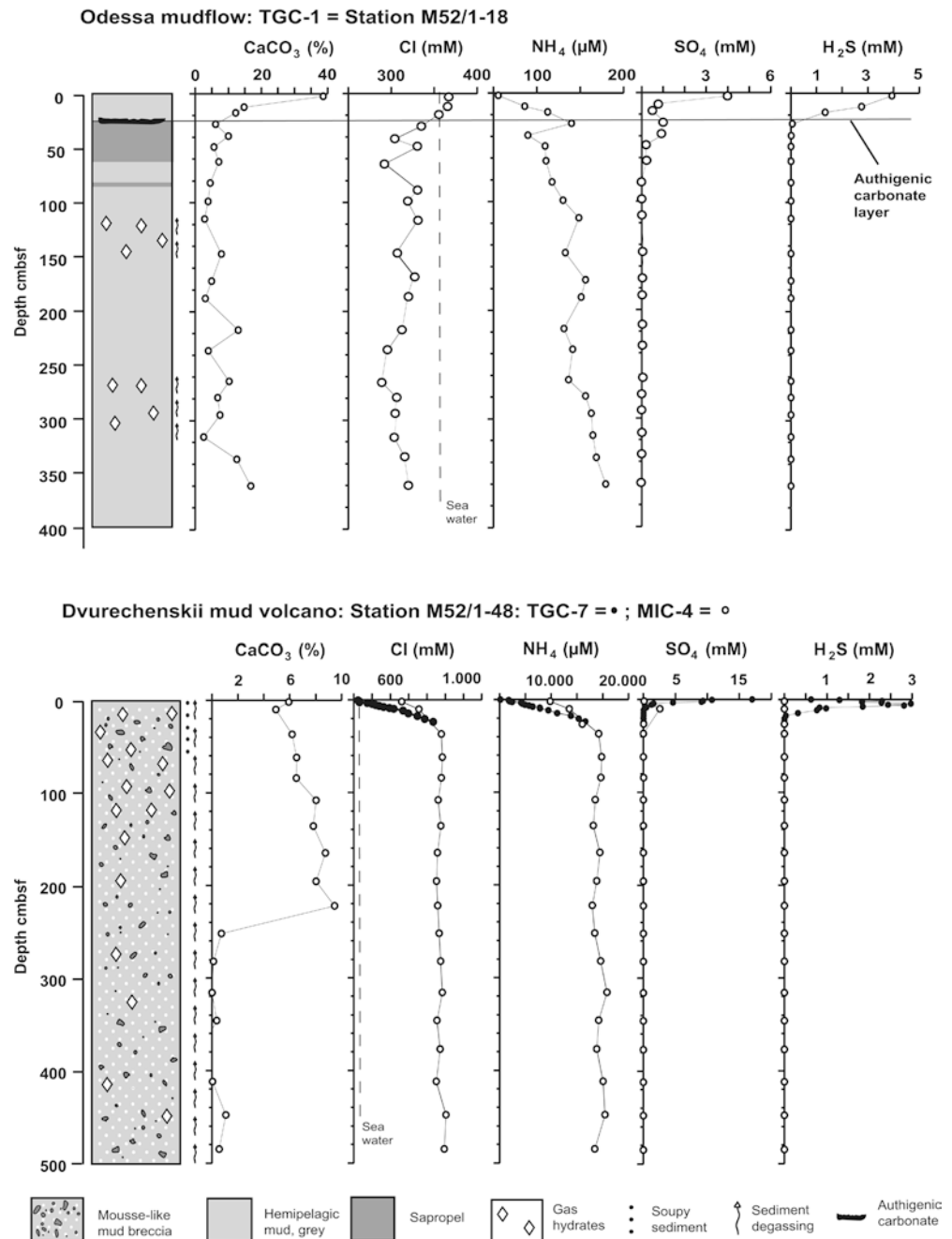


Fig. 7 Location map of seafloor temperature measurements taken on DMV with recorded mud temperatures

Fig. 8 Lithologic information and pore water data from Odessa mud flow (station M52/1-18) and Dvurechenskii mud volcano (station M52/1-48-1)



sapropel layer is present between 81 and 83 cm b.s.f. Small gas hydrate crystals are dispersed in the mud between 123 and 140 cm and occur as broken slabs a few millimeters thick between 260 and 310 cm (Fig. 4D).

TGC-7 was taken on the southern part of the summit of the Dvurechenskii mud volcano (Fig. 8) and was followed at the same position by MIC-4, which was recovered from the uppermost 50 cm of sediment for more detailed analyses. The core contained 500 cm of a mousse-like mud breccia. The non-matrix components are millimeter- to centimeter-sized, subrounded to sub-angular mudstone clasts that cleave along well-defined, parallel planes. The sediment is matrix-supported and has a carbonate content of less than 10%. Small gas

hydrate crystals are common throughout the core, but are particularly abundant in the top 1.5 m of the core.

Selected pore water data are plotted for both cores in Fig. 8. The chloride profiles are interesting because of their link to gas hydrates (Hesse and Harisson 1981; Suess et al. 2002). Dissolved chloride from the two cores shows patterns that differ extremely with regard to their concentration profiles as well as their maximum values. Core TGC-1 reveals chloride concentrations of between 355 and 363 mM in the upper 20 cm b.s.f., which are close to the sea water value of 355 mM. Below 20 cm b.s.f., chloride concentrations are lower and show some negative anomalies of up to 322 mM (Fig. 8). TGC-7 from DMV shows a much higher level of 850 to

905 mM for most of the core. The multicorer MIC-4 from the same location, however, shows a linear decrease from the high chloride values of 850 mM at 25 cm b.s.f. to sea water values of 357 mM near the sediment–water interface. Similar large differences occur in ammonia concentrations. TGC-1 reveals concentrations of 50–80 μM in the uppermost 25 cm b.s.f., which increase from below 25 cm b.s.f. to values of 180 μM (Fig. 8). Ammonia concentrations in the pore water of core TGC-7 show values of 19.000 to 20.000 μM and are, therefore, a factor of 100 to 150 higher than in TGC-1. At the same location, MIC-4 shows a concentration decrease from 16,000 μM at 25 cm b.s.f. to 130 μM close to the surface (Fig. 8). Other pore water constituents, such as sulfate and hydrogen sulfide, are totally depleted deeper in the cores and are only present close to the sediment surface. Sulfate concentrations in sediments of MIC-4 are 17.01 mM in the uppermost centimeter and decrease to values lower than 1.5 mM below 4.5 cm. In core TGC-1 from OMV, the resolution is not as good as in the cores from DMV because no MIC data are available. Even though the highest sulfate concentration of 5.59 mM may be an artifact, the downward gradient in sulfate decrease seems to be less steep in the cores from OMV than in the sediments from DMV.

Discussion

Presence of gas hydrates

Based on the temperature measurements carried out during the cruise, thermodynamic conditions for all sediment cores are within the methane hydrate stability field (Fig. 9). Taking the temperature values from the reference core as an estimate of the regional temperature gradient in the study area, we inferred a potential thickness of the methane hydrate-bearing sediment layer (GHSZ) of 400 m at a water depth of 2,000 m (Fig. 9). It is worth noting that the 16.5 $^{\circ}\text{C}$ temperature of core TGC-7 is close to the maximum temperature for methane hydrate stability at this depth (Fig. 9).

Depending on its concentration, methane occurs in sediment either as a dissolved component, as free gas, or if pressure and temperature are suitable gas molecules are included in the cage structure of clathrates. Free gas and gas hydrates can only co-exist when gas concentrations exceed methane solubility in the pore water. Due to the gas expansion phenomena during conventional coring procedures, it is often very difficult to evaluate whether methane exceeds its solubility in the host sediment or not, unless in situ tools are used (Paull and Ussler 2001). When gas hydrates are recovered in a sediment core, methane values in the host sediment must have exceeded their saturation concentration in the sediment. Using conventional coring techniques, gas hydrates may dissociate on their long way from the seafloor to the deck of the ship. However, several proxies

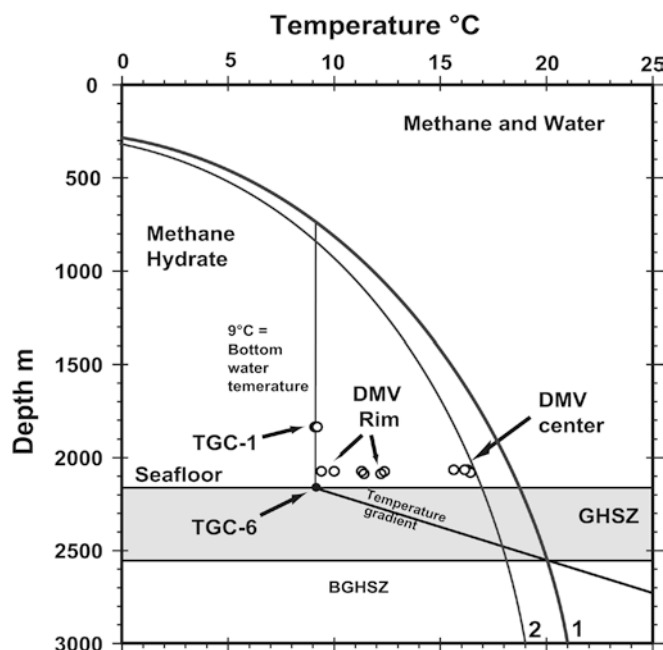


Fig. 9 Hydrate stability field calculated according to Sloan (1998) for pure methane and Black Sea water chlorinity of 355 mM (1) and pore water chlorinity of 900 mM in sediments from Dvurechenskii MV (2). Temperature measurements were taken during the M52/1 cruise. Thickness of the hydrate stability zone at 2,000 m water depth in the Sorokin Trough as graphically inferred from the bottom water temperature of 9 $^{\circ}\text{C}$ and a constant temperature gradient in sediments of 29 $^{\circ}\text{C km}^{-1}$

exist that can prove the former presence of gas hydrates after the hydrate has disappeared. One such proxy is the presence of chloride anomalies in the pore water. In core TGC-1, chloride concentrations lower than sea water values exist below 20 cm b.s.f. and were associated with strong sediment degassing. This observation is accompanied by the presence of gas hydrate crystals. The negative chloride anomalies result from the release of hydrate water during core retrieval, which causes freshening of the pore water. The hydrate water has no dissolved ions and its theoretical chloride concentration should be 0 mM. For a quantification of gas hydrates, the background concentration of chloride has to be known, which is usually a concentration of sea water. However, since the Black Sea changed from a freshwater to a marine environment, chloride concentrations in the sediment have varied through time and dissolved chloride in non-gas hydrate environments of the Black Sea decreases rather linearly with sediment depth, depending on sedimentation rates (Joergensen et al. 2001). As we do not know the ages of the cores, we are at present not able to calculate a background chloride content from the sediments. Future work may solve this problem and allow the use of a chloride proxy for gas hydrate quantification in the Black Sea cores. In addition to the negative chloride anomalies, positive excursions have recently been reported from the southern summit of Hydrate Ridge, where rapid gas hydrate formation occurs (Suess et al. 2002; Trehu et al. 2003). Due to water

uptake from the pore space during hydrate formation, the ions are excluded. Since hydrate formation appears to occur very rapidly, diffusion is too slow to compensate for this uptake. This results in residual pore water becoming enriched in ions. Chloride concentrations in core TGC-7 are up to 900 mM throughout the sediment core, which is, on average, 540 mM higher than the sea water value. Although gas hydrates clearly exist in the core, we do not think that the high chloride values are the result of hydrate formation and ion exclusion alone because of the constant high chloride values in the core and the high flux of several components from deeper sediments below.

Temperature anomalies are another gas hydrate proxy. As hydrate dissociation is a strongly endothermic reaction, cold spots are left behind in the host sediments after dissociation. Consequently, we measured sediment temperatures after the cores had been opened for sampling. In the gas-hydrate-bearing intervals of core TGC-7, the temperature was 6 °C, which is 10 °C colder than the in situ temperature of 16 °C measured by thermistor sensors (Fig. 6). This anomalous low temperature can only be explained by gas hydrate dissociation. The temperature measured in core TGC-1 was as low as 6.5 °C after retrieval, which is 2.5 °C colder than the temperature of 9 °C measured in situ. Based on the delta T of 10 °C in core TGC-7 in comparison to delta T of 2.5 °C in core TGC-1, we conclude that more gas hydrates exist in the sediment of the DMV than in the sediments of OMV.

Mud extrusion at Dvurechenskii MV

The sediments from DMV are unusual in many aspects. They are very mousse-like and probably contained much more gas hydrates than the sediments from OMV or other sediments that have been sampled during cruise M52/1. It is interesting to note that such gas-saturated, fluid-rich mud breccia occurs on a flat-topped mud volcano. This morphology is consistent with higher extrusion of relatively fluid mud volcanic products. Such flat-topped mud volcanoes have been described in the Barbados accretionary prism and have been termed “mud pies” (Henry et al. 1996). The chemistry of the pore water at DMV also seems to be unique because of high concentrations of several dissolved components, such as chloride and ammonium (Fig. 8), compared with other Black Sea sites. Ammonia concentrations show about the same downcore distribution as the chloride, which leads to the assumption that the profiles are shaped by a high outflow of fluid or/and mud (Fig. 8). High net flux rates of 12–24 cm year⁻¹ have been calculated preliminarily from high resolution pore water constituents. The high ammonia concentrations are probably the product of anaerobic degradation of organic matter at depth. In general, sediments that extrude at mud volcanoes in the Sorokin Trough and the central Black Sea originate from a source 4–5 km deep in the

stratigraphic level of the Oligocene to Lower Miocene Maikopian Formation. Clasts recovered from mud breccias of the DMV are composed of mudstones, laminated siltstones, sandstones and marls and preliminary shipboard analysis confirmed the Maikopian Formation as the source formation. Furthermore, high mud extrusion is indicated by elevated sediment temperature measured during M52/1 (Figs. 6 and 7). The ascent of fluid and mud in the mud volcano is much faster than the advective cooling, which leads to unusually high temperatures in the uppermost sediments of DMV.

Anaerobic methane oxidation

The sulfate profiles from both cores are controlled by sulfate reduction during anaerobic bacterial respiration as has been shown for other places in the Black Sea and elsewhere (Borowski et al. 2000; Joergensen et al. 2001). Below the pycnocline, sulfate is the main electron acceptor for bacterial respiration in the anoxic Black Sea. Methane diffusion and venting from sediments is significant as a carbon and energy source for the modern sulfur cycle in the water and sediments of the Black Sea (Reeburgh et al. 1991). Although the process of anaerobic methane oxidation (AMO) during sulfate reduction was often postulated, based on pore-water profiles (Claypool and Kaplan 1974), the microbes responsible for this biogeochemical process were only recently discovered (Boetius et al. 2000). Since its discovery, the consortium responsible for this coupled process of methane oxidation and sulfate reduction has been identified in several locations (Boetius, personal communication), including the north-western Black Sea, where the growth of up to 4-m-high microbial reefs is fuelled by AMO (Michaelis et al. 2002). Carbonate precipitation is generally associated with AMO because of increased pore-water alkalinity accompanied by reactions that maintain a high pH (Ritger et al. 1987; Peckmann et al. 2001). Hydrogen sulfide is another product of AMO and is often consumed in oxic water by chemolithotrophic bacteria such as *Beggiatoa* or symbiotic microbes (Sibuet and Olu 1998). In both pore water profiles presented here, AMO is well documented by sulfate and hydrogen sulfide profiles (Fig. 8). In addition, a 2-cm-thick carbonate crust associated with visible bacterial colonies seems to occur at a depth where AMO is currently active. Preliminary carbon isotope composition measurements from the carbonate crust reveal $\delta^{13}\text{C}$ values of -41.8 to -43.0‰ ($n = 5$), indicating methane as the main carbon source.

Conclusion

Our findings document that Dvurechenskii mud volcano is presently active. Mud of higher temperature and fluids enriched in chloride and other chemical constituents

appear to ascend from deeper stratigraphic levels, most probably from the Maikopian Formation. Although temperatures as high as 16.5 °C are reached in sediments close to the surface, gas hydrates are within their stability field and their presence was confirmed by gas hydrate sampling. Sediments from Odessa MV, Yalta MV and an unnamed mud volcano in the Sorokin Trough also contained gas hydrates. This was documented either by direct gas hydrate sampling or by gas hydrate proxies such as negative temperature anomalies, measured on opened sediment cores, or by negative chloride anomalies in the pore water profiles. High methane concentrations and advective fluid flow lead to a methane flux to the bottom water, which sustains anaerobic methane oxidation (AMO). Evidence for AMO was shown by pore water data and carbonate precipitation.

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