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Geological, geochemical, and microbial processes at the hydrate-bearing Håkon Mosby mud volcano: a review

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Abstract

Submarine mud volcanoes are point sources of fluid expulsion and oases of active geological, geochemical, and microbial processes in the deep ocean. The results of multidisciplinary investigations at the Håkon Mosby mud volcano (HMMV) in the Norwegian Sea at ~1250 m water depth are reviewed in this paper. Seafloor morphology, lithotypes, geochemical, and biological processes at the HMMV are concentrically zoned. The zonation is controlled by ejection of sediment, water, and gases (mainly methane) accompanied by high heat flow in the mud volcano crater. A structural gas hydrate accumulation is associated with the HMMV. Gas hydrate is abundant only in a relatively narrow zone where optimal conditions (low temperature and high gas concentration) exist for gas hydrate crystallization. Authigenic minerals, bacterial mats, and chemosynthetic communities typical of cold seep environments are present. Rapid anaerobic sulfate-dependant oxidation of methane is thought to be mediated by a consortium of methanogens and sulfate-reducing bacteria. Although methane is oxidized in sediments at high rates, a significant portion of this gas may escape into the ocean, mainly as diffuse flux. In the water column, methane is rapidly dissolved and oxidized. This observation supports the hypothesis that gas flux from deep-water mud volcanoes contributes to the oceanic carbon pool, but not to the atmosphere. The HMMV represents an important natural laboratory and provides insight to processes at the interface of methane-rich sediments and cold bottom water in the deep ocean. Future studies may best focus on accurate direct measurements of gas flux and quantification of the biogeochemical cycling of major chemical elements in shallow sediment.

Keywords: Mud volcano; Methane; Gas flux; Carbon cycle; Anaerobic methane oxidation; Gas hydrate

1. Introduction

Mud volcanoes occur worldwide onshore and offshore, on active and passive continental margins,

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and on abyssal plains (Milkov, 2000; Dimitrov, 2002). These constructional features form as a result of mud and fluid ejection in areas of rapid sedimentation or lateral tectonic compression (Milkov, 2000, and references therein). The study of mud volcanoes is important for a variety of reasons:

(1) Mud volcanoes are considered to be a significant source of fossil methane in the atmosphere and the ocean (Dimitrov, 2002; Milkov et al., 2003), although they are not included in the modern models of atmospheric methane sources/sinks (Crutzen and Lelieveld, 2001). Gas flux from individual mud volcanoes varies from 10^2 to 1.5×10^7 m^3 $year^{-1}$ during quiescent periods (Milkov et al., 2003), and may be as much as 10^7–10^{10} m^3 over periods of days during eruptions (Guliyev and Feizullayev, 1996; Dimitrov, 2002). Milkov et al. (2003) estimate that the global gas flux from mud volcanoes may be as much as 33 Tg $year^{-1}$. According to their study, 6 Tg $year^{-1}$ of gas (primarily methane) may escape from onshore and shallow offshore mud volcanoes directly to the atmosphere. The majority of the global gas flux comes from deep-water mud volcanoes, and gas appears to be oxidized, dissolved, and dispersed in the water column (Milkov et al., 2003). Other researchers (Etiope and Klusman, 2002; Dimitrov, 2002) also suggest that onshore and shallow offshore mud volcanoes may emit 2–20 Tg $year^{-1}$ of gas directly to the atmosphere.
(2) Submarine mud volcanoes represent a potential geohazard for petroleum exploitation (Bagirov and Lerche, 1999).
(3) Sediments and fluids expelled from mud volcanoes provide useful information on the geology and petroleum potential of deep sedimentary basins (Guliyev and Feizullayev, 1996).
(4) Gas hydrate associated with deep-water mud volcanoes is considered as a potential energy resource (Hovland, 2000).

This contribution is a review of more than 10 years of multinational and multidisciplinary studies of the Håkon Mosby mud volcano (HMMV) located in the Norwegian Sea (~72°00.3′ N and 14°44.0′ E)

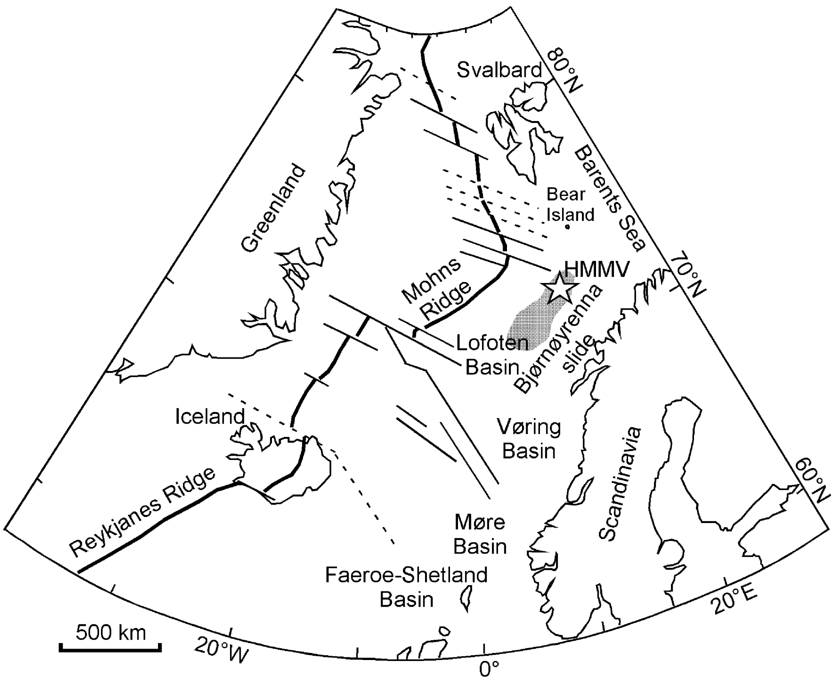

Fig. 1. Simplified tectonic map of the northeast Atlantic (after Lundin and Doré, 2002). The location of the HMMV and some other features mentioned in the text are shown. See Lundin and Doré (2002) for further details on the tectonic elements.

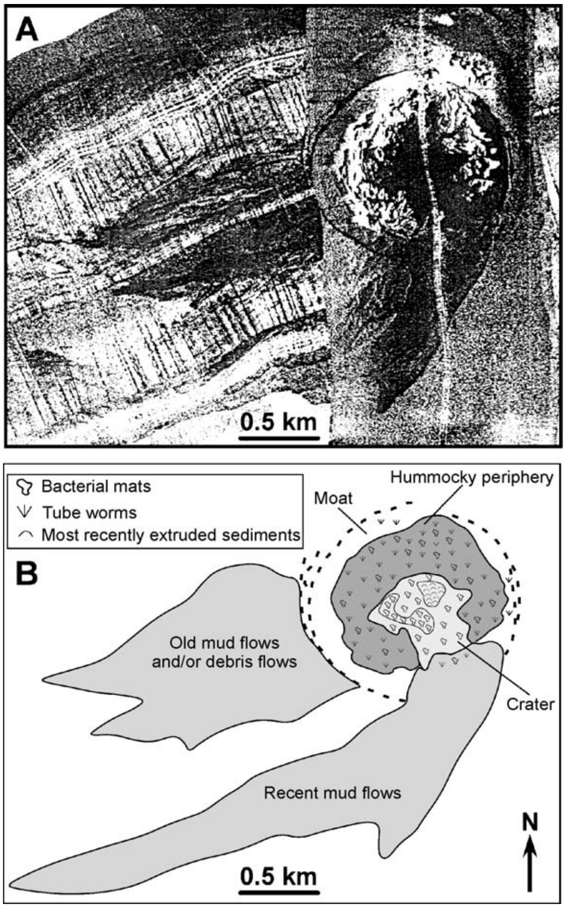

Fig. 2. (A) A 30 kHz deep-tow side-scan sonar mosaic in the area of the HMMV (Vogt et al., 1999). Darker tones denote stronger backscatter. (B) Major morphological element of the HMMV as inferred from sidescan images, photo and video surveys, submersible observations, and coring (same area as shown in A).

at ~1250–1260 m water depth (Figs. 1–3, Vogt et al., 1997). Vogt et al. (1999) describe early investigations. The HMMV was discovered in 1989–1990 as a side-scan sonar (SeaMARC II) feature on the Bear Island submarine fan during geophysical mapping campaign (Vogt et al., 1991). The feature was revisited on board *F/S Håkon Mosby* in 1995 when samples of tubeworms and gas hydrate were recovered (Vogt et al., 1997). The following cruise of *NIS Professor Logachev* in 1996 resulted in the collection of 102.6 km of 30 kHz side-scan images, 124 km of shallow acoustic profiles, 17 gravity and piston cores, plus CTD measurements. In addition, ~8000 m^2 of the seafloor were covered by video and photo surveys that allowed us to compile the first map of the HMMV landscape (Milkov et al., 1999). The investigations were continued in 1998 during the cruise of *NIS Akademik Mstislav Keldysh*, equiped with *Mir-1* and *Mir-2* manned submersibles. The morphology of the HMMV inferred from early side-scan sonar images and video survey was confirmed, and precisely located samples of sediment, bacterial mats, dimersal fish and other materials were collected during the 1998 cruise (Bogdanov et al., 1999).

The studies continued in 1998 (*NIS Professor Logachev*, Kenyon et al., 1999), 1999 (*R/V Jan Mayen*) and in 2001 (*R/V L'Atalante*). During investigations, the HMMV has become an important natural laboratory for the study of the complex interplay of geological, geochemical, and microbial processes fueled by the extrusion of sediments and the expulsion of fluids at the seafloor. This contribution reviews and synthesizes published results of previous investigations, and emphasizes the gas hydrate system that is believed to be typical of active deep-water mud volcanoes worldwide (Milkov, 2000).

2. Geologic setting and deep structure

The SW Barents Sea margin separates the oceanic Eocene–Early Oligocene oceanic crust in the Lofoten Basin from the continental crust in the Barents Sea (Fig. 1). The sedimentary section in the HMMV area is ~6.1 km thick and is underlain by oceanic crust formed ~34–37 Ma (Faleide et al., 1996). The initial breakup and seafloor spreading in early Eocene time (53.7 Ma) followed by a rotation of the opening direction in Oligocene time (35 Ma), led to the widening of the northern Norwegian–Greenland Sea (Lundin and Doré, 2002). Sediment accumulated at the continental margin since the beginning of the breakup as a result of erosion and redeposition from the Barents Sea shelf and Svalbard (Fiedler and Faleide, 1996).

Based on regional seismic studies, the Cenozoic sedimentary section is divided into preglacial (Eocene–Late Miocene–Pliocene) and glacial (Plio-Pleistocene) units (Faleide et al., 1996). Glacial units are suggested to include sediments deposited by slumps, debris flows, and mud flows (Laberg and Vorren, 1996; Vorren et al., 1998). Several large

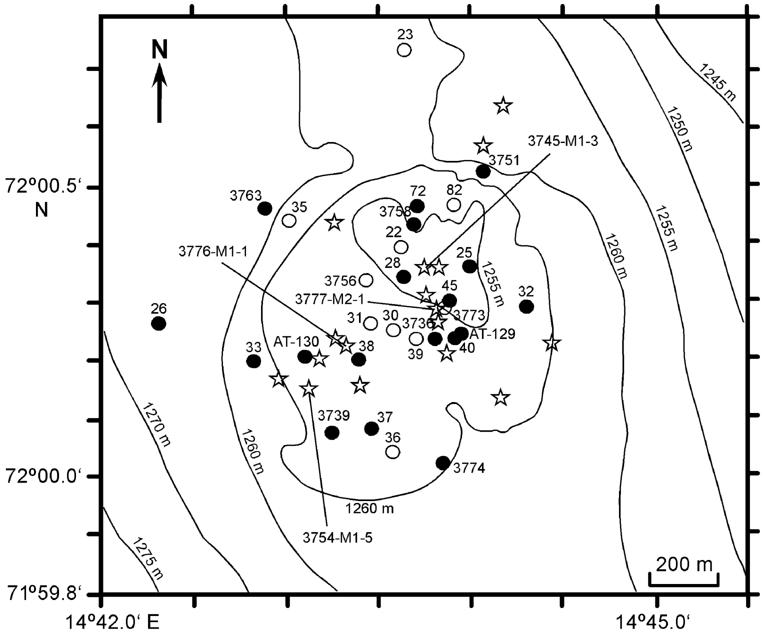

Fig. 3. Bathymetric scheme of the HMMV showing stations where hydrate-bearing sediments (solid circles) and hydrate-free sediments (open circles) were observed in cores (<3 mbsf). Stations where shallow sediments (0–0.2 mbsf) and biota were sampled by research submersibles are also indicated (stars). The figure is compiled using data presented by Ginsburg et al. (1999), Kenyon et al. (1999), and Lein et al. (2000b).

fans occur along the SW Barents Sea margin. The HMMV is located near the depocenter of the large Bear Island Trough Mouth Fan (Hjelstuen et al., 1999; Laberg and Vorren, 1996) that extends from the Barents Sea shelf to ~3000 m water depth in the Lofoten Basin. Rapid sedimentation is characteristic of the Bear Island Fan. The average sedimentation rate is estimated to have been 2.2 cm ka^{-1} prior to Late Pliocene time, and up to 172 cm ka^{-1} during Late Pliocene–Pleistocene time (Fiedler and Faleide, 1996). Several large Pleistocene slides complicate the morphology of the Bear Island Fan (Hjelstuen et al., 1999). The HMMV is within the scar of a large Late Pleistocene Bjørnøyrenna Slide, which may have failed between 313 and 194 ka (Laberg and Vorren, 1993). No other mud volcanoes were found near the HMMV, although several seafloor-piercing mud diapirs are recognized on seismic profiles and sonar images and sampled (Kenyon et al., 1999).

The deep structure of the HMMV has been imaged by seismoacoustic methods (Fig. 4). Regional subhorizontal seismic reflectors appear pulled down when plotted in two-way travel time and disrupted below the HMMV (Hjelstuen et al., 1999). This signature is typical of other mud volcanoes and diapirs (e.g., Langseth et al., 1988) and is caused by the presence of gas in mobilized and fluidized sediments in the migration conduit of the HMMV. This interpretation is supported by relatively low seismic velocities in the disturbed zone (Hjelstuen et al., 1999). The disturbed seismic reflectors are observed as deep as ~2.5–3 km (Fig. 4), suggesting that the "roots" of the HMMV may be located within the terrigeneous Late Pliocene sediments of unit GI (Fig. 4). This observation is consistent with the similar pore water compositions from the HMMV and from the unit GI sampled at the ODP Site 986, located 600 km north of the HMMV (Ginsburg et al., 1999).

3. Morphology and shallow sediments

Side-scan sonar images (Vogt et al., 1999; Fig. 2A), bathymetric map (Ginsburg et al., 1999; Fig.

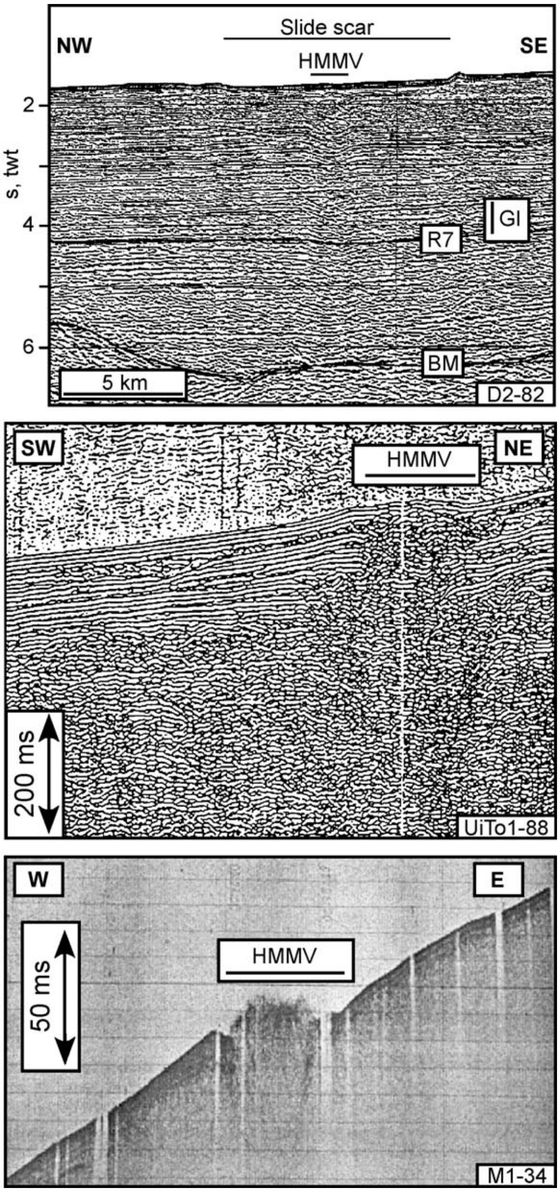

Fig. 4. Multichannel (D2-82, Hjelstuen et al., 1999), single-channel (UiTo1-88, courtesy of K. Andreassen), and 8.85 kHz acoustic (M1–34) profiles across the HMMV.

3), photo and video surveys (Milkov et al., 1999), and submersible observations (Bogdanov et al., 1999) suggest that the HMMV is a dome-like, low-relief constructional feature of sediment. The HMMV is ~1.4 km in diameter, ~1.2 km^2 in area (including the surrounding moat and excluding distal mud flows), and has ~7–15 m relief. Four major morphological elements (crater, hummocky periphery, mud flows, and surrounding moat) are defined within the HMMV. Specific lithotypes correspond to the morphological elements. A "normal" relatively flat, brown to gray-brown seafloor with numerous pits (traces of burrowing organisms) is observed outside the mud volcano (Milkov et al., 1999). Sediments sampled beyond the HMMV area are described elsewhere (Lein et al., 1998; Shilov et al., 1999).

A relatively flat, shallow crater is near the center of the HMMV (Figs. 2 and 3). The most active area of the HMMV at present is in the northern zone of this crater. Sediment appears to have been recently extruded in this area, which is characterized by high acoustic backscatter on sonar images (Fig. 2), and a high heat flow and geothermal gradient (Vogt et al., 1999). Linear (1 m long, few cm high) ripple-like seafloor swells occur locally within the crater (Fig. 5A). The southwestern zone of the crater is largely (up to 80%) covered with white bacterial mats (Figs. 2 and 5). Only non-stratified, homogeneous, anoxic gas-charged (mainly methane and H_2S) sediment is cored within the crater (e.g., Station 31, Fig. 6, Milkov, 1998; Lein et al., 1998, 1999). The extruded material is mostly greenish-gray carbonate-poor (<4% $CaCO_3$) and organic-lean (0.55–0.95% TOC) fine-grained mud with a small fraction of sand-sized grains (50–55% mud, 35% silt, 10–15% sand; Milkov, 1998; Shilov et al., 1999; Krupskaya et al., 2002; Lein et al., 2000b). Quartz, feldspar, carbonates, pyroxene, and gypsum are abundant in the sand fraction of sediment. The clay fraction consists of illite, chlorite, and kaolinite (Lein et al., 1998). A few rock fragments (sandstone and siltstone) found in the crater sediment are attributed to ice rafting. The rates of hydrocarbon-driven microbial processes in shallow sediments of the crater are high (Lein et al., 2000b; see Section 7 below).

A hummocky peripheral zone surrounds the crater (except where mud flows from the crater in southeast). Linear trough-like features and round hummocks (with a relief of 2–3 m based on submersible observations) are recognized on sidescan sonar images (Fig. 2). High heat flow (>1000 mW m^{-2}) and geothermal gradients (>0.817 °C m^{-1}) are measured in the

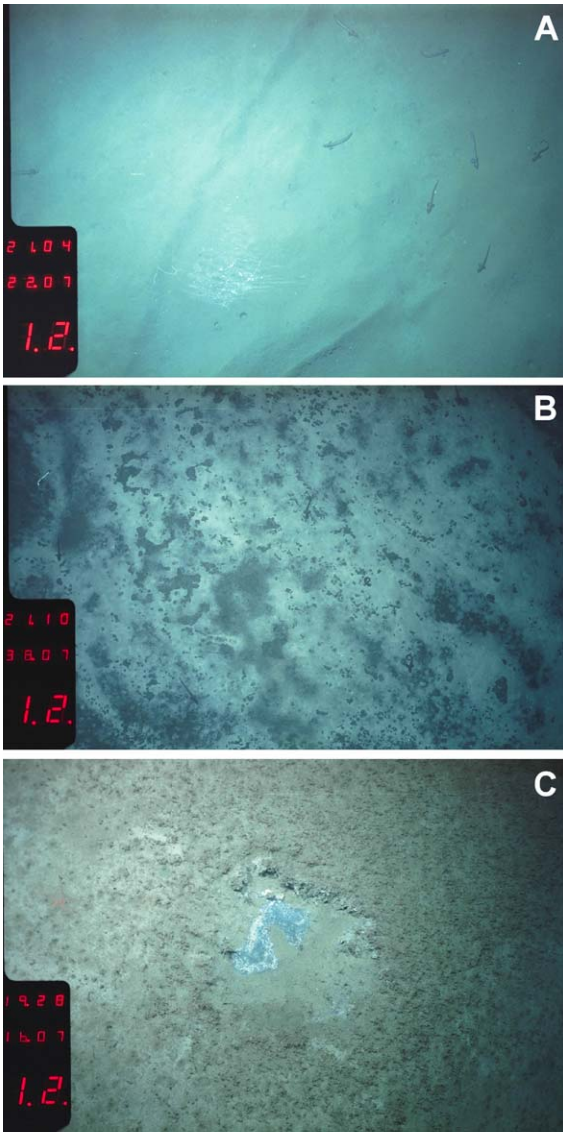

Fig. 5. Seafloor images from the HMMV area. (A) Seafloor near the most active area of the mud volcano (note linear ripple-like seafloor swells of recently extruded sediments). (B) Seafloor with abundant white bacterial mats in southwest part of the crater. (C) Seafloor typical of hummocky peripheral zone. Note a bacterial mat in the shallow depression. All images are 3.5 m long × 2.5 m wide.

peripheral zone (Eldholm et al., 1999), but appear to be lower than in the crater itself (Ginsburg et al., 1999) where sediments and fluids have been recently extruded. Video surveys, submersible observations, and coring data indicate a wide distribution of tubeworms (*Pogonophora*) and the sparse occurrence of bacterial mats and seafloor carbonate buildups (Milkov et al., 1999; Bogdanov et al., 1999). Core descriptions suggest that sediments are composed of material extruded from the crater (often gas-charged and hydrate-bearing) overlain by normally deposited material (e.g., Station 28, Fig. 6). Oxic yellowish-brown carbonate-rich (10–20% $CaCO_3$) and relatively organic-rich (0.73–1.3% TOC) sediments (thickness as much as 9 cm) with the remains of tubeworms commonly overly stratified anoxic sediments in the hummocky peripheral zone (Milkov, 1998; Lein et al., 2000b). The rates of microbial processes in shallow sediment in this zone are several orders of magnitude lower than in the crater itself (Lein et al., 2000b).

Sediment extruded from the crater formed mud flows (Fig. 2). At least two generations of mud flows may be recognized on sonar images. Sediments were most recently extruded from the southeast part of the crater and they flowed downslope to the southwest. Video-survey data suggest that the surfaces of recent mud flows are currently occupied by tubeworms and bacterial mats nearest the crater. At a great distance (>200 m) from the crater, the surface of mud flows appears to be similar to the "normal" seafloor with pelagic sediments. The mud flow sediment contains both material extruded from the crater and normally deposited hemipelagic components (Krupskaya et al., 2002). Mud flow sediment located to the southwest (downslope) from the mud volcano may also include material transported from the hummocky peripheral zone by bottom currents (Vogt et al., 1999; Milkov, 1998).

The hummocky peripheral zone is surrounded by a shallow moat ~200 m wide and ~2 m deep (Figs. 2 and 3). This may be a fault-related feature formed by mud extrusion and then subsidence of sediment surrounding the crater (Vogt et al., 1999). Similar concentric peripheral fault swarms are observed around other mud volcanoes onshore (Jakubov et al., 1971) and offshore (Prior et al., 1989). Video-survey data suggest that tubeworms may occur in some areas of the moat. However, across most of the moat, the seafloor is similar to the "normal" seafloor outside of the HMMV. Cores acquired in the moat contain stratified normal seafloor sediment with only a minor fraction of mate-

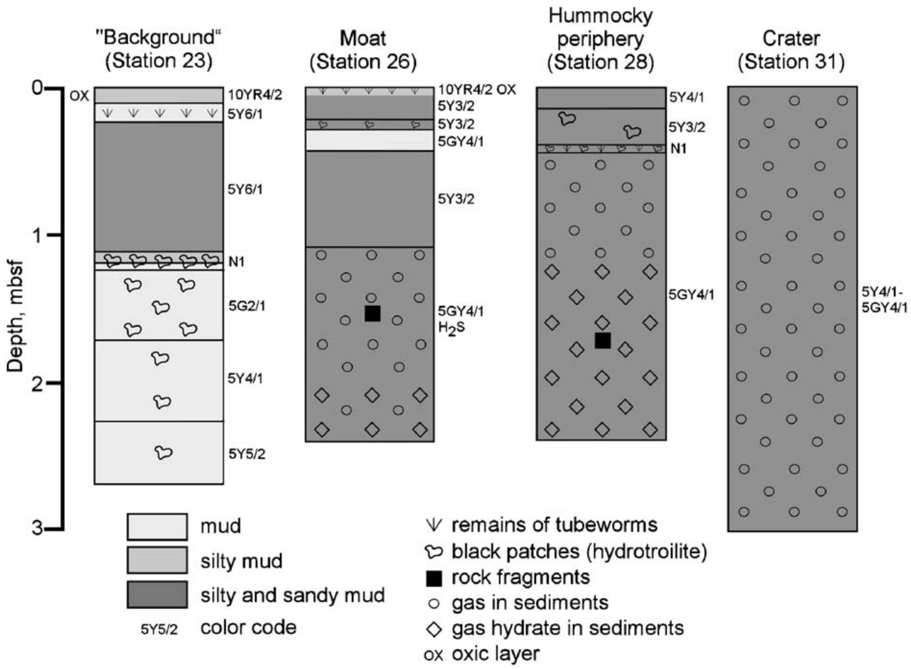

Fig. 6. Lithology of gravity cores acquired from the major morphological elements of the HMMV and from the background area outside of the mud volcano.

rial transported from the crater (e.g., Station 26, Fig. 6, Milkov, 1998).

4. Geochemistry of sediment pore waters

Three types of hydrochemical profiles that correlate with morphological elements and lithotypes are recognized at the HMMV. These types are similar to those found at other mud volcanoes (e.g., Martin et al., 1996). Pore-water in the most active part of the mud volcano (e.g., Station 31) is characterized by lower salinity ($\sim$22‰), lower concentrations of Cl^-, SO_4^{2-} (not shown), Mg^{2+} and other major ions, and higher concentrations of Br^- and I^- relative to seawater (Fig. 7; Milkov, 1998; Lein et al., 1998, 1999, 2000b; Ginsburg et al., 1999). The concentrations of the ions in the active crater vary little with depth in the sediment cores. Pore water is slightly depleted in ^{16}O ($\delta^{18}O$ varies between -0.125‰ and 0.470‰ relative to SMOW) and is strongly depleted in deuterium (δD varies between -22‰ and -24‰ relative to SMOW) (Ginsburg et al., 1999). Mud volcano water is similar to pore water from unit GI sampled at the ODP Site 986 at 750–850 m below seafloor (mbsf). The same unit is buried at depth 2.5–3 km in the HMMV area (Fig. 4), and may be a source of the mud volcano fluid (Ginsburg et al., 1999). Relatively low concentrations of major ions (Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, Na^+) appear to be a result of dehydration of clay minerals during rapid sedimentation. Relatively high concentrations of Br^- and I^-, high $\delta^{18}O$ and low δD values (Ginsburg et al., 1999) are consistent with dehydration of organic matter (e.g., Martin et al., 1996).

The ionic and isotopic compositions of pore water in sediment outside the HMMV (“background”, e.g., Station 23) is similar to that of seawater (Fig. 7; Lein et al., 1998, 1999; Ginsburg et al., 1999). Mixing of mud volcano water (e.g., Station 31) and pore water typical of “normal” marine sediments (e.g., Station 23) is characteristic of the hummocky peripheral zone of the HMMV (e.g., Station 25; Fig. 7). Low salinity and low concentrations of the major ions is observed in the deeper sections of cores and high salinity and high concentration of the major ions is measured in shallower sediments (e.g., Station 25; Fig. 7). Gas

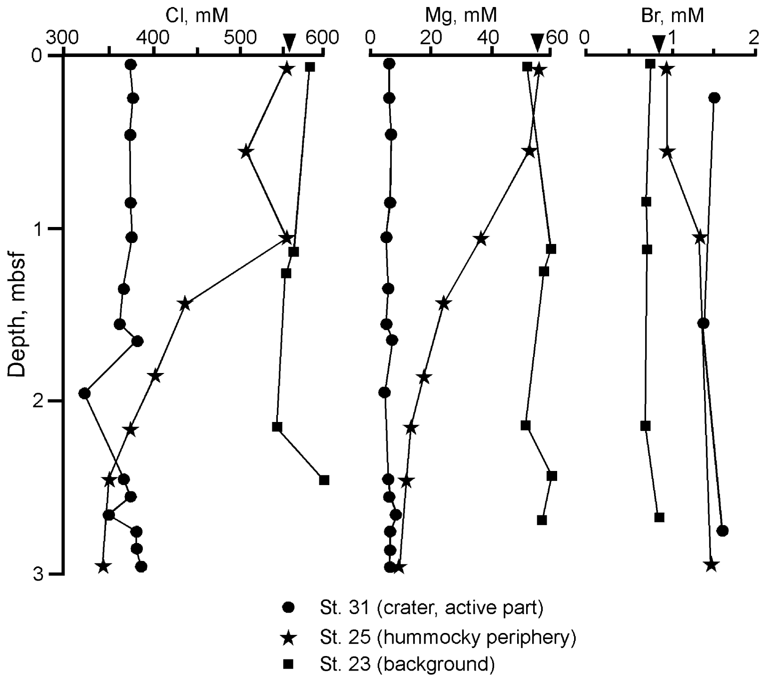

Fig. 7. Concentration of Cl^-, Mg^{2+}, and Br^- in sediment pore water acquired from the major morphological elements of the HMMV and from the background area outside of the mud volcano (based on data from Milkov, 1998).

hydrate commonly occurs in sediments of the hummocky peripheral zone. Only freshwater is incorporated in gas hydrate during crystallization (Sloan, 1998). Thus, the concentration of major ions in pore water of sediments may decrease if gas hydrate decomposes. This further complicates the hydrochemical profile of sediments at the hummocky periphery (see Ginsburg et al., 1999, for further discussion).

5. Gas flux

Mud volcanoes have been proposed to be a significant source of gas flux from the lithosphere to the atmosphere and the ocean (Etiope and Klusman, 2002; Milkov et al., 2003). More than 10^3 mud volcanoes may occur in deep-water areas on continental slopes and abyssal plains (Milkov, 2000). They may emit as much as 27 Tg year^{-1} of gases (largely methane) to the ocean (Milkov et al., 2003). No gas bubbles have been observed escaping from the HMMV seafloor during the 1996 video survey (Milkov et al., 1999), nor during the 1998 submersible observations (Bogdanov et al., 1999). Venting of free gas (bubbles) is not typical of the HMMV perhaps because the methane concentration in the bottom water does not reach high saturation values (1.2 l l^{-1}, Egorov et al., 1999), resulted from low bottom water temperature (-1 °C) and high pressure ($\sim$12.5 MPa), or because only microbubbles of methane form. Methane concentration in the bottom water is relatively high above the most active area of the crater (as much as 6000 μl l^{-1}). The concentration gradually decreases to background levels (<0.1 μl l^{-1}) above the hummocky peripheral zone and the moat, at a distance 300–400 m from the area of ongoing fluid expulsion (Bogdanov et al., 1999). The major gas flux from the mud volcano appears to be diffuse. Etiope et al. (2002) suggest that diffuse degassing is quantitatively more significant than discrete gas venting at mud volcanoes in Sicily, and probably elsewhere.

Using the data presented by Ginsburg et al. (1999), we estimate that the gas flux from the HMMV is of the order 1.5×10^5 m^3 year^{-1}. Sediment serves as a major barrier for gas flux and sequesters methane and other gases in gas hydrate and as authigenic carbonate depleted in ^{13}C. The average rate of methane oxidation in shallow sediments is estimated to be 0.15 l m^{-2} day^{-1} (Lein et al., 2000b). Nevertheless, relatively high concentrations of methane in bottom water (as much as 6000 μl l^{-1}) suggest that a significant portion of the methane escapes from sediment to the water column. Bogdanov et al. (1999) observe that methane concentrations in seawater are high only near the seafloor. The concentration decreases rapidly upward in the water column and is no different from "background" values at 45 m above the seafloor. Large gas bubbles coated with oil may escape to the atmosphere in deep-water areas (Sassen et al., 2001). At the HMMV, methane is rapidly (at rates as great as 48.5 nl CH_4 l^{-1} day^{-1}, Lein et al., 2000b) oxidized, dissolved, and diluted (i.e., removed by bottom currents) in the water column, as it probably is in most other areas of active methane venting from the seafloor such as the Eel River Basin offshore California (Valentine et al., 2001). This observation is consistent with a suggestion that gas flux from deep-water mud volcanoes is not a significant contributor to atmospheric methane, but may affect the mass and the isotopic composition of the oceanic carbon pool (Milkov et al., 2003).

6. Gas hydrate accumulation

Gas hydrate has been persistently recovered at the HMMV since the first coring cruise in 1995 (*F/S Håkon Mosby*, Vogt et al., 1997). Sediments (<3 mbsf) were sampled at 28 stations by gravity corers (Ginsburg et al., 1999; Lein et al., 2000a,b; Kenyon et al.,

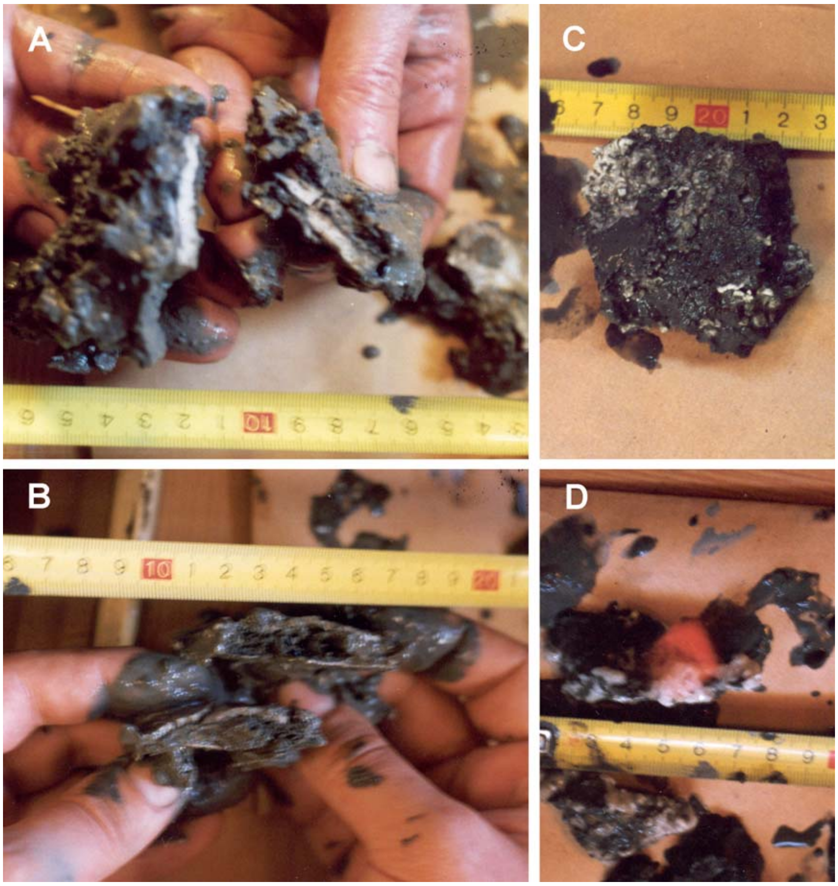

Fig. 8. Gas hydrate inclusions typical of the HMMV sediment. (A, B) White and grayish-white vein-fillings; (C) subrounded aggregate; (D) burning vein-filling. Note the flame in the middle part of the image.

1999), and gas hydrate was recovered at 18 stations (Fig. 3). Shallow sediment (<0.2 mbsf) was sampled at 15 stations by push corers (Lein et al., 2000a,b), but no gas hydrate was reported (Fig. 3). The HMMV gas hydrate accumulation is a typical of structural accumulations associated with mud volcanoes (Milkov and Sassen, 2002).

Milkov (1998), Ginsburg et al. (1999), Bogdanov et al. (1999), and Kenyon et al. (1999) describe the morphology of gas hydrate at the HMMV. Gas hydrate is observed in sediments largely as white and grayish-white vein-fillings (as much as 4 cm long, and 2 mm in thickness, Fig. 8). Massive gas hydrate vein-fillings occur in other gas hydrate provinces such as the Gulf of Mexico (Sassen et al., 2001), Black Sea (Ginsburg and Soloviev, 1998), and the Hydrate Ridge (Suess et al., 2001), and are thought to be indicative of high-flux environments (Ginsburg and Soloviev, 1998; Sassen et al., 2001). Isometric and rose-like aggregates of vein-fillings (as great as 5 cm thick) that contain small (<1 mm) lens-like voids are common. The vein-fillings appear to be randomly oriented with regard to sediment fabric. Relatively small gas hydrate inclusions of various shapes with length as much as 13 mm are also observed in sediment. Gas hydrate cementing sediment is observed in several cores (Ginsburg et al., 1999). Gas hydrate occurs near the seafloor (0–3 mbsf) in the crater, and at some depth below the seafloor (0.9–3 mbsf) in the hummocky peripheral zone. Visual observations suggest that gas hydrate content in sediments varies from 1 to 50 vol.% (Milkov, 1998; Ginsburg et al., 1999). More accurate estimates based on pore-water chlorinity analysis suggest that the maximum gas hydrate content is 25 vol.% (Station 28, 1.5–1.6 mbsf) (Ginsburg et al., 1999).

The C_1–C_4 (methane through butanes) hydrocarbons of hydrate-bound gas and gas from hydrate-bearing sediments collected in 1996 (n=15) are dominated by methane (99.8–99.97%; Table 1) (Ginsburg et al., 1999). C_2–C_4 hydrocarbons occur as minor components, and their concentrations are in the order: ethane>propane>*iso*-butane>*n*-butane. CO_2 is also present at low concentration. Gas from hydrate-bearing sediment appears to be slightly enriched in propane and butanes relative to hydrate-bound gas (Table 1). This may indicate molecular fractionation during gas hydrate crystallization observed at seep sites where gas in sediments is enriched in C_{2+} components (e.g., Sassen et al., 2001). Coffin et al. (2000) report slightly higher concentrations of non-methane hydrate-bound gases in their samples collected in 1998 (Table 1). Relatively low concentrations of noble

Table 1
Composition of gases (as vol.% of ΣC_n+CO_2) from decomposed gas hydrate (GH) and hydrate-bearing sediments (HS)

Site	Depth, cm	Sample	C_1	C_2	C_3	i-C_4	n-C_4	CO_2	Reference
Samples collected in 1996									
25	130	GH	99.80	0.07	0.0054	0.0025	<0.0001	0.12	Milkov, 1998
	190	GH	99.80	0.08	0.0018	0.0004	<0.0001	0.16	Milkov, 1998
	230	GH	99.90	0.04	0.0015	0.0005	<0.0001	0.06	Milkov, 1998
	300	GH	99.90	0.06	0.0023	0.0009	<0.0001	0.05	Milkov, 1998
28	125–130	GH	99.90	0.04	0.0023	0.0010	<0.0001	0.06	Milkov, 1998
	220–230	GH	99.90	0.02	0.0066	0.0047	<0.0001	0.05	Ginsburg et al., 1999
	240	GH	99.90	0.02	0.0008	0.0001	<0.0001	0.06	Milkov, 1998
32	70–80	GH	99.80	0.04	0.0002	<0.0001	<0.0001	0.10	Milkov, 1998
33	55	GH	99.90	0.11	0.0002	<0.0001	<0.0001	0.20	Ginsburg et al., 1999
45	0–5	GH	99.90	0.07	0.0002	0.0010	<0.0001	0.02	Milkov, 1998
	40–45	GH	99.80	0.03	0.0002	0.0001	<0.0001	0.20	Milkov, 1998
	90–100	GH	99.95	0.05	0.0006	<0.0001	<0.0001	0.10	Ginsburg et al., 1999
Mean		GH	99.87	0.05	0.0018	0.0010	<0.0001	0.10	
25	165–175	HS	99.80	0.1	0.0110	0.0030	0.0002	0.10	Ginsburg et al., 1999
	205–220	HS	99.97	0.02	0.0029	0.0009	<0.0001	0.02	Ginsburg et al., 1999
45	65–85	HS	99.90	0.09	0.0038	0.0048	0.0004	0.10	Ginsburg et al., 1999
Mean		HS	99.89	0.07	0.0059	0.0029	0.00023	0.07	
Samples collected in 1998									
Several samples		GH	99.35	0.24	<0.01			0.40	Coffin et al., 2000

gases (He, Ne, and Ar) are found in all samples of hydrate-bearing sediment except for one sample where an extremely high concentration of He (7080 ppm) is measured (Prasolov et al., 1999).

Molecular properties of the gas hydrate are consistent with structure I (Sloan, 1998). X-ray diffraction analysis of gas hydrates collected in 1998 confirms this structure I, and water ice is present in samples (Coffin et al., 2000). Hydrate-bound methane has δ^{13}C values (n=9, mean=−60.6‰) and δD value (−242‰) (Lein et al., 1999) consistent with a largely microbial origin, with minor admixture of thermogenic hydrocarbons (e.g., Whiticar, 1999).

Ginsburg et al. (1999) suggest that the HMMV gas hydrate accumulation has an approximately concentrically zoned morphology controlled by the structurally focused upward flow of warm fluid from depth. No gas hydrate is recovered in three cores from the geologically most active area of the mud volcano (Stations 31, 30, and 39 in zone "a" in Fig. 9). In this zone, recently extruded sediment (Milkov et al., 1999), high geothermal gradients (locally perhaps as

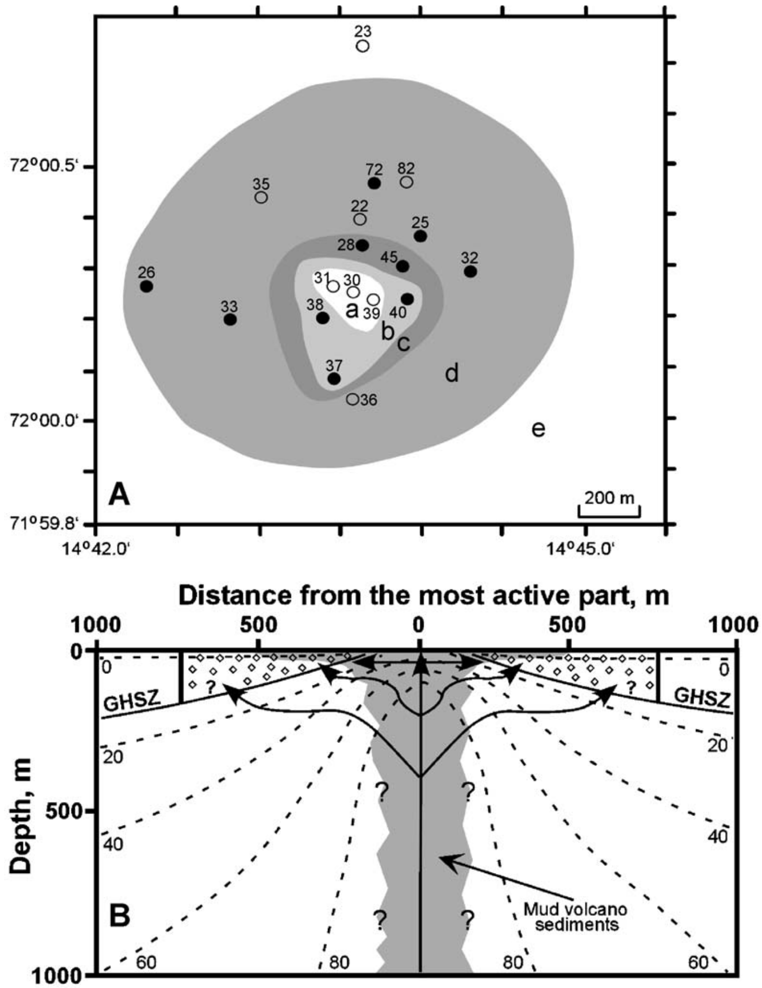

Fig. 9. Proposed distribution of gas hydrate in the HMMV. (A) Map view illustrating the variation of gas hydrate concentration in sediment. No gas hydrate is found in zones "a" and "e". Gas hydrate concentrations in zones "b"–"d" varies from a few percent by volume ("b"), to 10–20% ("c"), and to 0–10% ("d"). (B) Schematic cross-section illustrating the temperature field (isotherms are shown in °C), gas hydrate stability zone (GHSZ), and the distribution of gas hydrate in sediment. Note that horizontal scales for A and B are the same. Modified from Ginsburg et al. (1999).

high as 30 °C m^{-1}) and elevated sediment temperatures are observed. Temperatures as high as 16 °C were measured onboard immediately following core recovery (Ginsburg et al., 1999; Lein et al., 2000b). Gas hydrate appears unstable in this zone.

In the next zone "b", surrounding the most active area of the mud volcano, only small gas hydrate inclusions are observed in sediment (Stations 37, 38, and 40, Fig. 9). Sediment temperature is suggested to vary significantly in this zone in response to the pulsed fluid expulsion typical of mud volcanoes (e.g., in the Gulf of Mexico, MacDonald et al., 2000). Gas hydrate may be transiently stable in this zone, crystallizing when temperatures decrease and decomposing when temperatures increase.

In the next zone "c", large gas hydrate vein-fillings and high gas hydrate concentrations (as much as 25 vol.%) are observed (Stations 28 and 45, Fig. 9). This zone is characterized by optimal conditions for gas hydrate crystallization, because sediment temperature is well below the equilibrium temperature, and gas is abundant in sediments. In the next zone "d", gas hydrate is less abundant in the cores (Stations 26, 33, 36, 32, 25, 22, 35, 72, and 85), possibly because of lower gas flux. Gas hydrate is believed to occur as far as 750 m from the most active part of the mud volcano (Ginsburg et al., 1999). At the periphery of the HMMV, gas hydrate appears to crystallize both in sediments extruded from the crater in the past (e.g., Station 25) and in "normal" stratified sediments (e.g., Station 26 located in the moat).

Ginsburg et al. (1999) use the pore water Mg/Cl ratio to demonstrate that gas hydrate crystallizes from deep external mud volcano fluid (water and gas) around the presently active area of the HMMV. Based on this observation, Milkov (2000) suggests that gas hydrate crystallization is analogous to low-temperature hydrothermal processes of mineral formation. A mixture of mud volcano water and in situ water crystallizes in gas hydrate at the periphery of the HMMV (Ginsburg et al., 1999) suggesting that crystallization of gas hydrate may be compared to metasomatic processes (Milkov, 2000).

The distribution and concentration of gas hydrate in sediments is estimated based only on shallow cores (<3 m). In the simple model of Ginsburg et al. (1999), the gas hydrate stability zone is 160 m thick at the periphery of the HMMV. The volume of hydrate-bound gas at the HMMV is estimated using different approaches. Ginsburg et al. (1999) use an integral approach and assume that the gas hydrate accumulation may be modeled as a ring-shaped body with estimated boundary conditions (i.e., lateral and vertical boundaries of gas hydrate distribution and concentration). Milkov (1998) estimates the volume of hydrate-bound gas in each zone of varying gas hydrate concentration (Fig. 9) and calculates the volume of hydrate-bound gas at the HMMV as a sum of gas in different zones. Both approaches result in similar estimated volumes of hydrate-bound gas equivalent to $\sim 3\text{–}4 \times 10^8$ m^3 at STP. The gas hydrate resource is comparable with the reserves in very small conventional gas fields (Ivanhoe and Leckie, 1993). Milkov and Sassen (2002) suggest, based on considerations of economic geology, that gas hydrate resource in the HMMV is subeconomic at present time.

7. Microorganisms and their relation to chemosynthetic communities

Chemosynthetic communities using methane and sulfide as the principle sources of energy occur at many cold seep sites worldwide (MacDonald et al., 1989; Sibuet and Olu, 1998). At the HMMV, a relatively limited biological community dominated by tubeworms and demersal fish was observed during a video survey in 1996 (Milkov et al., 1999) and submersible operations in 1998 (Bogdanov et al., 1999). Living pogonophoran tubeworms were recovered in a box core acquired at the periphery of the HMMV (Station 85, Fig. 3) in 1995 (Vogt et al., 1997). Pimenov et al. (1999) report the occurrence of 17 species (classes *Pogonophora*, *Polychaeta*, *Crustacea*, and *Pantopoda*) in a box core acquired at Station 36 (Fig. 3) in 1996.

The biomass of pogonophoran tubeworms is estimated to be approximately 785 g m^{-2} (Gebruk et al., 1999). *Pogonophora* are found to be represented by two new species belonging to genera *Sclerolinum* (abundant on oxidized surface sediments) and *Oligobrachia* (abundant on reduced sediments) (Smirnov, 2000; Pimenov et al., 1999, 2000). The tissues of pogonophoran tubeworms are strongly depleted in ^{13}C ($\delta^{13}C$ varies from −34.9‰ to −56.1‰, Lein et al., 2000b). SEM studies of *Sclerolinum* tissues show endosymbiotic bacteria with intracellular membrane structures typical of methanotrophs (Pimenov et al., 2000). Thus, both geochemical and microbiological evidence suggest that methane is a major source of organic carbon in cells of the *Sclerolinum*. Pimenov et al. (2000) failed to detect methane oxidation and typical membrane structures in *Oligobrachia* tissues and suggest that sulfate-reducers supply carbon. In addition to tubeworms, only gastropods and demersal fishes (eight identified species) are found to occur at the HMMV (Milkov et al., 1999; Lein et al., 2000b). These fish consume pogonophoran tubeworms and are enriched in light carbon isotope (δ^{13}C=−51.9‰, Lein et al., 2000a,b). In contrast to the Gulf of Mexico (MacDonald et al., 1989) and other cold seeps (Sibuet and Olu, 1998), methanotrophic mussels and clams are not observed at the HMMV. This may be because the HMMV is a geologically young feature.

The wide distribution of bacterial mats at the HMMV was first observed during a 1996 video survey (Milkov et al., 1999) and further documented during submersible observations in 1998 (Bogdanov et al., 1999). White bacterial mats (0.1–0.5 cm thick) occur on the seafloor within the crater, the hummocky peripheral zone, and the proximal area of mud flows (Fig. 2). The total area of the mats may be as large as 0.2 km^2 (Gebruk et al., 1999). Mats are most abundant in the southwestern area of the crater (Milkov et al., 1999) where they cover up to 80–90% of the seafloor over strongly reduced sediment (Eh=−300 mV; Bogdanov et al., 1999). No bacterial mats are observed in the active part of the crater where sediments and fluids appear to have been most recently extruded and expelled (Milkov et al., 1999; Bogdanov et al., 1999). Within the hummocky peripheral zone, bacterial mats largely occur in the middle of bare tubeworm-free depressions as wide as 1–1.5 m and 30–50 cm deep (Fig. 5, Milkov et al., 1999; Bogdanov et al., 1999). Shallow sediments in the depression are thought to be strongly reduced and rich in H_2S (Pimenov et al., 2000). No bacterial mats are observed in the surrounding moat or on the "normal" seafloor outside of the mud volcano (Fig. 2B) where shallow sediments are oxidized to a depth of 5–8 cm (Milkov et al., 1999). Although gas hydrate is observed to occur in shallow sediment immediately beneath thick and continuous bacterial mats (Bogdanov et al., 1999), so far there is no evidence of direct physical association of gas hydrate and microbes as, for instance, in the Gulf of Mexico (Sassen et al., 1999; Lanoil et al., 2001).

Pimenov et al. (1999, 2000) studied bacterial mats and associated sediments sampled by box core and by the *Mir* submersibles, and results are summarized below. SEM observations show that the bacterial mats are composed of large filaments (length >100 μm, width 2–8 μm; Fig. 10), short rods and coccoid cells (Pimenov et al., 2000). Pimenov et al. (2000) suggest that filamentous bacteria are related to the genera *Leucothrix* (non-sulfur bacteria) and *Thiothrix* (sulfide oxidizing bacteria) common at deep-sea hydrothermal vents (Wirsen et al., 1993). Bacterial mats are generally depleted in ^{13}C (δ^{13}C varies between −17.6‰

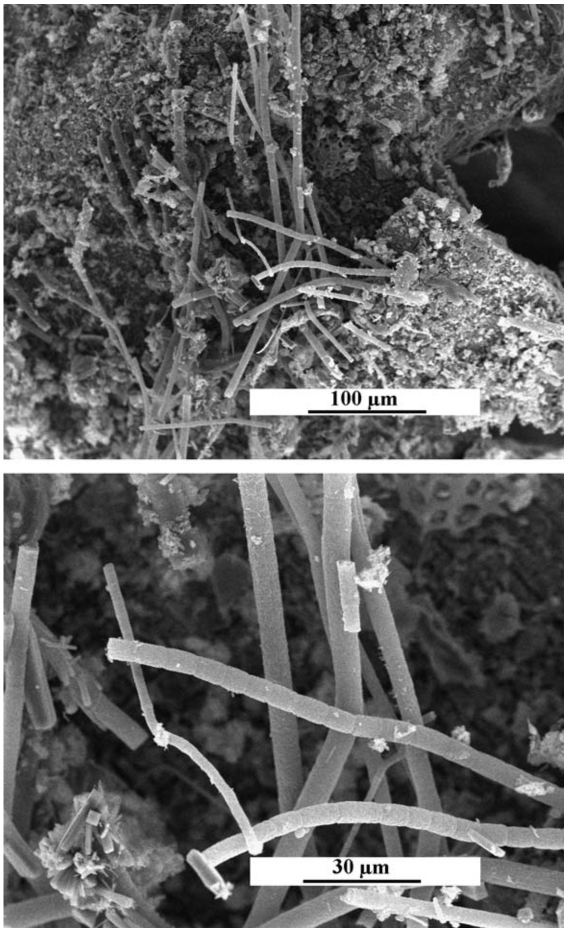

Fig. 10. SEM images of large filamentous bacteria predominant in bacterial mats on the seafloor of the HMMV.

and −53.0‰, Lein et al., 2000b). In contrast, *Beggiatoa*, a giant sulfide-oxidizing bacterium are common overlying gassy sediment and gas hydrate in chemosynthetic communities of the Gulf of Mexico slope (Sassen et al., 1993).

The total number of microorganisms in shallow sediments of the HMMV varies from 2.5×10^6 to 1.8×10^8 cells cm^{-3} (Pimenov et al., 2000). Sulfate-reducing (10^3–10^7 cells m^{-3}), methanotrophic (10^3–10^6 cells m^{-3}), and sulfur-oxidizing (10^2–10^6 cells m^{-3}) bacteria are most abundant in sediments, but methanogens (0–10^4 cells m^{-3}) are less abundant. The highest concentrations of methanotrophic and sulfur-oxidizing bacteria are found within mildly reduced surface sediment (0–0.5 cm), whereas sulfate-reducing and methanogenic bacteria mainly occur at greater depth (3–10 cm) (Pimenov et al., 2000). The biomass of bacterial mats overlying reduced methane-rich sediments is estimated to be 200–1000 g C m^{-2} (Lein et al., 2000b).

Microbial processes appear to be most rapid in the crater of the HMMV, within the upper 20 cm of sediments. The rates of glucose consumption (125–1490 nmol C dm^{-3} day^{-1}) and dark CO_2-assimilation (395–1850 μg C dm^{-3} day^{-1}) suggest high overall activity of microorganisms (Pimenov et al., 2000). The rate of sulfate reduction (135–13390 μg S dm^{-3} day^{-1}) and of methane oxidation (115–1570 μl dm^{-3} day^{-1}) are among the highest measured in marine sediments, although there is not a simple relationship between them (e.g., there is no positive correlation between the two rates, Fig. 11). In contrast, the rate of methanogenesis is found to be relatively low (<0.1–3.5 μl dm^{-3} day^{-1}) (Pimenov et al., 2000). These observations suggest that bacterial mats physically retain fluids in sediment. Bacterial mats at the HMMV and at cold seeps elsewhere appear to be biological barriers that may retard loss of hydrocarbon gases and other fluids to the water column (Sassen et al., 1993).

Submersible observations (Bogdanov et al., 1999), geochemical (Lein et al., 2000a,b), and microbiological (Pimenov et al., 2000) evidence suggest that the bacterial mats occur exclusively over strongly reduced sediment enriched in methane and H_2S. Pimenov et al. (2000) argue that the methanogens in the methane-rich sediments of the HMMV oxidize methane and produce hydrogen in accordance with the reaction reverse to methanogenesis:

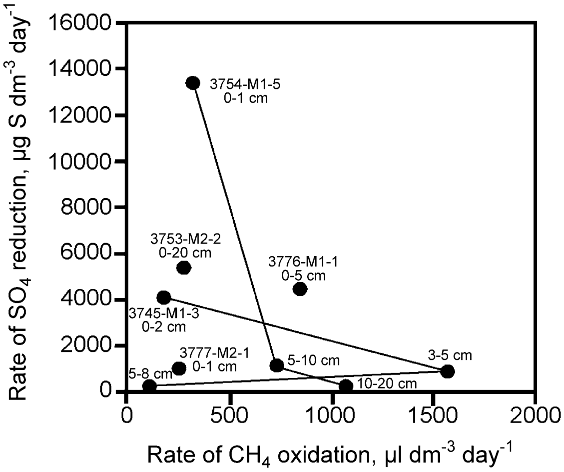

Fig. 11. Rates of sulfate reduction and methane oxidation in the HMMV sediment (based on data from Pimenov et al., 2000).

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (1)$$

Then, sulfate-reducing organisms oxidize hydrogen (e.g., Hoehler and Alperin, 1996):

$$SO_4^{2-} + 4H_2 + H^+ \rightarrow HS^- + 4H_2O \quad (2)$$

The net reaction

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + 4H_2O \quad (3)$$

yields ∼ −25 kJ mol^{-1} methane oxidized depending on environmental conditions (Valentine and Reeburgh, 2000). This pathway is suggested to occur at cold seeps offshore California (Hinrichs et al., 1999, 2000), in the Aleutian trench (Elvert et al., 2000), at the Cascadia margin (Boetius et al., 2000), in the Black Sea (Schouten et al., 2001), in the Mediterranean Sea (Pancost et al., 2000), and in the Gulf of Mexico (Zhang et al., 2002). Hoehler et al. (1994) propose that "reverse methanogenesis" involves a consortium of methanogens and sulfate-reducing bacteria. Such a structured consortium (with Archaea as methanogens) is shown to occur at methane seeps at Cascadia Margin (Boetius et al., 2000), and in the Eel River Basin offshore California (Orphan et al., 2001). However, Valentine and Reeburgh (2000) point out that "reverse methanogenesis" as the mechanism responsible for sulfate-dependent methane oxidation is uncertain. These authors consider alternative mechanisms of anaerobic methane oxidation including (1) the formation of acetic acid and hydrogen by methanotrophs and their subsequent consumption by sulfate-reducers; and (2) formation of acetate from CO_2 and methane by methanotrophs and subsequent consumption of acetate by sulfate-reducers (see also Zehnder and Brock, 1979). On the other hand, Sorensen et al. (2001) suggested that a methane-oxidizing consortia is not likely to be based on inter-species transfer of hydrogen and acetate, and suggest formate as a possible substrate. A comprehensive overview on recent progress in the study of the microbially mediated anaerobic oxidation of methane is presented by Hinrichs and Boetius (2002), and the readers are referred to that paper for future discussion.

8. Authigenic carbonate rock

Precipitation of authigenic carbonate at mud volcanoes (Aloisi et al., 2000) and other sites of hydrocarbon fluids discharge on passive (e.g., Gulf of Mexico (Roberts and Aharon, 1994) and the Black Sea (Peckmann et al., 2001)), and on the active (e.g., Hydrate Ridge offshore Oregon (Greinert et al., 2001) and Makran accretionary prism (von Rad et al., 1996)) continental margins is well documented. Lein et al. (2000a) report on the authigenic carbonate from the HMMV, and results are summarized below.

Seafloor carbonate buildups and crusts of various shape as high as 30 cm were observed during video survey (Milkov et al., 1999) and from the *Mir* submersibles (Bogdanov et al., 1999) within the hummocky peripheral zone and within the crater of the HMMV (Lein et al., 2000a). Two types of carbonate

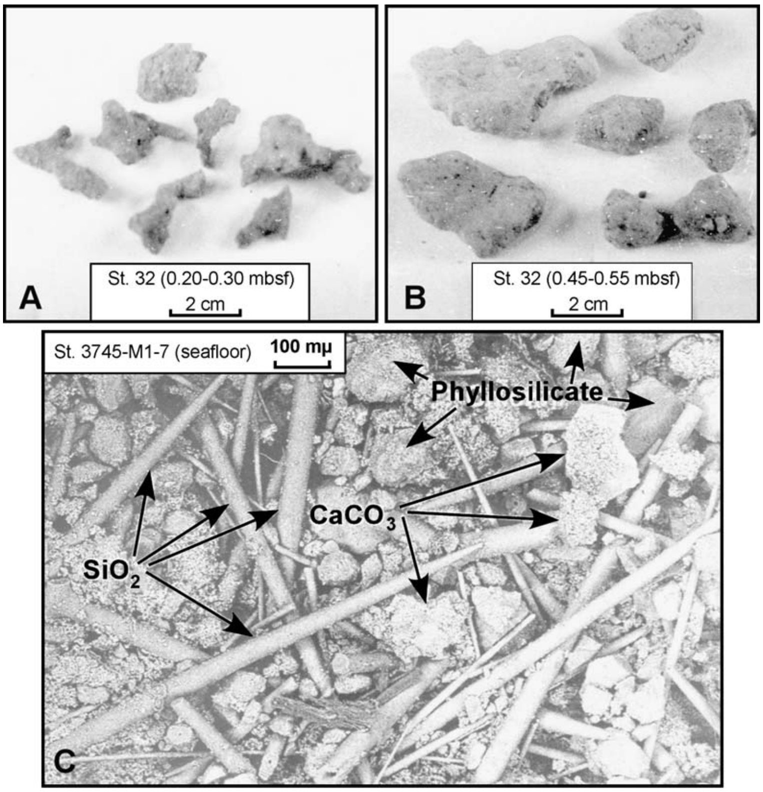

Fig. 12. Carbonate nodules from the HMMV sediment. (A) Elongated coral-shaped nodules; (B) subspheroidal nodules; (C) SEM image of carbonate buildup (Lein et al., 1998, 2000a).

nodules are found in sediments at Stations 32 and 36 at depth below 15 cm. These are elongated coral-shaped (<5 cm long) aggregates of silt and sand material cemented by carbonate, and subspheroidal nodules (Fig. 12; Milkov, 1998; Lein et al., 1998, 2000a). A buried carbonate "chimney" 17 cm long was also recovered from a box core at Station 36 (Lein et al., 1998, 2000a).

Petrographic studies show that the nodules consist of clay–carbonate matrix with embedded terrigenous material (grains of quartz, rock fragments (mainly quartzite), feldspar, chlorite and biotite) accounting for 40–60% of nodule volume. Skeletal remains include spicules of sponges, foraminiferal tests, and fragments of shells, together comprising ~5% of nodules (Fig. 12; Milkov, 1998; Lein et al., 2000a). Calcite is the main carbonate phase in the nodules (Fig. 12). High-Mg calcite, aragonite, and dolomite typical of authigenic carbonate sampled at other mud volcanoes and seeps (e.g., Aloisi et al., 2000; von Rad et al., 1996; Roberts and Carney, 1997) are not present, perhaps because of low bottom water temperature (−1 °C) (Lein et al., 2000a). Barite occurs, which is typical of some authigenic carbonate in the Gulf of Mexico (Fu and Aharon, 1997). Moreover, zeolites are identified (Lein et al., 2000b).

The carbon isotopic properties of most carbonate nodules typically vary in the narrow −28.4‰ to −29.6‰ PDB range, oxygen isotopic properties are in the 4.3‰ to 5.4‰ SMOW range (Fig. 13; Lein et al., 2000a,b). However, in one carbonate nodule, a $\delta^{13}C$ value of −16.6‰ PDB is measured. The relative enrichment in ^{13}C in the atypical sample is caused by mixture with skeletal carbonate (>10% of the nodule) (Lein et al., 2000a). The carbon and oxygen isotopic properties of carbonate nodules are similar to those of nodules from mud volcanoes in the Mediterranean Sea (Aloisi et al., 2000, Fig. 13) and suggest that carbon is derived from methane in shallow sediments. Lein et al. (2000a) show that carbonate nodules and crusts form at sites of intense anaerobic methane oxidation (at rates 1.1–1.57 ml CH_4 dm^{-3} day^{-1}) and sulfate reduction (at rates 1–15 mg S dm^{-3} day^{-1}). Both isotopic and geochemical evidence suggest that carbonates at the HMMV are authigenic and precipitate on the seafloor from CO_2 derived by anaerobic methane oxidation (Eq. (1)) (Lein et al., 2000a,b; Pimenov et al., 2000). Thus, it is possible that authigenic carbonate buried in sediments at Stations 32 and 36 at depth >15 cm did not form in situ, but were transported and buried by mud flows.

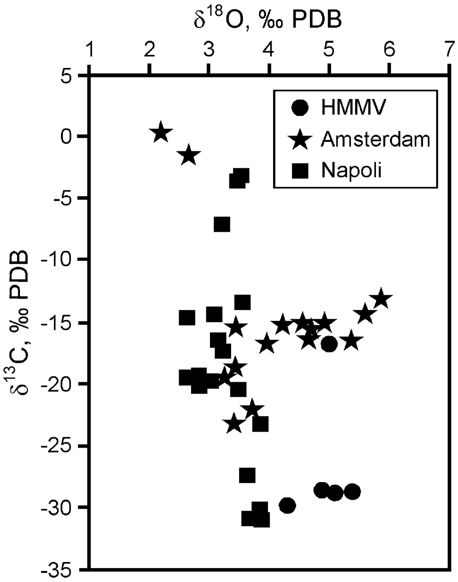

Fig. 13. Carbon and oxygen isotopic composition of carbonate nodules from the HMMV (based on data from Lein et al., 2000a) in comparison with authigenic carbonates from the Napoli and the Amsterdam mud volcanoes in the Mediterranean Sea (based on data from Aloisi et al., 2000).

The measured radiocarbon ages of five authigenic carbonates vary from 7960±410 to 11380±530 years BP (Lein et al., 2000a,b). In their estimate of the fluid balance of the HMMV, Ginsburg et al. (1999) envision two periods of mud volcano activity (200 and 12 ka) based on the timing of the large Late Pleistocene Bjornoyrenna Slide (Laberg and Vorren, 1993; Hald and Aspeli, 1997). Although various carbon sources affect the absolute age measured in shallow authigenic carbonates (Lein et al., 2000a,b), the measurements suggest that the HMMV is likely to be older than 12 ka. This is consistent with the suggestion of Bogdanov et al. (1999) that the HMMV formed during the Last Glacial Maximum, between 18 and 15 ka.

9. Conclusions and directions of future research

(1) Submarine mud volcanoes are widespread and potentially significant sources of carbon in the

ocean. The HMMV is a deep-water site where geological, geochemical, and bacterial processes are active at the present time. The multidisciplinary studies at the mud volcano provide a useful insight into the interplay of these processes.

(2) Concentric zonation is a major characteristic of the HMMV, and perhaps other active submarine mud volcanoes. The seafloor morphology, heat flow and geothermal gradient, dissolved methane concentration in the bottom water and seafloor sediments, sediment pore-water composition, occurrence of gas hydrate, distribution of bacterial mats and chemosynthetic organisms all show an approximately concentric zonation. This is governed by extrusion and expulsion of sediments and methane-rich fluids at the seafloor in the crater of the HMMV. However, in detail the HMMV is much more complex, particularly in the hummocky peripheral zone. This complexity needs to be addressed in further studies.

(3) The structural gas hydrate accumulation at the HMMV appears to be typical of deep-water mud volcanoes studied to date. Gas hydrate is stable in sediment, and sequesters hydrocarbon gases that migrated from ~2 to 3 km depth in section. However, the gas hydrate accumulation is not likely to be profitably exploited at the HMMV because of relatively low total gas resource in place and the lack of infrastructure.

(4) The HMMV appears to be a site of rapid anaerobic methane oxidation in shallow sediment. It is suggested that "reverse methanogenesis" mediated by a consortium of methanogens and sulfate-reducing bacteria is the mechanism responsible for methane oxidation. However, no such consortium has yet been shown to exist at the HMMV. Further microbiological studies are required to better understand the process of anaerobic methane oxidation, which also appears to occur in many other areas (Valentine and Reeburgh, 2000).

(5) In addition to microbially mediated processes, precipitation of authigenic minerals, diffusion of major and minor ions in pore-water, gas and water fractionation during gas hydrate crystallization, and other geochemical processes appear to be active at the HMMV. However, studies to date have not addressed the cycling of carbon, sulfur, and other elements at the interface of shallow sediments and bottom water in this area. Future quantification and modeling of geochemical cycles are necessary to study the balances of organic and inorganic components at this cold seep area that may be typical of others worldwide.

(6) Although bacterial methane oxidation is rapid in shallow sediment, gas flux from the HMMV nevertheless appears to be significant. This supports the suggestion that gas flux from the deep-water mud volcanoes may affect the mass and the isotopic composition of the oceanic carbon pool. In the future, direct measurements of gas flux from the HMMV and other mud volcanoes should be made to determine how important this flux might be from a global carbon perspective.

(7) The HMMV is a geologically active site. Temporal variability of the fluids flux, generation of new mud flows, possible eruptions, and the evolving chemosynthetic communities should be studied in future, possibly via long-term observations at the seafloor and in situ measurements.

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