Linking Mediterranean Brine Pools and Mud Volcanism

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Methane seepage at mud volcanoes around the world continues to be of broad international interest for a number of reasons.

Among these, seafloor methane is a potentially important contributor to global warming. In addition, dewatering and degassing of sediments and the formation of fluid migration pathways is important not only to sedimentologists, but also to hydrocarbon reservoir engineers and hydrologists.

Also of interest are the role of mud volcanoes on the chemical budget of the bottom waters, considering the large number of seeps and mud volcanoes in the Mediterranean basin; and the deep stratigraphy of an ocean basin otherwise available only by deep sea drilling. Studying erupted rock fragments from mud volcanoes is a relatively inexpensive, if haphazard, alternative to drilling down through the formations cut by the diatreme to determine the stratigraphy.

Intense emission of methane occurs not only at Mediterranean mud volcanoes, but also at seeps and vents along related fault systems. The fluid emissions are linked to carbonate pavements up to several tens of centimeters thick and a varied benthic fauna with symbiotic bacteria. Continuing deformation by mud from below creates a landscape with large crevasses and graben structures several meters wide in mud flows forming the summit of the mud volcanoes. These are a few of the results observations from a joint French-Dutch effort carried out in 1998 in which, for the first time, these phenomena were observed in the Mediterranean by submersible.

Fluxes of methane through the floor of the eastern Mediterranean are therefore greater than expected, even on the basis of the large number of mud volcanoes, because of the fluid seeps along faults. Furthermore, extensive gas fluxes imply that there may be wide spread occurrences of gas hydrates. Gas hydrate occurrence would be moderated by the regional presence of highly saline pore waters and hydrogen sulphide. Even relatively small accumulations, however, are susceptible to rapid release of large volumes of methane (over 160 times the volume concentrated in hydrate form at sea surface conditions) should there be periods of greater brine fluxes through the sediment, increases in bottom water temperature, or decreases in sea level.

The linkage of fluid seeps and mud volcanoes also provides new clues to the mechanisms of mud volcanism; for example, through fault control. In addition, monitoring brine lake levels could be a proxy for tracking variations in the flux of methane through the seafloor in this case.

Diving to the Mud Volcanoes

The submersible observations were made by the Dutch-French MEDIterranean expedition of NAUTile (MEDINAUT), which investigated cold seeps and mud volcanoes in two distinctive tectonic settings in the eastern Mediterranean Sea using the French research submersible *Nautile* from support vessel *N/O Nadir*. Another effort, the MEDIterranean NETHerlands expedition (MEDINETH), was organized as a follow-up by the Dutch group in 1999 to complete sampling with longer cores, as well as further geophysical surveying using a deep tow sidescan sonar and subbottom profiling device.

The French and Dutch teams were both complementary and multidisciplinary, with microbiologists, organic biogeochemists, inorganic geochemists, sedimentologists, benthic ecologists, geophysical, and geotechnical specialists.

Most of the participants had extensive experience in investigating mud volcanoes and fluid seeps in other parts of the world. They were interested principally in detailed, multidisciplinary investigations of mud volcanoes that already had been well studied. Two of them—the "Milano" and "Napoli" mud volcanoes—had even been drilled by ODP Leg 160 [*Emeis et al.*, 1996] to determine the controls, triggers, and processes of mud volcanism.

Mud volcanoes from two different settings were studied. One of the settings was the Olimpi Mud Volcano field (OMV area) on the Mediterranean Ridge [*Cita et al.*, 1996; *Mascle et al.*, 1999], the accretionary prism associated with subduction along the Hellenic Arc south of Greece (Figure 1). The other setting was in the Anaximander Mountains (AM area), a group of continental fragments rifted from Turkey in post-Miocene time and now caught up in the plate convergence between Africa and Eurasia via the active Anatolian and Aegean microplates [*Woodside et al.*, 1997, 1998].

There are two principal differences between the mud volcano settings. Messinian evaporites occur within the Mediterranean Ridge but are absent in the Anaximander Mountains, and the Anaximander Mountains are formed by older, consolidated rocks than the active accretionary prism sediments of the Olimpi area. What the two settings have in common is strong compressional tectonics with superposed faulting.

A good review of the current state of understanding about the Mediterranean mud volcanoes was made following the ODP results [*Robertson and Kopf*, 1998]. One surprising ODP result was that these mud volcanoes showed episodic eruptions dating back over 1 Ma. MEDINAUT observations clearly showed that mud volcanoes can lie dormant for relatively long periods of time before reactivating. The "Kula" mud volcano in the AM area is a smooth dome covered by over 1.5 m of normal pelagic sedimentation, except for a small but very active area of fresh eruptions on its summit with a patch of mud flows no more than 200 m across. However this seems to be the exception because most of the explored volcano summits show very little pelagic sedimentation.

Most of the mud volcanoes are conical topographic features several kilometers across and on the order of 100 m high. None have craters but a few have relatively flat summit areas with low relief on the order of 5–10 m). Eruption centers are of limited areal extent, and submersible observations show that parasitic cones are centers of mud eruption on the outer summit areas of some mud volcanoes, for example, on "Kazan" and "Amsterdam" mud volcanoes (AM area; Figures 2b and 3).

Several distinct mud flows can generally be mapped at the surface of the mud volcanoes. Mud flows extend out onto the surrounding seafloor for several kilometers from the central upper reaches of the mud volcano. Young flows show thin carbonate crusts, widespread benthic fauna, and surfaces that are rough

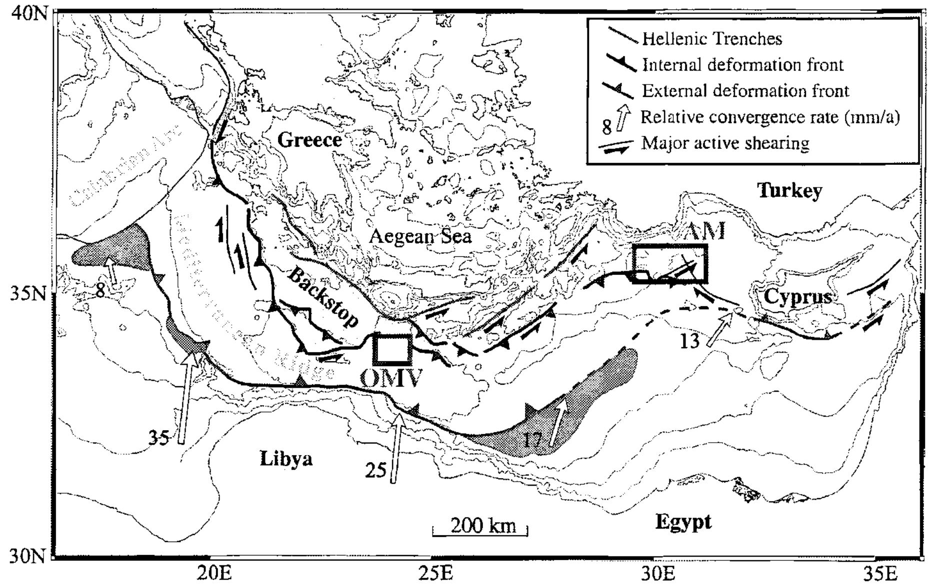
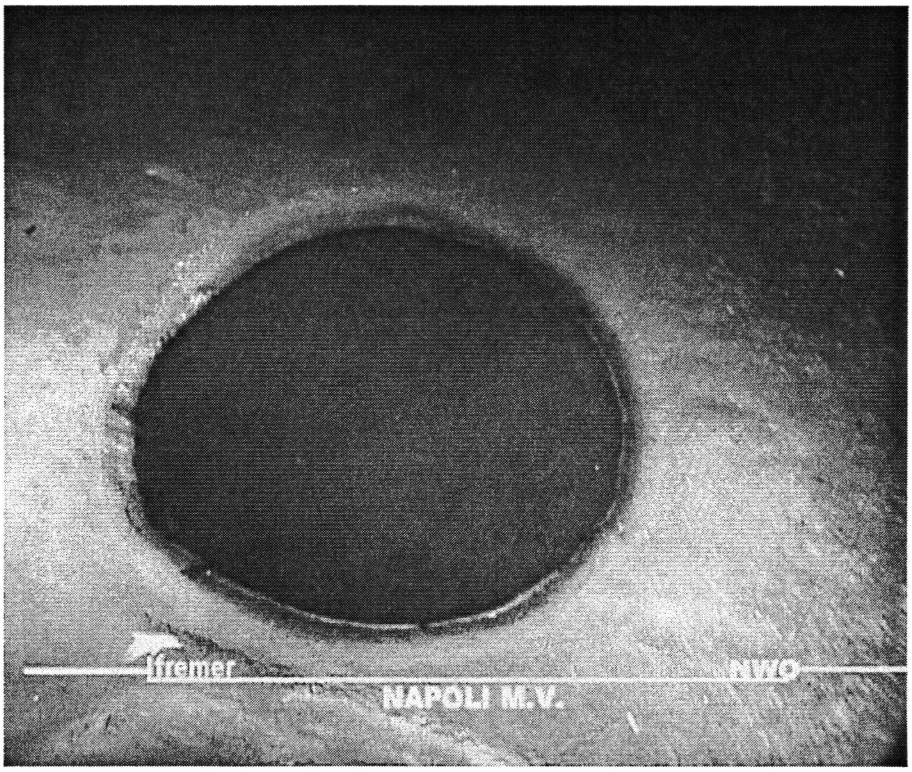


Fig. 1. Location map showing the Olimpi Mud Volcano Field (OMV) and Anaximander Mountains (AM) (in boxes) in their general eastern Mediterranean context. Original color image appears at the back of this volume.



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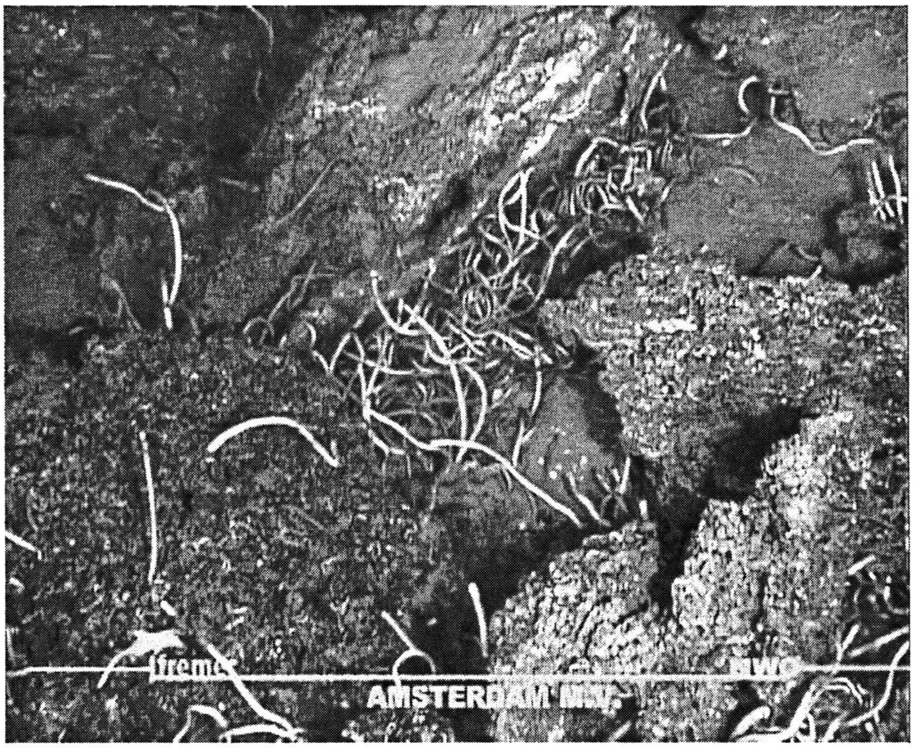

(b)

Fig. 2. Photographs from submersible Nautile of (a) a brine pool about 2-3 m in diameter at 1950-m water depth on top of Napoli mud volcano in the OMV area, and (b) a cold seep at a depth of 1970 m on top of a small parasitic cone on the west side of "Amsterdam" mud volcano (see Figure 3) in the AM area. Note the broken crusts and associated vestimentiferan worms at the active cold seep. Original color image appears at the back of this volume.

with projecting clasts and crevassing. Crevasses vary from a few centimeters deep and wide on mud volcanoes like "Milano," "Maidstone," and "Moscow" (all in the OMV area), to roughly 7–10 m wide and deep as observed on the "Amsterdam" mud volcano (AM area; Figure 3). They are thought to be the result of slow continuous or episodic mud motion inside the volcanoes, which would take place over a much longer time scale than the probably short-lived eruption events themselves.

These are not dead features in any way. Slight expansion or deflation of the mud volcano in response to mud movements driven from below, or surficial gravitational creep of mud flows on the flanks of mud volcanoes, may all be involved in the crevassing. Some scarps of several meters high were inferred to be faults at "Maidstone" and "Napoli," where they are in apparent continuity with longer faults observed on deep tow sidescan images at a regional scale on the Mediterranean Ridge. Indeed, broad scale PRISMED II multibeam mapping emphasizes the importance of a system of long faults crossing the Mediterranean Ridge obliquely [*Mascle et al.*, 1999].

Brine Lakes and Mud Volcanoes

Brine lakes on the Mediterranean Ridge are a well-known phenomenon [e.g., *MEDRIFF Consortium*, 1995], but their occurrence in association with the mud volcanoes is an important new observation. This is because the pathways and driving mechanisms must generally be the same and the flux of methane can be seen as being much more widespread than previously thought for mud volcanoes alone. Release of fluids from the Mediterranean Ridge ranges from simple seeping of brines and gas to more energetic, possibly explosive, emissions with sediment at mud volcanoes. Not only are brine pools associated with faults, as speculated by Woodside and Volgin [1996], but the "Napoli" mud volcano (OMV area) is covered with shallow pools in its most active central area (Figure 2a). The pools form in small depressions on the relatively flat summit of Napoli, where relief of only a few meters is measured. From the submersible, the summit of the "Napoli" mud volcano appears to form a vast salt marsh where brines, emitted by numerous small vents, have accumulated in the shallow depressions on the seafloor. Brine accumulations were also discovered outside the volcanoes in the Nadir Brine Lakes where hypersaline fluids have migrated to the seafloor along deep faults. These brines are also rich in methane and carry dissolved gas to the seafloor.

Sidescan sonar records suggested the presence of brine lakes lying in a north-south fault zone between the "Maidstone" and "Moscow" mud volcanoes in the OMV area [*Woodside and Volgin*, 1996]. MEDINAUT confirmed both their presence and their control by faults; thus they were named after the research vessel *Nadir* from which they were explored. These brine lakes, and at least one of the brine pools on "Napoli" (Figure 2a), are circular, with diameters up to about 250 m for the principal Nadir brine lake. They give the impression of a pock mark or large crater formed on the seafloor actively in response to fluid emissions.

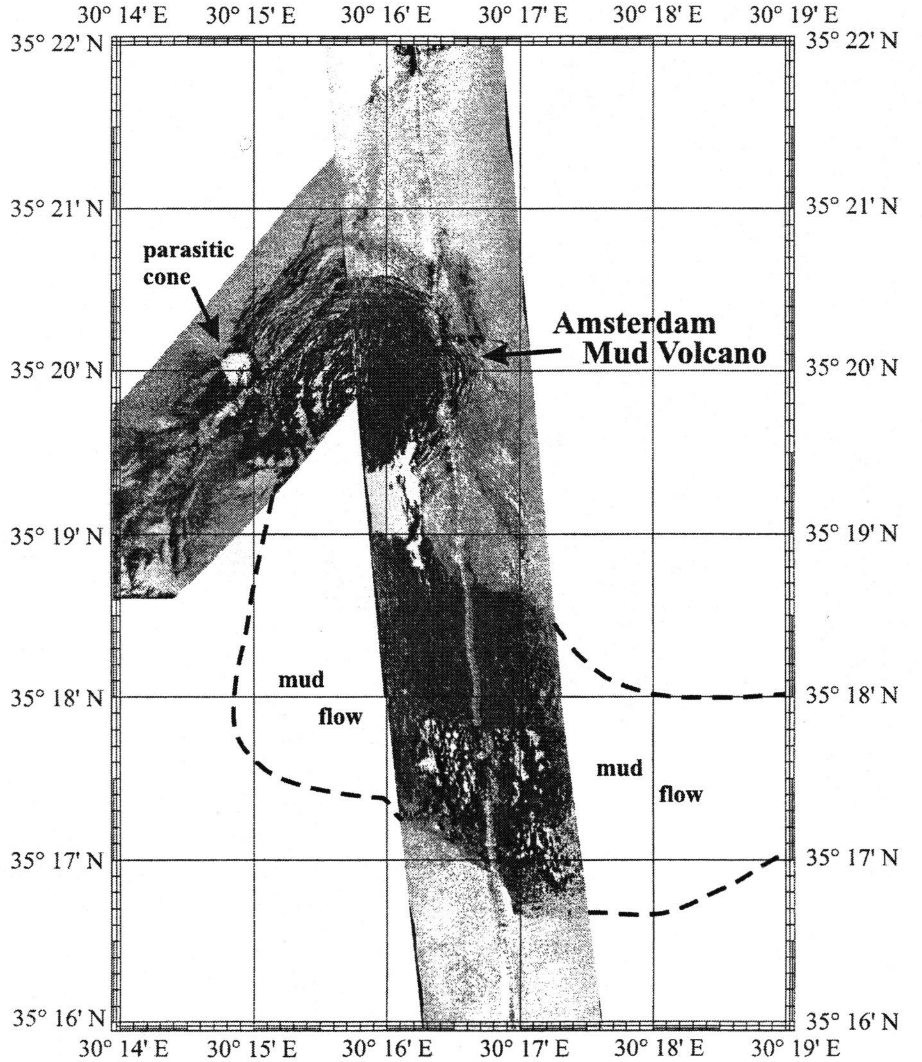

Fig. 3. Mosaic of MAK-1 (oblique strip) and ORETech (long central strip) deep tow sidescan records of "Amsterdam" mud volcano in the Anaximander Mountains. The mud volcano is the large circular area of high backscatter (dark) in the upper center and part of a large flow is seen to the south of it, also with high backscatter. The flow alone is over 300 m thick and comprises around 13 km³ of erupted mud. The light-colored spot on the left rim of the mud volcano is a very active parasitic cone on a NNE-SSW-oriented fault (see Figure 2b).

The observation of empty brine pools, evidence of directional flow in some brine lakes (suggesting the occurrence of overflow), and margin variability (for example, "bathtub ring" zoning of crusts, sediment color) indicate that the level of brine in the lakes varies on a short time scale. The implied variability and episodicity of brine expulsion must also correlate with variable release of dissolved methane into the water column.

Some vents occur at the bottom of the brine pools while others are linked to the pools by shallow gray-stained channels from seeps on slightly higher terrain. The channels have the appearance of river systems with tributaries emanating from small source holes on the order of 10 cm in diameter. Vents and channels are color-zoned, with white rims (from inferred microbial aggregates), gray areas of reduced sediment, and dark brown areas farther away. In the main Nadir brine lake the levels of methane are as high as 133 ml/l. In contrast, the shallow brine pools on the "Napoli" mud volcano and also in the OMV area have levels of only 0.1 ml/l, probably because of greater mixing with normal, less saline, bottom water.

Carbonate Crusts

Carbonate crusts are present at most seeps. In some cases, they build up large, mushroom-like structures above vents by adding material from the bottom. In other cases, they form a general cover on mud flows, varying in thickness from centimeters to decimeters. Where the crusts are absent or thin, the mud flows are inferred to be relatively freshly erupted. The carbonate is predominantly aragonite with calcite and minor dolomite, and the crusts incorporate shells and tube worms from the benthic communities that develop around the vents. The isotopic composition of the crusts indicates that they are derived from oxidation of the methane that issues from the vents: $\delta^{13}C$ values range from 0 to -47 per mil, and $\delta^{18}O$ values vary from about 2 to 5.4 per mil (all values are relative to the Peedee belemnite standard). Further investigation will determine whether the crusts build episodically, as the gas venting is thought to occur.

Methane

Large methane concentrations measured in the water column above mud volcanoes indicate intense degassing. Background levels of methane in the eastern Mediterranean basin are normally around 10 nl/l away from the mud volcanoes. Methane concentrations of 1 to 20 μl/l, up to about one thousand times the background value, were recorded above Napoli and Milano (OMV area). Similar extensive methane emissions above large areas of the Amsterdam mud volcano (AM area) produce water column readings of between 3 and 13.5 μl/l, which is indicative of significant expulsions of gas-enriched fluids from the sediments. This was confirmed by higher nephelometric values, which indicate enhanced bottom-water turbidity everywhere above the Amsterdam mud volcano.

There is considerable variability in terms of gas seepage from one volcano to another despite the generally intense fluxes observed above all the mud volcanoes studied by MEDINAUT and MEDINETH. General degassing probably occurs throughout fresh mud flows initially, with specific vents developing later where pathways have formed through the flows. The focused seeps are likely fed from deeper, less ephemeral sources below the flows. Preliminary analysis of the methane suggests principally biogenic origin in the OMV area and both thermogenic and biogenic components in the AM area.

Gas Hydrates

Salinity profiles obtained from pore water samples suggested that gas hydrates were present on several mud volcanoes. This had already been observed at Milano mud volcano (OMV area) in ODP Leg 160 cores [*De Lange and Brumsack*, 1998]. Decreasing salinity with depth in MEDINAUT cores from the upper 30 cm of sediments from mud volcanoes "Milano" and "Moscow" (OMV area) and from "Kazan" (AM area) indicates the presence of shallow gas hydrates in the absence of other plausible explanations. On the "Moscow" mud volcano, the salinity decreased to about 8 per mil in the upper 30 cm compared to 30 per mil for the bottom water. A plentiful supply of gas under prevailing seafloor conditions (13–14°C and depths greater than 1900 m) also indicates that gas hydrates would be stable there. The favored interpretation is that gas hydrates were present in the cores obtained by submersible and would have dissociated during the slow return of the submersible to the sea surface, producing methane, which would escape relatively quickly, and fresh water that would dilute the normally salty pore water. Bubbles were observed leaving the cores at least once during the submersible's ascent. In 1996, small nodules of gas hydrates were sampled in a gravity core from the "Kula" mud volcano (AM area) in a hydrogen sulphide-rich section below 50 cm [*Woodside et al.*, 1998].

During the 1999 MEDINETH expedition, an extensive field of gas hydrates was sampled on Amsterdam mud volcano, with smaller quantities on the "Kula" mud volcano, and on the "Texel" mud volcano on the Florence Rise just west of Cyprus. In each case the presence of the gas hydrates confirmed the original inference.

Benthic Life

Both the submersible observations and follow-up investigations revealed a profound ubiquity of life ranging from microbes to macrofauna. At all mud volcanoes visited in both the OMV and AM areas, abundant organisms were observed including vestimentiferan worms, mollusks (small bivalves, gasteropods), crabs, urchins, sponges, shrimps, and fish (even rays). Vestimentiferan worms, in particular, are characteristic of cold seep settings such as these [e.g., *Sibuet and Olu*, 1998] and were common at all sites, occurring either in isolation or in small clusters of up to several hundred organisms. The tubes range from 10 cm to 40 cm in length and approximately 0.5–1 cm in diameter. They commonly protrude from beneath the crusts where the greatest concentration of methane is likely to be (Figure 2b).

Also striking are widespread deposits of mollusk shells throughout the investigated areas. The impression was of a catastrophe that had killed off a far more extensive molluskan community than currently exists there. These mollusks may have thrived during degassing of recent mud flows and then died off as the gas supply from the flow diminished. Living mollusks were not nearly as abundant on the seafloor, but they may be living below the seafloor. Nevertheless, living mollusks were recovered from several mud volcanoes, sometimes from within the sediment but also from the lower side of crusts.

Bivalves *Lucinidae*, *Vesicomyidae*, and *Mytilidae* are all represented, expanding on previous observations of these organisms in sediments from the "Napoli" dome [*Cita et al.*, 1996] and the Anaximander Mountains. Macrofauna are concentrated generally at sites where fluid emission is greatest, suggesting a causal relationship between methane concentration and the prosperity of the ecosystem [*Sibuet and Olu*, 1998]. Initial investigations have revealed the presence of methylotrophic and sulphur-oxidizing chemoautotrophic endosymbiont bacteria in some bivalves and provide direct evidence of this connection.

Bacteria aggregates are also common and were visually discernible from the *Nautile*. White, filamentous bacteria were abundant on the "Milano" mud volcano (OMV area) but were also observed in other parts of both study areas. They appear to be similar to Beggiatoa aggregates, and initial carbon isotope evidence is consistent with a chemoautotrophic physiology. Further phylogenetic analyses will directly confirm this assignment. In addition, black gelatinous mats, approximately 0.5-cm thick, were observed throughout the OMV area. These mats appear to sit over methane seeps but were also recovered from the bottom of a brine pool. Isotopic and molecular analyses indicate that these are microbial aggregates containing a consortium of organisms thriving on net anaerobic methane oxidation. This was confirmed by pore-water geochemistry.

Lipid analyses clearly indicate that diverse bacteria and archaea also thrive in the upper 1 m of mud volcano deposits. The structures of these lipids, their carbon isotopic compositions, and pore-water profiles of sulfate and methane concentrations all indicate that these communities are sustained by the pronounced flux of methane, which is oxidized anaerobically by the archaea in syntrophic cooperation with sulfate-reducing bacteria and perhaps other types [*Pancost et al.*, 2000]. Initial results clearly indicate that the pronounced methane flux from mud volcano deposits sustains a diverse and robust ecosystem comprised of bacteria and archaea. Consequently, net methane oxidation by this microbial ecosystem could be one of the dominant sinks for methane released from mud volcano sediments.

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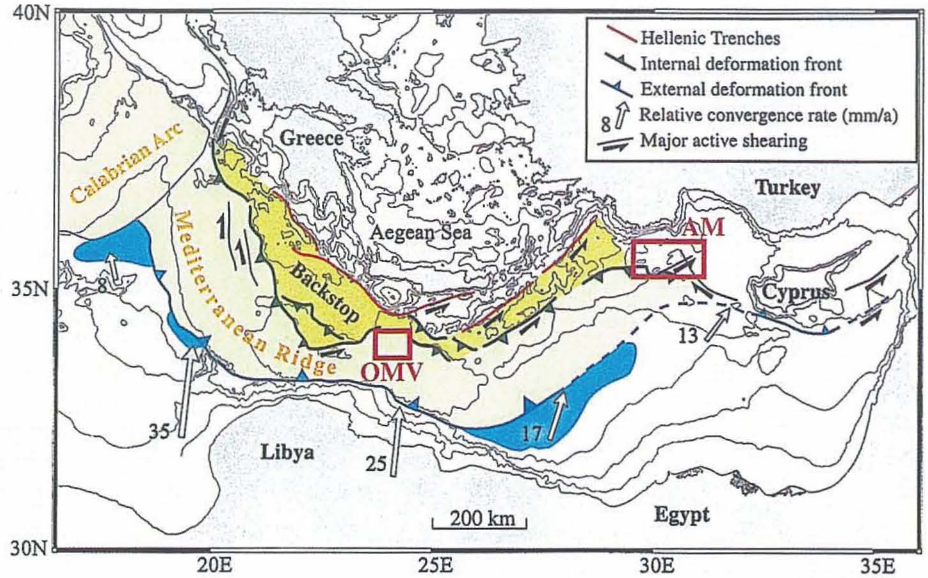

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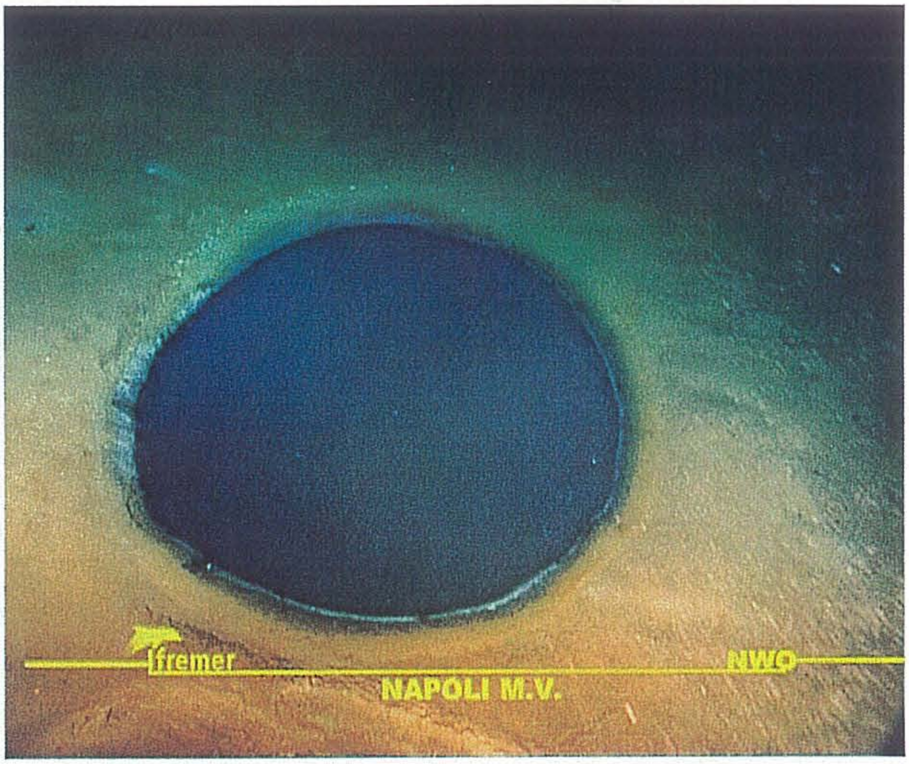

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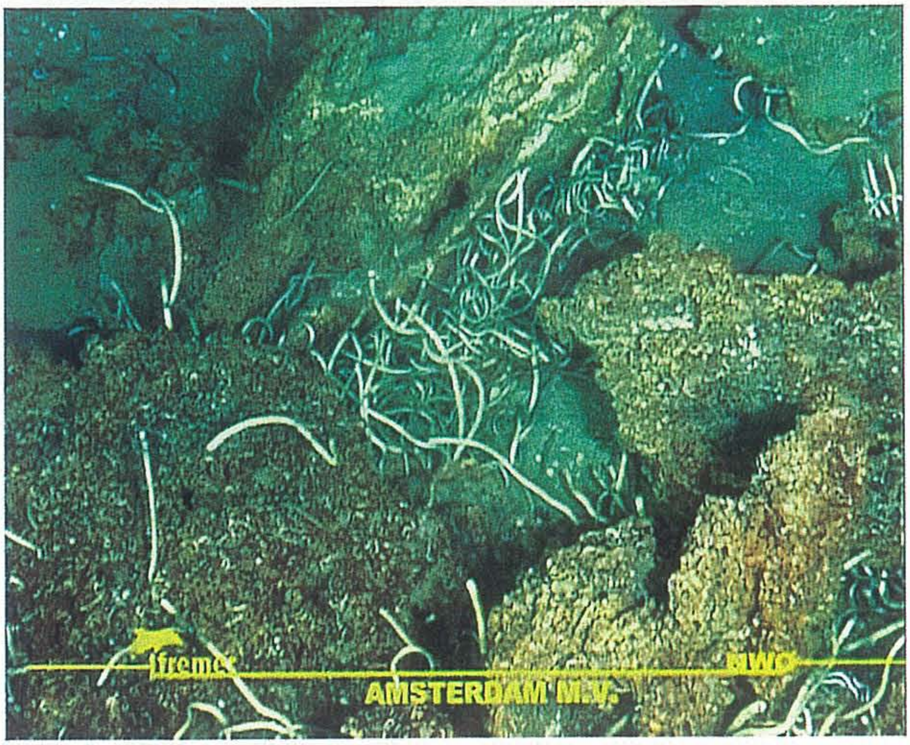

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