

Research Article

Thessaloniki Mud Volcano, the Shallowest Gas Hydrate-Bearing Mud Volcano in the Anaximander Mountains, Eastern Mediterranean

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A detailed multibeam survey and the subsequent gravity coring carried out in the Anaximander Mountains, Eastern Mediterranean, detected a new active gas hydrate-bearing mud volcano (MV) that was named Thessaloniki. It is outlined by the 1315 m bathymetric contour, is 1.67 km² in area, and has a summit depth of 1260 m. The sea bottom water temperature is 13.7°C. The gas hydrate crystals generally have the form of flakes or rice, some larger aggregates of them are up to 2 cm across. A pressure core taken at the site contained 3.1 lt. of hydrocarbon gases composed of methane, nearly devoid of propane and butane. The sediment had a gas hydrate occupancy of 0.7% of the core volume. These characteristics place the gas hydrate field at Thessaloniki MV at the upper boundary of the gas hydrate stability zone, prone to dissociation with the slightest increase in sea water temperature, decrease in hydrostatic pressure, or change in the temperature of the advecting fluids.

1. Introduction: Purpose of This Study

The occurrence of mud volcanoes (MVs), mud diapirs, and fluid seeps has long been known in various different geological environments of the Eastern Mediterranean [1] and in the Aegean Sea [2]. They occur not only in regions of compressional stress present in subduction zones (e.g., Calabrian Arc [3], Mediterranean Ridge [4], and orogenic belts [1, 5–7]), but also on passive rifted margins such as the Egyptian offshore [8, 9] and areas of mixed tectonic signature like the ANAXIMANDER Mountains where mud volcanism is related to faults with normal and transcurrent faulting components [10–12]. Especially the accretionary prism of the Hellenic Arc (Mediterranean Ridge) is an area where a large number of mud volcanoes have been studied following

their discovery in the late 1970s [13]. Mud volcanoes are also known for their high methane fluxes, advecting methane-rich fluids at seafloor seeps, gas hydrates, and favorable environments for chemosynthetic symbiotic fauna [5, 10, 12].

The Anaximander Mountains are situated between the Hellenic and Cyprus Arcs at the junction of the African Plate with the Anatolian and the Aegean microplates, an area accommodating the relative motion between the African and Eurasian plates [6, 10, 14]. The mountains have thus undergone a complex deformation including southward directed thrusting, northeast-southwest shearing in the west (Strabo Trough trend) and northwest-southeast shearing in the east (Florence Rise trend), and cross-cutting normal faulting, all defining the current structure of the mountains [10, 12, 15, 16]. They are comprised of three

main seamounts: Anaximander, Anaximenes, and Anaxagoras (Figure 1(a)).

The setting of the Anaximander Mountains is clearly favorable for the occurrence of mud volcanoes (Figure 1) thanks to the presence of overpressured fluids and faults that act as conduits for the fluids to escape [12, 17, 18]. Discovered during the Dutch ANAXIPROBE project by multibeam surveying in 1995, seven large mud volcanoes were sampled in 1996 [6, 7, 11] when the first gas hydrates samples in the Mediterranean Sea were collected from Kula MV. By 2002 the Amsterdam and Kazan MVs were also discovered to have hydrates. Between 2003 and 2005 the EC-funded project ANAXIMANDER targeted these mud volcanoes in a study of the gas hydrates and associated deep biosphere in the area, and this was followed by the HERMES project (2005–2009). During these projects gas hydrates from Amsterdam and Kazan MVs were collected and studied, and two new mud volcanoes named Athina and Thessaloniki were also discovered, sampled, and studied (Figure 1(b) [17, 19–21]).

Since Thessaloniki MV is the shallowest known GH bearing MV in the Eastern Mediterranean, very briefly described earlier [17, 21], the purpose of this study is to carry out detailed analyses and examination of all data collected in this area and discuss the conditions and characteristics of the GH present.

2. Materials and Methods

The data examined in this study were acquired mainly during two cruises of the R/V *Aegaeo* in May 2003 and October–November 2004. During the first cruise detailed swath bathymetry and backscatter imagery of the study area was obtained using a hull-mounted SEABEAM 2120 swath system operating at 20 KHz. It has an angular sector of 150°, with 159 beams and a swath width from 7.5- to 11.5- times the water depth, for depths from 1 to 5 km respectively. Navigation was carried out with a Trimble 4000 GPS providing the ships position to within ±10 m. The bathymetric map of Thessaloniki MV (Figure 2) was produced using a 20 m grid interval and plotted with a Mercator projection at a scale of 1 : 20,000 with 5 m contours. Sediment was sampled with a 3 m long 73 cm i.d. Benthos Instruments Gravity Corer with presplit sleeves to reduce the time needed to open and sample the cores. The time between coring the seafloor and on board sampling of cores from a depth of 2000 m was thus reduced to between 20 and 25 minutes to ensure the least possible gas hydrate dissociation and sediment distortion. As soon as the cores were opened, the temperature of the sediments was measured, and any gas hydrates were collected and placed in a freezer at –70°C. Detailed sampling of the sediment followed.

The pressure coring was carried out using the APCA (Autoclave Piston Corer Anaximander) [22] designed and fabricated by Technical University of Berlin as part of the ANAXIMANDER project. The APCA retrieves cores of 10 cm diameter and up to a length of 250 cm in water depths of up to 2500 m. It preserves the sediment cores under *in situ* pressure conditions [22]. Upon retrieval on

deck the autoclave corer was placed upright for controlled degassing and kept in an ice bath to prevent warming to deck temperatures. The degassing, gas collection, and gas-subsampling were carried out using a valve system as described by Heeschen et al. [19], a method used and described also by others [18]. The pressure was constantly monitored and the increasing volume of released gas was read off from a converted graduated cylinder. Gas subsamples were taken via a three-port valve and were stored for analysis in the laboratory [22]. A total of four gravity cores and one autoclave core were collected at Thessaloniki MV (Figure 2, Table 1). The trace and main elements were analyzed by the X-ray diffraction method using a SIEMENS D-500 instrument. The crystalline phases were determined using the Joint Committee Power Diffraction Standards and their final semiquantitative analyses by using the EVA program from Siemens/Bruker/Socabimo.

3. Results and Discussion

3.1. Bathymetry and Backscattering Imaging. Anaximenes Mountain (Figure 1) is a slightly northwestward concave feature occupying the shallowest (680 m) and smallest area in the Anaximander Complex, and therefore is characterized by steep slopes and rugged relief. To the south the Mediterranean Ridge is terminated in the form of a flat slightly wavy or folded area lying at a water depth of about 2800 m. It is separated from Anaximenes Mountain by a deep valley (>3000 m). The study of the combined 3D seabed morphology and backscatter intensity revealed in the southeastern slope of Anaximenes Mountain numerous dome-like morphological features with strong backscatter that constitute potential mud volcano sites. Following image processing of the backscatter data, a number of high backscatter areas implying potential active mud volcanism were identified. One of these sites at a depth of 1798 m was subsequently surveyed in 2003 and discovered to be a mud volcano which was named Athina MV (Figure 1, [17, 20]). In the same area, about 9 km northeast of Athina MV (at 35° 28.60 N – 30° 15.06 E), and at water depths between 1320 and 1260 m the Thessaloniki MV was discovered after surveying and sampling in November 2004 (Figures 1 and 2 [17, 21]). This mud volcano had not been fully examined in previous cruises because of its small size and location at the base of a very steep sloping cliff (Figure 2), although its eastern side was crossed during the ANAXIPROBE ORETech side scan survey [7] (Figure 2). It is an oval submarine hill with its long axis about 1750 m as defined by the 1315 m isobath, with steep northern and eastern slopes and an area of about 1.67 km². In the inner part, near the summit, it becomes more circular where three peaks are distinguished, two in the west outlined by the 1260 m contour and one in the east at 1265 m. Its small size and location on a steep slope made it a lower priority for investigation during earlier research projects.

3.2. Sedimentology. Five cores were collected from Thessaloniki MV: four gravity cores (AX46-GC1, AX47-GC1,

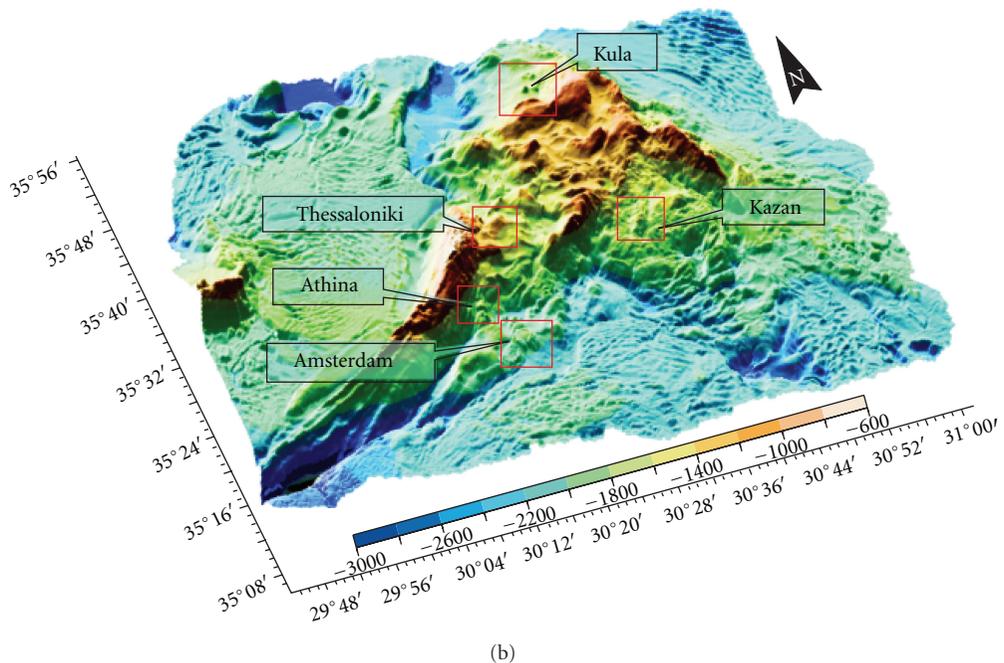
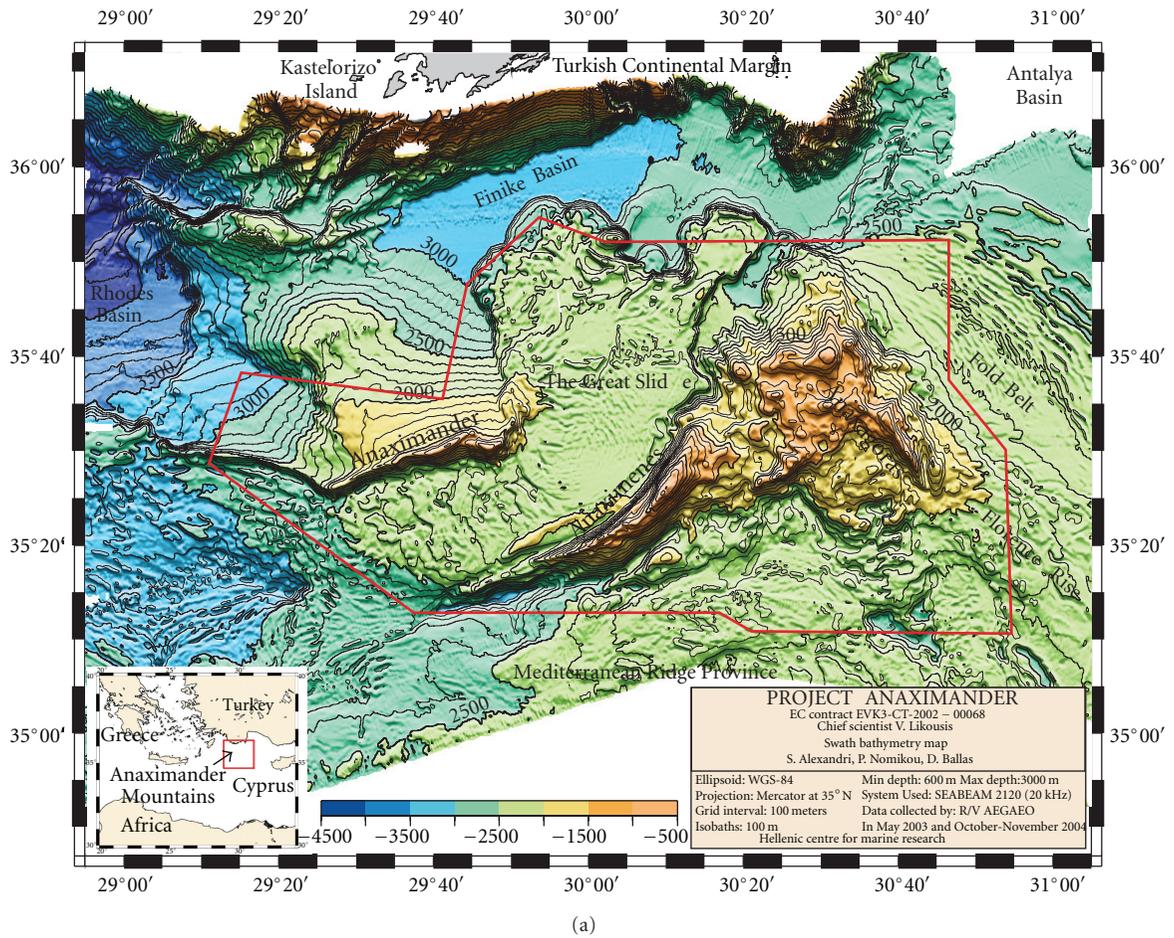


FIGURE 1: Bathymetry-physiography of the Anaximander complex (a), and swath bathymetry with locations of the five surveyed mud volcanoes ((b) from [17] supplemented with ANAXIPROBE data to outline each MV area [11]).

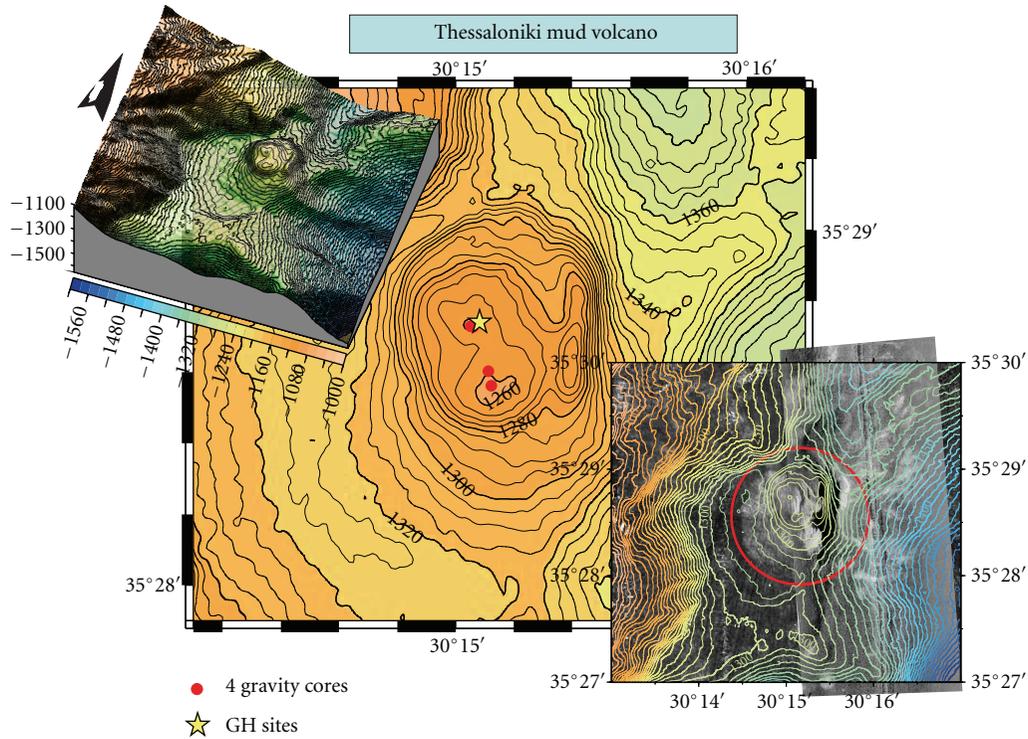


FIGURE 2: Swath bathymetry map of Thessaloniki MV and location of the collected cores (black dots). Upper left, greater swath map with the volcano at the center, lower right, ORETech side scan image from ANAXIPROBE cruise on top of SEABEAM backscatter intensity map. Gravity cores AX46-GC1, AX47-GC1, and autoclave core AX49-AP1 were retrieved from the northern peak, nearly at the same location. Gravity cores AX-48 and AX-49 were retrieved from the southern peak (from [17] supplemented with back scatter data and location of APCA core).

TABLE 1: (a) Gravity cores. (b) Autoclave core.

(a)							
Core no.	Latitude	Longitude	Water depth (m)	Sediment temperature	Length (cm)	G.H. presence (visual identification)	Smell of H ₂ S gas
AX46-GC1	35°28.603'	30°15.113'	1263	14,4° C	110	No	Yes
AX47-GC1	35°28.562'	30°15.123'	1265	12,3° C	167	No	Yes
AX48-GG1	35°28.729'	30°15.052'	1264	8.4–10.7° C	130	Yes	Yes
AX49-GC1	35°28.728'	30°15.060'	1264	No data	228	Yes	Yes

(b)							
Core no.	Latitude	Longitude	Water depth (m)	Length (cm)	Pressure (bars)	GH presence	Gas vol. (litres)
AX49-AP1	35°28.728'	30°15.060'	1.264	0.70	105	Yes	3.1

AX48-GC1, and AX49-GC1) and one autoclave core (AX49-AP1). They are located in similar sedimentary environments on the two western highs on the summit of Thessaloniki MV (Figure 2), in water depths from 1263 to 1265 m. Table 1 presents the details of the core locations and characteristics, with the initial deck observations made to determine whether there were gas hydrates (even if not actually observed; for example, with sediment temperatures below the seafloor temperature, ~13.7°C, there is likely to have

been dissociating gas hydrates present). These observations confirmed that this MV is an active gas hydrate bearing mud volcano, the fourth discovered in the Mediterranean.

The general appearance of typical mud breccia cores (Figure 3) is of a very poorly sorted sediment with muddy matrix-supported angular to subangular clasts (xenoliths) of different compositions and grain sizes (0.5 to 2.5 cm). The clasts reflect the geological units through which the overpressured sediment passed before erupting on the



FIGURE 4: Section 99–124 cm of core AX48-GC1. Note the soft character of section 110–120 cm which contained gas hydrates.

with many degassing features produced from the dissociation of GH dispersed throughout the whole length of the core.

3.3. Geochemical Results. A geochemical analysis was made of both the mud flow (trace element) and the rock clasts (main element) of the gravity cores.

The results of the trace element analysis in the mud flow of two gravity cores (Table 2(a)) indicate that organic carbon (C_{org}), Na_2O , Mg, Rd, Sr, and Cu do not vary down core. The total carbon (C_{tot}) is higher at the top of the cores than in the lower sections whereas the values of S and Zn are usually lower at the top of the cores than below.

Calcite is the dominant mineral in the rock clasts from gravity core AX 48-GC1 (Table 2(b)). This combined with the presence of the other main elements shown in Table 2(b), and the low dolomite content, support earlier interpretations that bedrock here is related to the Miocene flysch deposits present on land to the north ([6] see Section 3.4).

These results also indicate that the composition of the Thessaloniki MV sediments are comparable to those reported in other Mediterranean mud volcanoes like Athina [20] and even those from the Gulf of Cadiz [29].

The methane concentration was measured in both gravity cores. No gas hydrates were observed in core AX47-GC1 but the sediment was wet and in some places “soupy.” On the other hand, gas hydrates were observed throughout core AX49-GC1 when it was opened on deck (Figures 3 and 4). Methane concentrations in core AX47-GC1 were about $2800 \mu\text{mol/kg}$ wet sediment, with a maximum of $4000 \mu\text{mol/kg}$ wet sediment at a core depth below sea floor of 100 cm. In core AX49-GC1, the methane concentration was $3000 \mu\text{mol/kg}$ wet sediment, decreasing to $2000 \mu\text{mol/kg}$ wet sediment below this maximum at 100 cm down core (Figure 5). Thus the methane concentrations at both western highs on the summit of the mud volcano were high despite the apparent differences in gas hydrate content seen in the sediment. However, due to the degassing of these conventional cores during recovery, and the consequent loss of up to 90% of the methane [19], we could not determine significant differences in methane concentrations because the concentrations are far below methane saturation in the presence of gas hydrates ($\sim 100 \text{ mmol/kg}$ pore water [19]).

It is possible that observations of gas hydrates in one core, but not in another with similar concentrations of methane, can be explained by differences in the size of the gas hydrate deposits between the two cores, with the smaller GH crystals disappearing more quickly.

The *in situ* methane concentration in the autoclave core at northern site AX49 (core AX49-AP1) was calculated to be about 180 mmol/kg pore water at depths where there is no sulfate present. To calculate gas hydrate volumes from methane concentrations in relation to the core volume, the amount of collected gas ($\sum \text{CH}_4 = 3.1 \text{ L}$) is related to the core volume between the bottom of the core and the sulfate depletion depth, assuming an even distribution throughout this depth range with dissolved and hydrate-bound CH_4 to be present. The saturation concentration (c_{eq}) of CH_4 is subtracted before calculating gas hydrate volumes. For details see [30]. In core AX49-AP1 gas hydrates occupy about 0.7% of the core volume. The gas collected from the pressure core is nearly devoid of propane and butane thus allowing structure I gas hydrates to be formed [19]. No pressure corer was taken on the southern peak of this western high.

3.4. Study of the Mud Breccia Rock Clasts. The presence of a yellowish-brown oxidized layer in the upper few centimetres of the two gravity cores, where there were no gas hydrates observed, probably indicates that at these two sites mud volcano activity was low to absent during the last few hundred years. Freshly erupted mud breccia is characterised by grey reduced sediment and the lack of an oxidised hemipelagic sediment cover. An estimate of the age of eruptions can sometimes be made using the thickness of the overlying sediment and a good estimate of the rate of sedimentation, in this area about $2\text{--}5 \text{ cm/ka}$ [24]. The composition of the mud in all cores was mainly silty clays with a sand fraction between 5 to 7% and a mean grain size between 6.2 and 7.8 phi; it is consisted of terrigenous material with minor amounts of biogenic components, mainly planktonic foraminifera.

As noted previously, rock clasts that erupted through a mud volcano are comprised of a chaotic mixture of material from the overpressurized source formation and the rock units through which the eruption occurred. This material can provide significant geological information about the deeper geological units underlying the mud volcano, as well as the stratigraphy. A litho-micropalaeontological study of 39 samples of mud breccia clasts from Thessaloniki MV was undertaken.

These rock clasts of various size (2–5 cm in length) and supported in a homogeneous mud breccia matrix were sampled from the gravity cores collected during the second cruise of the ANAXIMANDER project. They were subsequently washed and classified by their general characteristics (composition, color, grain size, reaction with HCl, and roundness). Several clasts were selected then for further thin section analysis using a NIKON polarizing petrographic microscope. The most informative samples were also washed and sieved through a $150 \mu\text{m}$ sieve. This fraction is also used for analyzing the planktonic foraminifera assemblages. Typical examples of thin sections are shown in Figure 6.

TABLE 2: (a) Trace element analysis of the mud flow in cores AX48GC1 and AX49GC1. (b) Main element analysis (%) of the rock clasts from core AX48-GC1.

(a)										
Core	Sample depth (cm)	C _{tot} * %	C _{org} * %	S %	Na ₂ O %	Mg %	Sr %	Rb %	Zn ppm	Cu ppm
AX48GC1	9 cm	2,57	0,37	0,27	1,48	0,142	0,022	0,08	87	56
"	30 cm	2,05	0,35	0,44	1,75	0,146	0,019	0,10	94	78
"	65 cm	2,20	0,32	0,48	1,62	0,134	0,027	0,08	100	74
"	110 cm	1,70	0,32	0,40	1,75	0,137	0,023	0,08	104	78
AX49GC1	12 cm	2,85	0,44	0,58	1,75	0,151	0,024	0,09	89	73
"	50 cm	2,25	0,48	0,62	1,75	0,150	0,023	0,09	102	72
"	70 cm	1,45	0,39	0,48	1,75	0,158	0,016	0,08	86	69
"	105 cm	1,75	0,43	0,58	1,62	0,146	0,023	0,08	94	76

(b)	
Mineral	%
Calcite	57
Quartz	12
Montmorillonite	5
Kaolinite	8
Glaucophane	4
Albite	6
SiO ₂	5
Dolomite	3

* C_{tot} is total carbon, C_{org} is organic carbon.

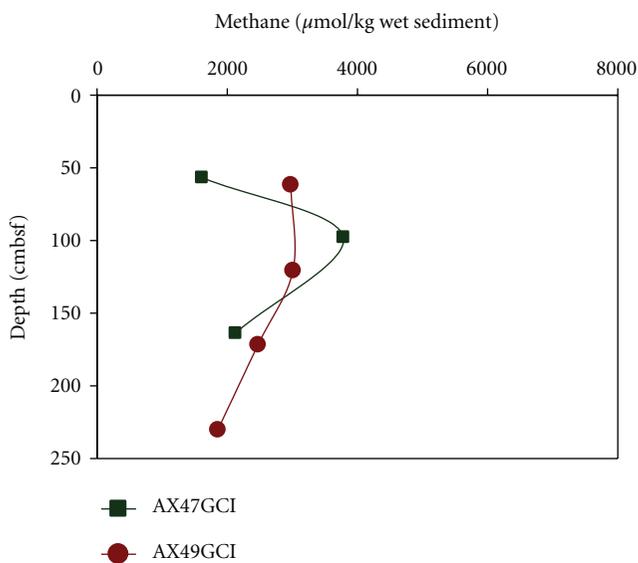


FIGURE 5: Methane concentrations of one of the southern (AX47-GG1) and northern (AX49-GG1) gravity core stations at Thessaloniki MV.

Rock clasts from the Thessaloniki MV cores (AX46GC1, AX47GC1, AX48GC1, AX49GC1, and AX49AP1) belong to two rock groups: fossiliferous micrites and detrital biomicrites. Both these two groups were recognized also in the other ANAXIMANDER mud volcanoes during this project [24, 25]. The fossiliferous micrites exhibit mainly

an angular-subangular form, are small in size, have light-gray colour, are consolidated, and contain (10–60%) well-preserved pelagic foraminifera in a micritic calcite matrix. The foram chambers are usually filled by sparitic calcite or pyrite. The planktonic species present are *Orbulina suturalis*, *Globigerinoides trilobus*, *Globigerinoides sp.*, and *Globoquadrina dehiscens*, which indicate a Lower to Middle Miocene age and an open marine environment [17, 24, 31]. The detrital biomicrites are angular-subangular in form, gray-brown in colour, contain tests and fragments of planktonic foraminifera, with fine grained aggregates of calcite and silty sized angular quartz grains in a micritic arenite matrix. Among the main fossils recognized are the species *Orbulina universa*, *Orbulina suturalis*, *Globigerinoides trilobus*, *Globoquadrina nepethens*, and *Globigerinoides obliquus*. which indicate an Upper Miocene age [31], and an open marine depositional environment.

Comparable microfaunal associations of Miocene deposits were also identified in the clasts sampled by gravity coring in the upper parts of mud flows in Amsterdam, Athina, Kazan, and Kula MVs. These data support the conclusion that part of the basement of the Anaximander Mountains in this area contains Miocene deposits that are comparable in age and facies with the geological units of the neighbouring land area of SW Turkey. Considering that these units are probably *in situ*, it can be concluded that the onshore Miocene flysch deposits of the Antalya Complex [24, 31] extend southward into the Anaximenes and Anaximander Mountains, thus supporting similar conclusions by Woodside et al. and other authors [6, 7, 12, 32, 33].

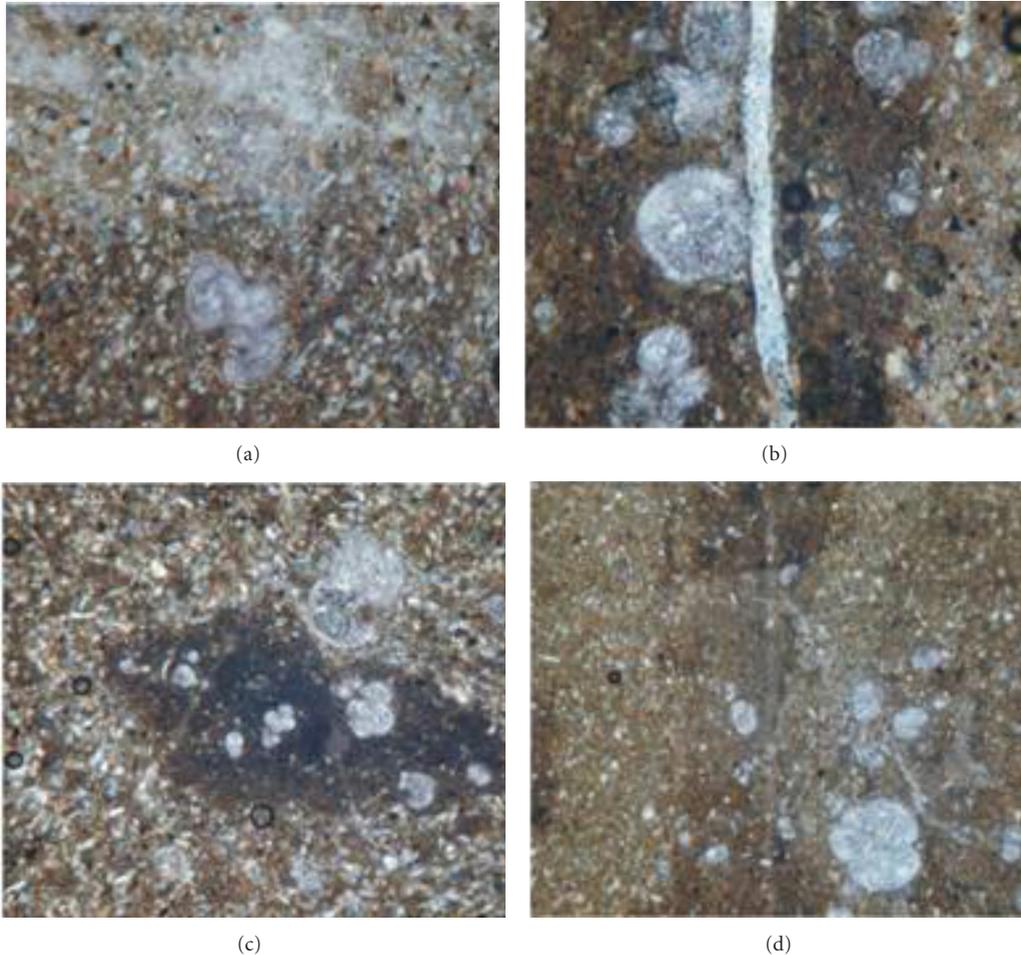


FIGURE 6: (a–d) Polarized microscope pictures of thin sections of mud breccia rock clasts; bioclastic carbonate pack/wackestones (grading into mudstones/claystones) with Globigerinidae planktonic foraminifera.

4. Gas Hydrate Stability Field

As noted above, the sediment cores with gas hydrates were all from relatively recently erupted mud breccia, as indicated by the lack of hemipelagic cover or surface oxidation of the mud flow. Thessaloniki MV is the shallowest mud volcano bearing gas hydrates in the Mediterranean (1265 m). At this depth the gas hydrates are just within, and near the edge of the gas hydrate stability zone (Figures 7(a) and 7(b)) as determined by the pressure (12.9 Mpa at 1265 m depth) and seafloor temperature ($\sim 14^{\circ}\text{C}$). The field data collected at Thessaloniki MV indicated that the GH occur at 1265 m sea floor depth and in subbottom sedimentary layers at least to 220 cm below seafloor. The sea bottom water temperature is 13.75°C and the geothermal gradient is expected to be $30\text{--}35^{\circ}\text{C}/\text{Km}$ or more, based on heat flow measurements made in the Olimpi mud diapir field [34]. During the MIMES cruise in 2004, one heat flow measurement made by Feseker and Foucher on Amsterdam Mud Volcano showed a significant warming of the sediments by over 3°C in the upper 10 m of mud [35, 36]. In other mud volcano areas the heat flow implies much higher geothermal gradients which,

for example, were as high as $2.78^{\circ}\text{C}/\text{m}$ in the active centre of Isis mud volcano [35].

A gas hydrate stability diagram, based on the parameters just described, indicates (Figures 7(a) and 7(b), [27, 36]) that the gas hydrates at Thessaloniki MV are just at the limit for the occurrence of stable methane hydrate, and do not extend more than a few meters above the known Thessaloniki MV depth. This means that with only small changes in the environmental parameters the gas hydrates could disassociate releasing water and methane. Such changes could result from a decrease in seafloor pressure (e.g., by tectonic uplift or sea level decrease) or by slight increase in the bottom water temperature (e.g., from an event like the recent increase in bottom water temperature in the Ionian Sea [37]). These small changes in temperature and sea level are both possible and sufficient to destabilize the gas hydrates at Thessaloniki MV.

Although the amount of methane produced from the autoclave core from Thessaloniki MV is minor in quantity, and the volume of gas hydrates is unlikely to be large at this site (based on the maximum depth at which gas hydrates in this area can be stable, as indicated in Figures 7(a) and 7(b)), we do not know the potential areal extent of the GH

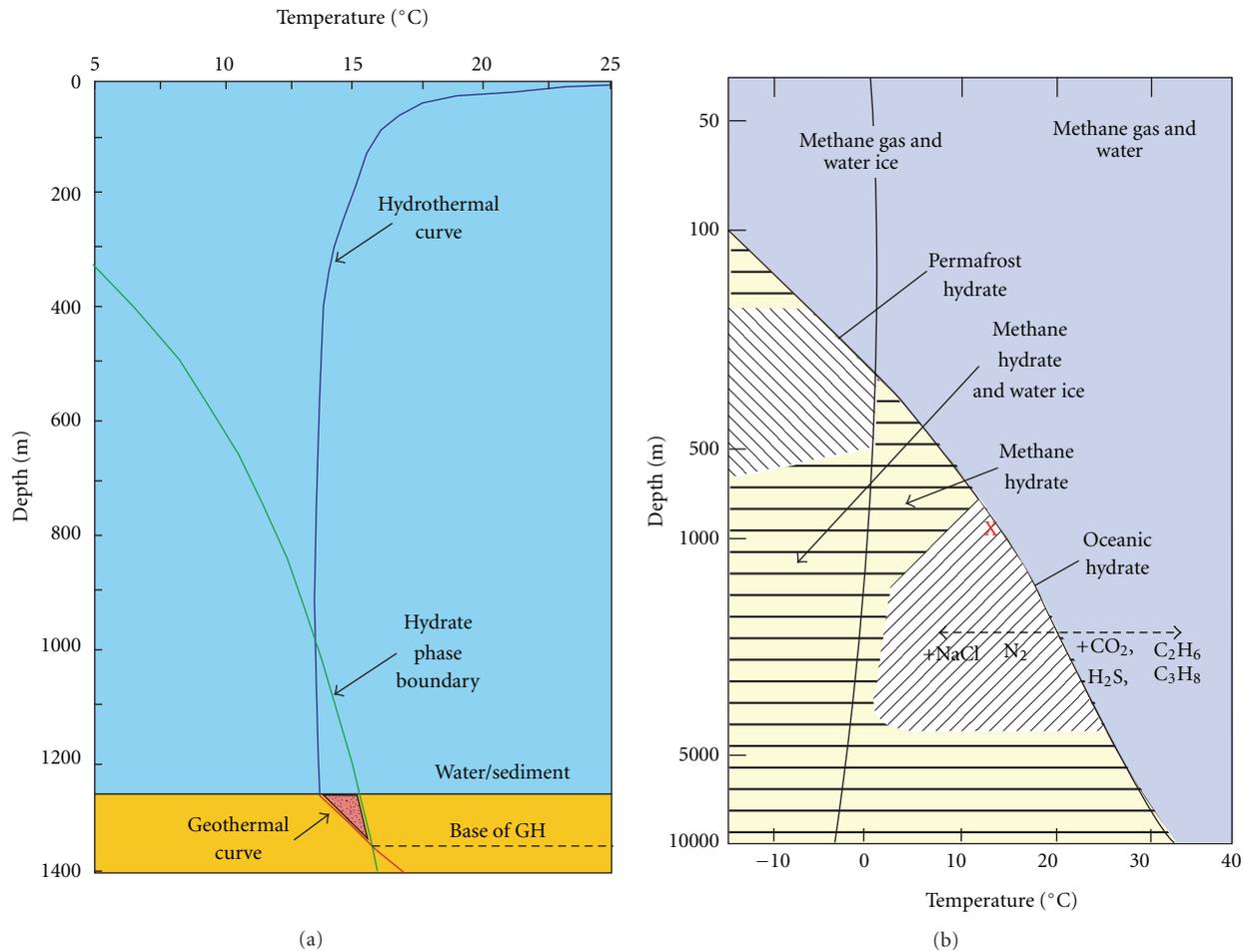


FIGURE 7: (a) Gas hydrate stability diagram for the Thessaloniki MV greater area (based on [36]), (b) gas hydrate stability diagram [27] depicting with an X the location of Thessaloniki gas hydrate field.

at these water depths in the Eastern Mediterranean. Since these GH are at the upper boundary of the GH stability diagram their distribution and presence should be studied more thoroughly.

5. Conclusion

A new gas hydrate bearing mud volcano named Thessaloniki was discovered in the Anaximander Mountains on the basis of its seafloor expression and an analysis of cores containing gas hydrates in a matrix of mud breccia typical of mud volcanoes. It is the shallowest mud volcano there, lying at depths between 1315 and 1260 m, with an areal extend of about 1.67 km² and comprising three peaks on its summit. GH were collected from three cores (two conventional gravity cores and one autoclave core). The GH crystals have the form of flakes or rice. The degassing of the 228 cm long autoclave core provided 3.1 liters of gas (mostly methane). Rock clasts from the mud breccias indicate a lower middle Miocene age for the source rock formation. The sea bottom temperature (13.7°C) and the pressure (12.9 MPa)

at Thessaloniki MV indicate that the GH there are at the upper limit of the stability zone, and prone to dissociation with the slightest temperature increase or pressure decrease. Therefore it could be a particularly suitable site for studying not only the mud volcano activity, but also the stability of natural gas hydrates and their potential environmental impact should they dissociate.

Acknowledgments

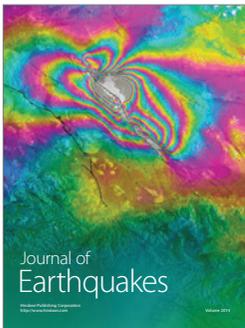
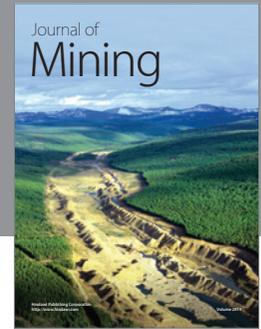
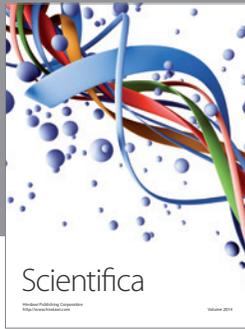
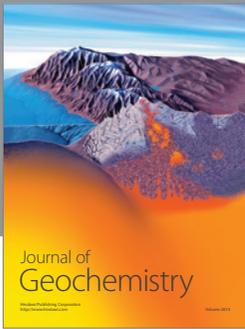
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