GEOLOGIC NOTE

Methane and hydrogen sulfide seepage in the northwest Peloponnesus petroliferous basin (Greece): Origin and geohazard

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ABSTRACT

Gas seepages along the Ionian coast of the northwestern Peloponnesus (Greece), at Killini, Katakolo, and Kaiafas reflect deep hydrocarbon-generation processes and represent a real hazard for humans and buildings. Methane microseepage, gas concentration in offshore and onshore vents, and gas dissolved in water springs, including the isotopic analysis of methane, have shown that the seeps are caused by thermogenic methane that had accumulated in Mesozoic limestone and had migrated upward through faults, or zones of weakness, induced by salt diapirism. A link between local seismicity and salt tectonics is suggested by the analyses of hypocenter distribution. Methane acts as a carrier gas for hydrogen sulfide produced by thermal sulfate reduction and/or thermal decomposition of sulfur compounds in kerogen or oil. Methane seeps in potentially explosive amounts, and hydrogen sulfide is over the levels necessary to induce toxicological diseases and lethal effects.

INTRODUCTION

The northwestern Peloponnesus (Greece) is one of the main hydrocarbon-prone areas of Greece. Petroleum fields occur in deep carbonates and clastic sequences from the Jurassic to the Eocene, belonging to the external Ionian tectonic unit of the Hellenides (Kamberis et al., 2000a). Deep faults act as preferential pathways

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for the upward migration of natural gas, producing gas seeps along the Ionian coast both offshore and onshore.

These seeps are of interest for three main reasons.

1. They reflect deep hydrocarbon-generation processes and high-temperature maturation, including gas-rock interactions in the reservoir; hence, they provide useful information on the nature of the exploitable natural gas.
2. They reflect the function of gas permeability of the rocks and faults; the Ionian zone faults are seismogenic, but nothing is known about the relationships between seismic activity, energy release, and gas discharge variations.
3. They represent hazards for humans and buildings because of the explosive and toxicological properties of methane and hydrogen sulfide, respectively.

This article tries to assess the gas origin, the factors leading to its surface seepage, and its environmental impact. Two gas surveys were performed in April and July 2004 at the three main seeping areas: Killini, Katakolo, and Kaiafas. The geochemical data have been compared with local brittle tectonics, stratigraphy, and seismic data. The study included methane microseepage measurements and analysis of the gas concentration in the atmospheric air above the soil in offshore and onshore vents and water springs, including isotopic analysis of methane.

GEOLOGICAL SETTING AND HYDROCARBON OCCURRENCE

The three study areas (Killini Peninsula, Katakolo Peninsula, and Kaiafas) are located in the northwest Peloponnesus, 50–60 km (31–37 mi) east of the northwestern end of the Hellenic subduction zone (Figure 1). Active subduction of the Ionian oceanic crust has been occurring beneath the outer Hellenic Arc since the late Neogene (Monopolis and Bruneton, 1982). Three northwest-southeast–trending tectonostratigraphic zones are defined in the External Hellenides, from west to east: the Preapulian, the Ionian, and the Gavrovo zones (Figure 1a, b). Sediments that accumulated in the basins formed in the tectonostratigraphic zones during the Neogene and the Quaternary (Zelilidis et al., 1998). Deep seismic data show that the development of Neogene basins was controlled by the westward-propagating Gavrovo thrust sheet (Kamberis et al., 2000a). As a result of this orogenic migration, an asymmetric basin (foredeep) in front of the thrust belts and piggyback basins on the propagated thrust sheets was developed.

Jurassic–Eocene carbonates and thick clastic sequences are separated by Triassic evaporites (mainly anhydrite), which penetrated the carbonate series through diapiric movements related to the thrusting of the Gavrovo nappes. This style of squeezed evaporites above the carbonate formations is common throughout the

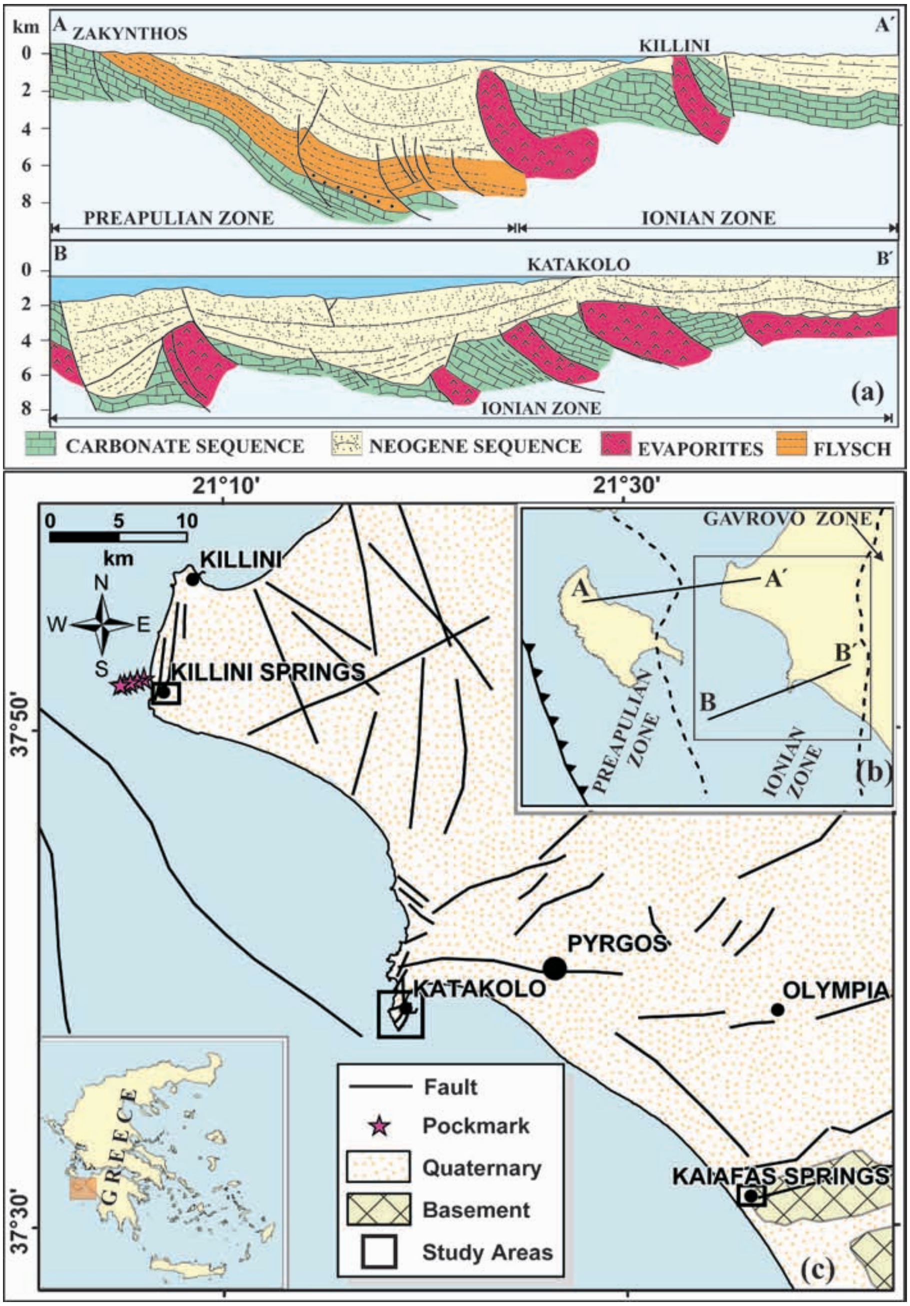

Figure 1. (a) Simplified cross sections showing the structural evolution of Neogene basins (modified from Kamberis et al., 2000a). (b) General map showing the position of the study area in relation to the Hellenic Trench and the three tectonostratigraphic zones. The two lines (AA′ and BB′) indicate the traces of the cross sections shown in (a). (c) General tectonic setting of northwest Peloponnesus (modified from Koukouvelas et al., 1996; Lekkas et al., 2000; Kamberis et al., 2000b; Hasiotis et al., 2002).

Ionian belt up to Albania (Velaj, 2001); here, even if they are older, the evaporites form the cap rock of the Mesozoic reservoirs. The diapirs, however, are also associated with thrust faults, which can potentially act as preferential pathways for upward fluid migration. Offshore diapirism also occurs between the Kefallinia–Zakynthos islands and west Peloponnesus (Brooks and Ferentinos, 1984). Moreover, offshore from the Killini Peninsula, a string of five large gas-induced pockmarks, whose formation is related to salt tectonics, has been discovered (Hasiotis et al., 2002).

Hydrocarbon production in the Ionian zone is caused by sapropelic and humic kerogen maturation and consequent oil and gas accumulation in the deep Jurassic carbonates (oil and thermogenic gas) and shallower Neogene sediments (biogenic gas), respectively (Kamberis et al., 2000b). An estimate of the oil contained in the Katakolo limestones is 40 million bbl, of which the maximum recoverable quantity is between 10 and 12 million bbl (ICAP, 2001).

Offshore from the Katakolo Peninsula, an oil and gas field has been discovered in Jurassic–Eocene carbonates underlying cap rocks made up of Pliocene clastic sequence and Triassic evaporites (Figure 1a). The north-northeast–south-southwest–trending Katakolo diapiric structure was formed at the base of the clastic sequence (Kamberis et al., 2000b). Normal faults associated with the Katakolo diapiric structure formed two grabens: the Katakolo graben, which is associated with north-south–trending normal faults and the Vounargon graben, which is controlled by northeast-southwest to east-northeast–west-southwest normal faults. Kamberis et al. (2000b) suggested that the main trends of the faults at the base of Neogene are quite similar to those of the Pliocene–Pleistocene synsedimentary faults. The latter created northwest- to northeast-trending extensional structures, which transect the older normal faults forming a structurally complex area.

The Zakynthos strait and northwest Peloponnesus are considered a very seismically active zone, the epicenters of many earthquakes being located along the three study areas (Papazachos and Papazachou, 1989). In 1993, a M_s 5.5 earthquake was preceded by three foreshocks of comparable size (33 min before, M_s 4.9; 5 min before, M_s 5.0; and 2 min before, M_s 5.1) and reactivated the structurally complex Katakolo–Pyrgos area, causing significant damage to the town of Pyrgos (Koukouvelas et al., 1996; Lekkas et al., 2000). The main event was followed by many aftershocks with $M_s > 2.8$ recorded by seismic networks. The focal depths for all the shocks were estimated within 20 km (12 mi). The focal mechanism solution had a slight dextral horizontal component associated with a northwest-southeast–striking fault (Lekkas et al., 2000).

GAS SEEPAGE

Anhydrite, as discussed below, is a fundamental factor in the composition of the gas seeps and presence of hydrogen sulfide. The Killini and Kaiafas seeps are, in fact, associated with sulfur water springs, which are local tourist attractions as spas called thermal baths. The term ''thermal,'' however, represents a misnomer because the water is not warm (22–23°C) and has no relationship with any geothermal environment (the Ionian zone is a cold sedimentary basin). In this respect, Killini and Kaiafas are an uncommon type of sulfur springs, where the carrier gas is methane (and not carbon dioxide), and the sulfur compounds are not produced by geothermal processes but by petroleum-generation processes.

Katakolo seeps occur both offshore and onshore at the local tourist harbor (Figure 2). Offshore bubbling plumes are widespread throughout the harbor docks. Bubbles are visible from the wharf over a wide area (order of 10^3 m^2 [10^4 ft^2]); divers have found bubbles of the order of 20–30 cm (8–12 in.) diameter issuing from cracks in the seabed, which is covered by a white bacterial mat (Figure 3a, b). Onshore seeps have penetrated and damaged the asphalt pavement of the harbor area at two main points: the entrance of the customs building and the duty-free shop (Katakolo is a port of call for tourist cruise ships), where, in 1972, a flame blew out from the pavement of the main wharf destroying a pole.

Other impressive onshore Katakolo seeps are located at the base of a hill, about 0.5 km (0.3 mi) north of the harbor. In this site, named ''Faros'' (Figure 3c), several bubbling pools, highly degassing soil, and oil seeps occupy a linear morphological depression, about 100 m (330 ft) long. Some vents can be easily ignited with a lighter, producing flames about 20 cm (8 in.) in height. The seep cannot be considered a mud volcano, as local people call it, because no actual mud emission and no conical morphology exist. However, it seems to be the largest onshore methane seep ever reported in Greece.

Beyond the localized seeps (vents, bubbling pools), gas is also released diffusely from the soil, without any visible manifestation. This microseepage is common and pervasive in many sedimentary hydrocarbon-prone basins of the world (Klusman et al., 1998; Etiope and Klusman, 2002; Etiope, 2004). In normal, dry-soil conditions, methane flux from the soil is generally nil or negative (0 down to -5 mg m^{-2} day^{-1}), with gas moving from the atmosphere to the soil because of methanotrophic consumption. In areas with microseepage from natural-gas reservoirs, the flux is positive, reaching values of tens to hundreds of milligrams per square meter per day (up to thousands of milligrams per square meter per day in exceptional cases, such as in mud volcanoes and macroseepage zones; Etiope et al., 2004).

METHODOLOGY

Microseepage

Microseepage flux was measured by the closed chamber method (Klusman et al., 2000; Etiope et al., 2004) at Killini (19 points), Katakolo harbor (9 points), and Faros macroseep (9 points). Gas that accumulated

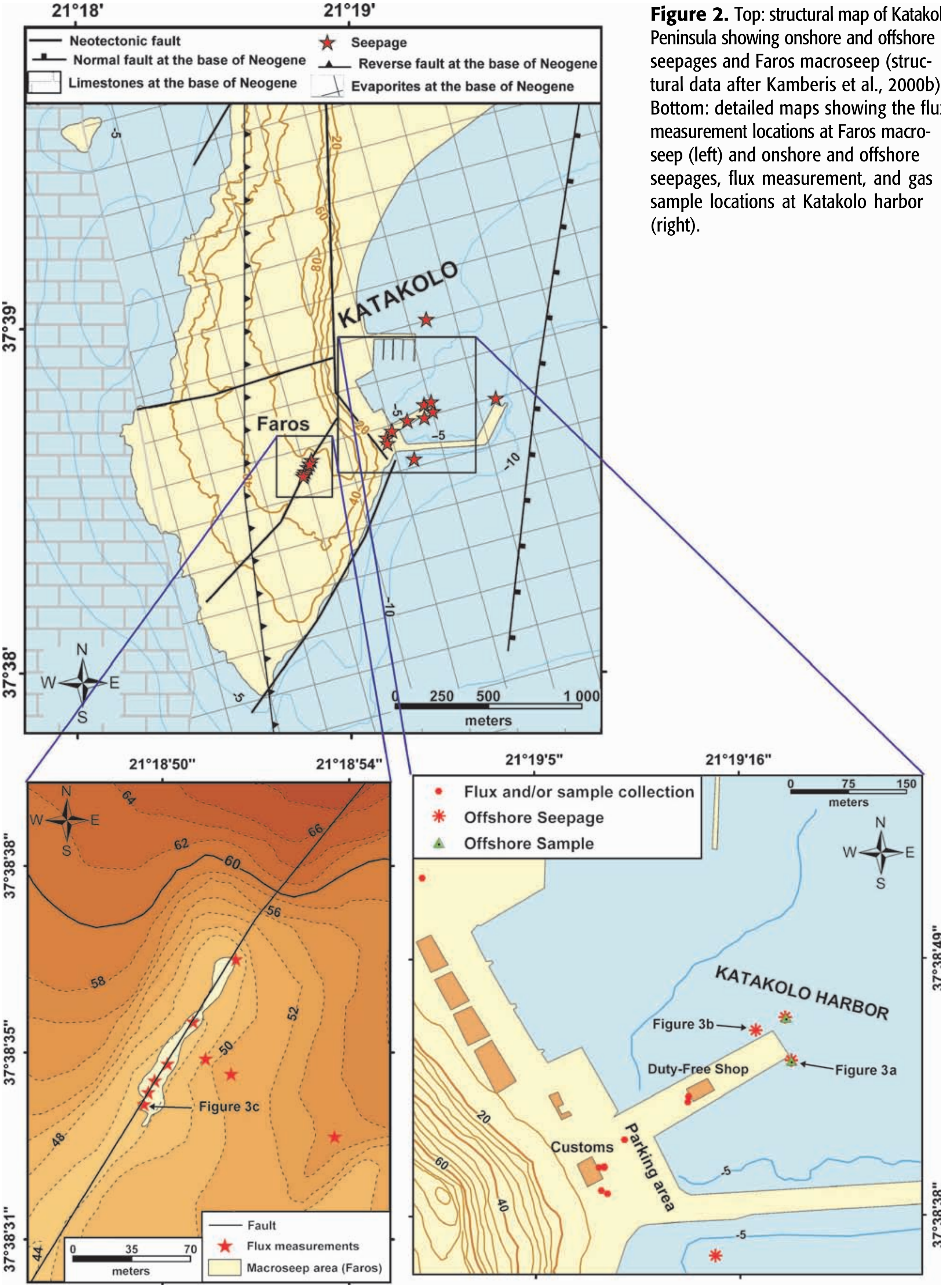

Figure 2. Top: structural map of Katakolo Peninsula showing onshore and offshore seepages and Faros macroseep (structural data after Kamberis et al., 2000b). Bottom: detailed maps showing the flux measurement locations at Faros macroseep (left) and onshore and offshore seepages, flux measurement, and gas sample locations at Katakolo harbor (right).

in a 10-L chamber was collected twice into syringes at time intervals ranging from 5 to 20 min after the deployment of the chamber. Methane was analyzed in

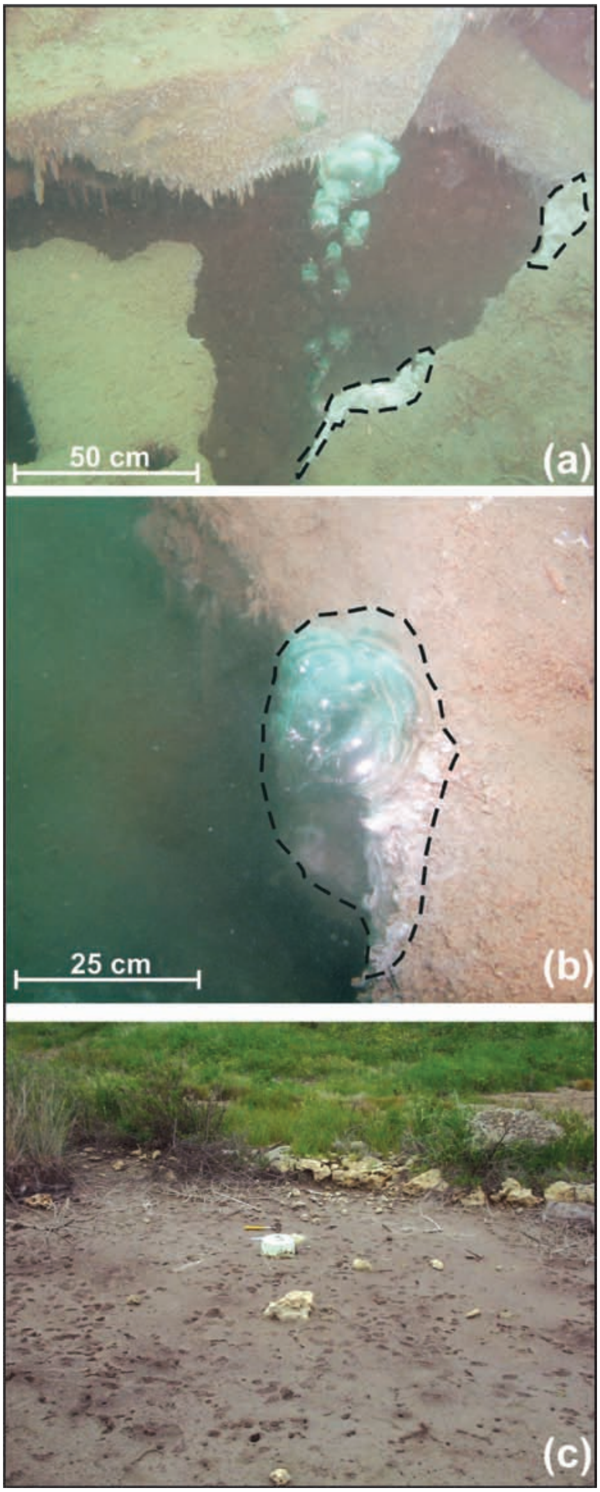

Figure 3. Bubbles and bacterial mat at the offshore Katakolo seeps (a, b); closed chamber (30 cm [12 in.] in diameter) for flux measurement at the Faros macroseep (c).

duplicate by a gas chromatograph with a flame ionization detector (FID) (Autofim II, Telegan; detection limit 0.1 ppm, accuracy 4–5%). The flux measurement reproducibility is within 13 and 20% for fluxes below and above 5000 mg m^{-2} day^{-1}, respectively.

A portable FID was also used as a sniffer to record the methane concentration in the atmospheric air within 20 cm (8 in.) above the soil surface. All the sites were monitored throughout tens of square meters with 75 recordings in total.

Gas Vents

Two offshore gas vents (bubble plumes 10 m [33 ft] deep) were sampled by divers at the Katakolo harbor. Gas bubbles were easily collected in a 200-cm^3 (12-$in.^3$) glass bottle sealed at seabed with silicone septa and aluminum caps.

Onshore gas vents were collected at the Katakolo harbor, Faros macroseep, and Killini bubbling pools using inverted funnels or chambers, and the gas was stored in the 200-cm^3 (12-$in.^3$) glass bottles.

All the samples were analyzed for C_1, C_2, C_2H_4, C_3, iC_4, nC_4, iC_5, nC_5, C_6+, $\delta^{13}C_1$, δDC_1 (deuterium isotope of methane), He, H_2, Ar, O_2, CO_2, N_2, CO, and H_2S by gas chromatography (Carle AGC 100–400 thermal conductivity and FID; detection limit: CO_2, N_2, Ar, and O_2, 40 ppmv; H_2S: 150 ppmv; He and hydrocarbons: 10 ppmv; accuracy 2%; 10% at the detection limit) and mass spectrometry (Finnigan Delta Plus XL; accuracy ± 0.1‰ on ^{13}C and ± 2‰ on ^2H) at Isotech Labs Inc. (Illinois, United States). Rapid onsite analyses were also made for CH_4 by the same portable FID used for microseepage and for H_2S and CO_2 by RAE Systems colorimetric tubes and sampling pump (accuracy < 10%).

Gas Dissolved in Spring Waters

Ground water was collected from Killini and Kaiafas springs at the main discharge points. Kaiafas spring is a pool inside a cave, instead of at the spring discharge, and some degassing can be expected into the cave air. Water was stored in 200-cm^3 (12-$in.^3$) glass bottles with silicone septa and aluminum caps. Gas was extracted by the head-space method and analyzed for C_1, C_2, C_2H_4, C_3, iC_4, nC_4, iC_5, nC_5, C_6+, $\delta^{13}C_1$, δDC_1, δDC_1, He, H_2, Ar, O_2, CO_2, N_2, CO, and H_2S as for the gas vent samples at the Isotech Labs. Rapid onsite

Table 1. Methane Microseepage

Location	Position	Number of Measurements	Flux* (mg m^{-2} day^{-1})
Killini	On the border of bubbling pools	5	from 40 to 185
	Close to the main spring	3	700–2200–2520
	>20 m (>66 ft) from the spring	5	from 60 to 320
	Road (>100 m [>330 ft] from the spring)	6	from −5 to 50
Katakolo harbor	Wharf (duty-free shop)	1	165,000
	Customs building	3	5600–4800–6900
	Parking (holes in the pavement)	2	57,000–80,000
	>30 m (>98 ft) far from the seeps	3	44–365–450
Katakolo Faros	Macroseep area	6	from 6800 to 285,000
	Hill slope (90, 30, and 10 m [295, 98, and 33 ft] from the seep)	3	260–650–7100

*The range is given for the sites in which more than three measurements were performed.

analyses were made on head-space gas for CH_4 by portable GC-FID and for H_2S and CO_2 by RAE colorimetric tubes.

RESULTS

Table 1 shows the microseepage flux measured at Killini and Katakolo. At Killini, the highest flux, on the order of 10^2–10^3 mg m^{-2} day^{-1}, occurs close to the main spring, picked up by a borehole. Tens to hundreds of milligrams per square meter per day are emitted around the bubbling pools. More than 100 m (330 ft) from the spring and pools, the microseepage drops to a few tens or single digits of milligrams per square meter per day down to negative values.

Katakolo seepage is up to two orders of magnitude higher than that in Killini. The values reach 285,000 and 165,000 mg m^{-2} day^{-1} at Faros and at the harbor, respectively. Throughout the Faros macroseep area (about 800 m^2 [8611 ft^2]), fluxes are on the order of 10^3–10^5 mg m^{-2} day^{-1}. The highest values are closer to the vents that sometimes form small fires. The flux decreases down to tens of milligrams per square meter per day at 90-m (295-ft) distance along the hill flank (Figure 2). In the harbor, where the asphalt pavement has been shattered by the gas leakage, the fluxes are at the 10^3–10^4-mg m^{-2} day^{-1} level.

Above the soil surface, up to 50 cm (19 in.), the air is generally enriched in CH_4, with concentrations rising from 2 ppmv (background) to tens of parts per million by volume across wide areas and up to hundreds of parts per million by volume at the Katakolo harbor (duty-free shop and customs buildings) and the Faros macroseep (Figure 2).

Table 2 shows the gas concentration in the vents. The Killini gas in the bubbling pools has about 80%

Table 2. Gas Concentration in Gas Vents and Soil Gas*

Location	Sample Type	CH_4	H_2S	C_2	C_3	iC_4	nC_4	C_5	C_6+	He	Ar	O_2	CO_2	N_2
Killini	Bubbles**	80	0.01	–	–	–	–	–	–	–	–	–	–	–
Katakolo offshore	Bubbles	40	0.23	0.722	0.154	0.045	nd†	nd	0.0214	0.011	0.52	10.94	2.42	45.10
Katakolo harbor	Soil gas (10 cm [4 in.] deep)	9.3	0.005	0.135	0.006	0.002	nd	nd	0.0105	0.003	0.84	18.97	0.86	69.88
	Dry vent**	85	0.02	–	–	–	–	–	–	–	–	–	0.12	–
Katakolo Faros	Dry vent**	94	–	–	–	–	–	–	–	–	–	–	–	–

*In % volume per unit volume.
**Onsite analyses by portable GC-FID (CH_4) and colorimetric tubes (H_2S and CO_2).
†nd = not detected.

CH_4, whereas Katakolo gas vents are greater than 85% CH_4. About 9% CH_4 occurs in the Katakolo harbor soil at one point where the asphalt was drilled to 10-cm (4-in.) depth. Offshore vents have 40% CH_4. The Katakolo gas has H_2S levels of 0.01–0.2% (hundreds to thousands parts per million by volume), and significant amounts of other light hydrocarbons such as ethane (C_2), propane (C_3), isobutane (iC_4), and C_6 alkanes.

Table 3 shows the composition of the gas dissolved in the springs of Killini and Kaiafas. These waters are also enriched in CH_4 with significant amounts of H_2S and ethane. From all the sites investigated, methane is clearly thermogenic as evidenced by $\delta^{13}C$, δD isotopes, and the $C_1/(C_2 + C_3)$ ratio (Table 4; Figure 4) in the Schoell and Bernard plots (Schoell, 1980; Whiticar, 1999). The Katakolo data are coherent with one analysis previously reported by Kamberis et al. (2000b) for gas collected from a well at 2376 m (7795 ft) in depth. The seeps have a higher $C_1/(C_2 + C_3)$ ratio as a result of migration. Soil gas CH_4 has $\delta^{13}C$ slightly higher than the other samples probably because of a fractionation by methane-oxidizing bacteria occurring in the soil, which tend to consume more $^{12}CH_4$ than $^{13}CH_4$.

DISCUSSION

CH_4 Origin

The gas seeping onshore and offshore from the northwest Peloponnesus is thermogenic methane coming from the deep Mesozoic limestone reservoirs. The isotopic data suggest catagenetic maturation from sapropelic kerogen (type II), in agreement with previous partial analyses by Kamberis et al. (2000b) and the organic matter analysis of limestones by Rigakis and Karakitsios (1998).

Biogenic methane, occurring in the Neogene clastic sequences, does not lead to surface seeps.

H_2S Origin

Methane acts as a carrier gas for hydrogen sulfide, whose generation must be related to the kerogen, oil, and/or the anhydritic formations. In general, H_2S in petroleum reservoirs can originate from three processes: bacterial sulfate reduction, thermal decomposition of sulfur compounds in kerogen or oil, and thermochemical sulfate reduction (TSR). Bacterial sulfate reduction and thermal decomposition of sulfur compounds generally lead to low levels of H_2S in gas (<3–5%). Thermochemical sulfate reduction is the only process able to produce larger amounts of H_2S and is dominant in the presence of evaporites (mainly anhydrite) in contact with limestone at temperatures generally above 120°C (Worden et al., 1995). Temperatures down to 80°C, however, have also been reported (Hunt 1996; Noth, 1997).

The basic TSR reaction is (Worden and Smalley, 1996)

$$\text{anhydrite} + \text{hydrocarbons} \rightarrow \text{calcite} + H_2S + H_2O \pm S \pm CO_2$$

The dominant reaction involves methane:

$$CaSO_4 + CH_4 \rightarrow CaCO_3 + H_2S + H_2O$$

The significant amounts of H_2S in the Jurassic limestones of northwest Peloponnesus (up to 10% at a depth of 2500 m [8202 ft]; Kamberis et al., 2000b) and the presence of anhydrite are consistent with a TSR origin. The geothermal gradient is quite low (around

Table 3. Composition of Head-Space Gas from Spring Waters*

Location	Sample Type	CH_4	H_2S	C_2	C_3–C_6	He	Ar	O_2	CO_2	N_2
Killini	Spring	10.01	3.50	–	–	–	–	–	–	–
	Spring**	8.1	1.9	0.0001	nd†	–	–	–	6.4	–
	Bubbling pool	17.21	2.08	0.093	nd	nd	1.18	1.19	10.85	67.40
	Bubbling pool**	10.2	1.3	0.002	nd	–	–	–	8.5	–
Kaiafas	Spring	8.54	1.40	0.04	nd	nd	1.16	1.56	6.99	80.31
	Spring**	6.8	0.7	–	nd	–	–	–	–	–

*In % volume per unit volume.

**Onsite analyses by portable GC-FID (CH_4) and colorimetric tubes (H_2S and CO_2).

†nd = not detected.

Table 4. Methane Isotopic Composition

Location	Sample Type	$\delta^{13}C_1$ ‰	δDC_1 ‰
Killini	Dissolved gas	−49.05	−174.0
Katakolo offshore	Bubbles	−36.11	−140.1
Katakolo onshore (harbor)	Soil gas (10 cm [4 in.] deep)	−31.25	−135.5
Kaiafas	Dissolved gas	−47.5	−166.5

2°C/100 m [2°C/330 ft]; N. Rigakis, 1990, personal communication), with temperatures of about 70°C at a depth of 2500 m (8202 ft), corresponding to the top of the main diapiric bodies. This means that the conditions for TSR are not fully met at that depth; it is possible that H_2S migrated from deeper and warmer (about 120°C) anhydrite-limestone contacts, such as those at 4000–5000 m (13,100–16,400 ft) (see Figures 1, 5). However, the TSR origin can only be demonstrated by verifying that $\delta^{34}S$ of H_2S and anhydrite are similar (Worden et al., 1995; Hunt, 1996). These isotopic analyses are therefore needed.

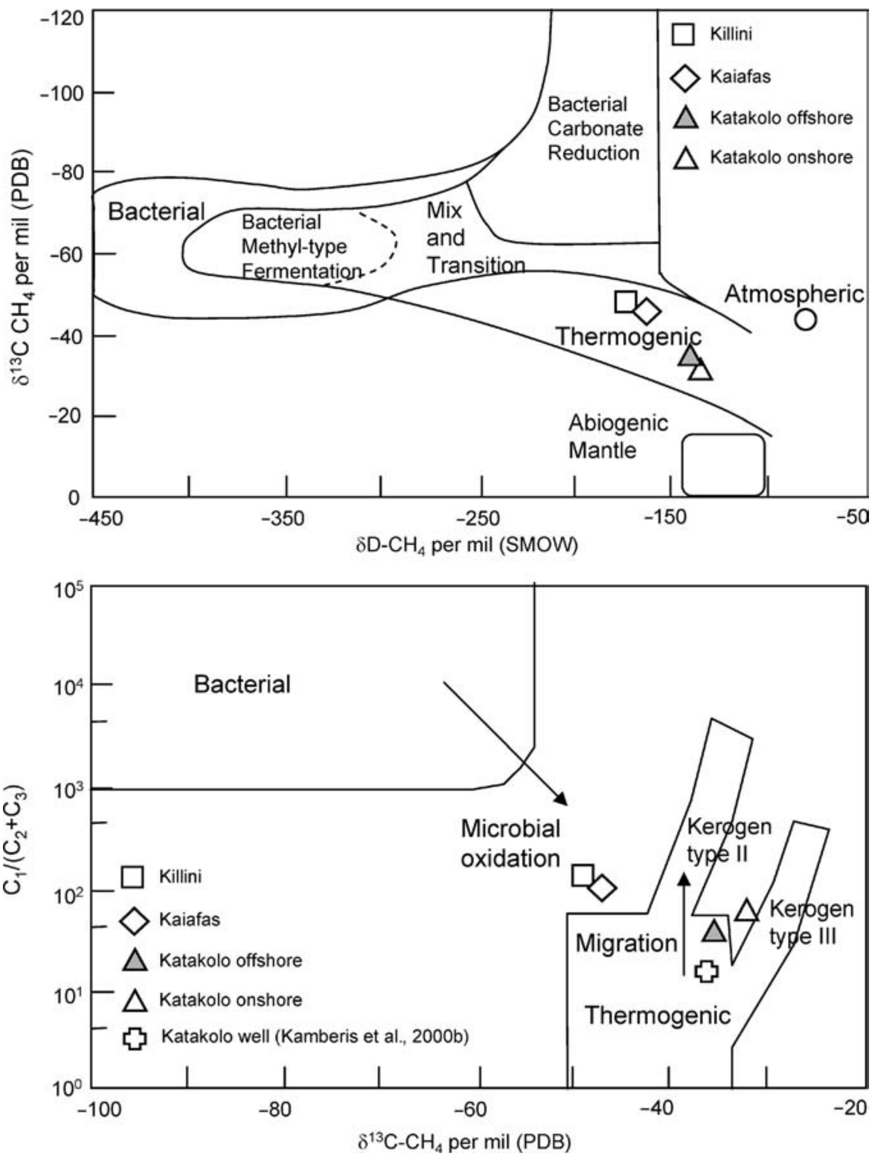

Figure 4. Methane classification diagrams by $\delta^{13}C_{CH_4}$ versus δD_{CH_4} (top, Schoell diagram; Schoell, 1980) and $\delta^{13}C_{CH_4}$ versus molecular composition of hydrocarbon gases (bottom, Bernard diagram; Whiticar, 1999). PDB = Peedee belemnite standard, SMOW = standard mean ocean water.

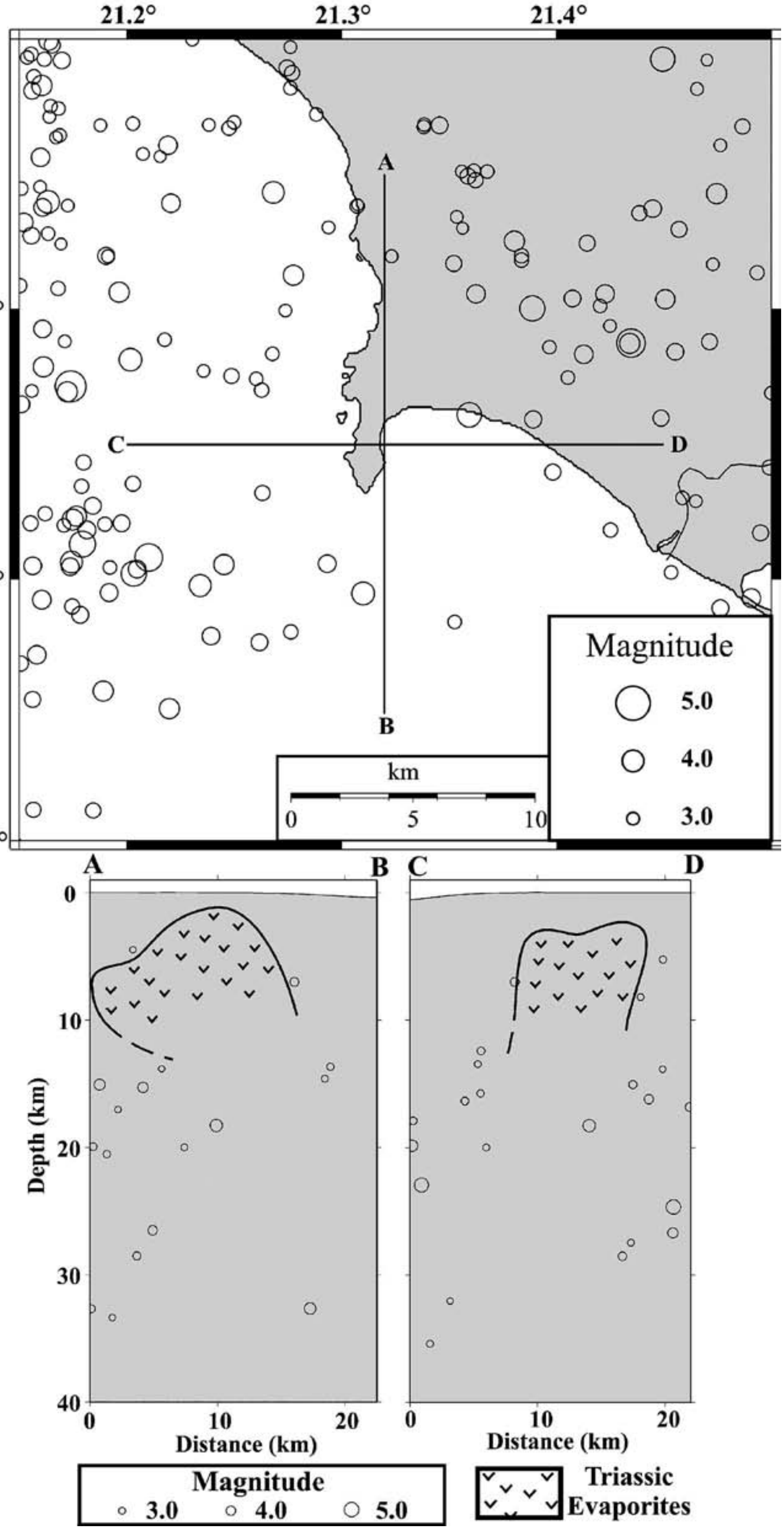

Figure 5. Map showing earthquakes (M_L > 3.0) located in the area of Katakolo Peninsula for the period 1991–2003 and cross sections showing the distribution of earthquake hypocenters in a 6-km (3.7-mi)-wide bound centered along AB and CD lines (data from Patras Seismic Network [PATNET]). Position and size of the diapiric body are drawn on the basis of data by Kamberis et al. (2000b).

A contribution from the thermal decomposition of sulfur compounds in kerogen or oil cannot be disregarded. The sapropelic (marine) kerogen, responsible for the origin of the Ionian thermogenic hydrocarbons, is enriched in sulfur with respect to the humic (terrestrial) kerogen of the Neogene clastics, and the carbonate rocks do not have enough iron to eliminate H_2S as pyrite (Worden and Smalley, 1996). Neogene sediments, where H_2S could be produced by a bacterial reduction, can instead have up to 12 times more iron, strongly reducing the H_2S level. This supports the fact that H_2S seeps, independently from the H_2S genesis, are associated only with thermogenic methane.

Salt Diapirism and Gas Migration

All the gas seeps investigated are associated with the salt diapirism, which induced sediment deformation and faulting. This link, initially suggested by the association of thermogenic CH_4 with high levels of H_2S, can easily be verified in the Katakolo peninsula, where exploratory wells and seismic and neotectonic data are available. Deep seismic profiles show that the diapiric structure developed at the Katakolo peninsula is bound to the west by an eastward-dipping reverse fault (Figure 1a) (Kamberis et al., 2000b). The diapiric movements are active, affecting the overlying detrital sequences and forming synsedimentary faults, as well as typical positive flower structures. As a result, a great number of east-west to west-northwest–east-southeast–trending extensional structures (Alfios graben, Pyrgos fault) were formed (Koukouvelas et al., 1996). At the Katakolo peninsula, the north-south–trending faults mapped at the base of Neogene and the associated west-northwest– and northwest-trending newly formed normal faults provided the preferential conduit for the gas migration, from the Jurassic carbonates and Triassic evaporites toward the surface. This hypothesis is further supported by (1) the position of the Faros macroseep located along a southwest-trending fault (Figure 2) and (2) the clustering of the onshore and offshore gas seeps at the intersection area of three west-southwest– to southwest-trending faults at the Katakolo harbor (Figure 2).

A first insight into possible links between salt tectonics and seismicity is suggested by Figure 5, which shows the seismicity (magnitude > 3.0) of the Katakolo area recorded by the Patras Seismic Network (PATNET) from 1991 to 2003. The PATNET consists of 19 stations (17 short period and 2 broad band), and the seismicity is located with a good degree of accuracy. The seismicity is predominantly concentrated to the west and northeast of Katakolo area, whereas it does not seem to affect the Katakolo area itself. This zone has to be considered a sort of aseismic area (at least with the chosen minimum threshold in magnitude, >3.0), corresponding to the presence of the Triassic diapiric body. The cross sections in Figure 5 show that some earthquake hypocenters located at depths ranging from 5 to 15 km (3.1–9.3 mi) occur at the periphery of the diapir; these events could be related to the activation of normal faults associated with the diapiric movement, the same faults as those inducing upward gas migration and seepage. A much deeper insight into the relationships between seismicity and salt tectonics could be achieved by adding a dense coverage of temporary seismic stations in the offshore and onshore Katakolo area.

Evidence of gas seepage related to salt tectonics is also provided by a string of five large gas-induced pockmarks discovered offshore from the Killini Peninsula, about 2 km (1.2 mi) east of the Killini springs (Hasiotis et al., 2002) (Figure 1c). Sparker seismic profiles adjacent to the pockmark string showed that the subbottom sediments were disturbed by diapirism. Fractures (small faults and joints) in the subbottom sediments develop radically around the diapir, providing the conduit for the gas migration and pockmark formation (Hasiotis et al., 2002). Thus, the five gas-induced pockmarks have been formed as a result of gas migration along the trace of a weakness zone because of salt tectonics. Similar scenarios have been reported in the Norwegian Trench (west of Bergen), where strings of pockmarks occur above faults and in a weakness zone in soft sediments (Hovland et al., 1996), and in the eastern Corfu shelf (Ionian Sea), where seismic data show gas seeps from around a Triassic salt diapir piercing the seabed (Papatheodorou et al., 1993). Gas migration toward the surface through a weakness zone related to salt tectonics can also explain the high percentage of methane and hydrogen sulfide in the Killini and Kaiafas springs.

Effects of Gas Seepage

The seeps investigated pose severe risks for people and buildings. The high methane content can produce explosions or flames at the surface, especially when conditions suitable to form explosive mixtures (5–10% CH_4) occur, like below the asphalt pavement in the Katakolo harbor. The risk is particularly worrying because the harbor is commonly used by tourists embarking or disembarking from cruise ships. The offshore methane emissions and shallow gas pockets can produce catastrophic blowouts during drilling operations or damage to offshore structures. It is well known that gas in marine sediments is a factor contributing to the initiation of sediment failures and enhances the liquefaction process (Hovland and Judd, 1988). Gas bubbles in the pore spaces of the seabed sediments exert an upward buoyancy force on the sediments, and if gas continues to migrate upward and accumulates, then pressure builds up, and the shear strength of the sediments decreases. Under normal circumstances, the increase of pore pressure will not result in a significant weakening of the bearing capacity of the sediments; but in the case of sudden cyclic forces (earthquake and waves), the pore pressure can equal the overburden pressure, and the sediments lose their bearing capacity. Thus, the gas-charged sediments, when subjected to cyclic loads, can collapse more easily than the gas-free sediments. In the Katakolo harbor, the area's high seismicity and high percentage of gas in the sediment pores, as indicated by the intensive seepages, are considered important factors in triggering sediment failures. However, earthquake activity is also a direct trigger for gas seepage (Field and Jennings, 1987; Papatheodorou et al., 1993; Hasiotis et al., 1996). A positive correlation between seismic activity and gas migration and seepages over time has been well documented in western Greece (Hasiotis et al., 1996).

Hydrogen sulfide is the most dangerous and toxic geological gas. It is classified as a chemical asphyxiant because it immediately chemically interacts with the blood hemoglobin to block oxygen being carried to the body's vital organs and tissues. Its characteristic rotten-egg smell is easy to detect at low concentrations, but at higher concentrations, it paralyzes the sense of smell. This can give one a false sense of security during exposure to hydrogen sulfide. Generally, 10 ppmv causes eye irritation; 200–300 ppmv causes eye inflammation and respiratory tract irritation after 1-h exposure; 500–700 ppmv may lead to the loss of consciousness and possible death in a span of 30–60 min; 1000 ppmv gives diaphragm paralysis on first breath and rapid asphyxiation. The H_2S levels of Katakolo seeps (hundreds to thousands of parts per million by volume) are impressive.

CONCLUSIONS

The resulting picture of the origin, tectonics, and geohazards of the northwest Peloponnesus gas seeps are summarized in the block diagram model of Figure 6.

Basically, the gas seeps consist of thermogenic methane coming from the carbonate reservoirs and carrying hydrogen sulfide probably originating from a thermochemical sulfate reduction, with a minor contribution from thermal decomposition of sulfur compounds in kerogen or oil; biogenic methane, existing in the Neogene sediments, does not seep to the surface.

The gas seeps are associated with intense microseepage in the surrounding areas (orders of 10^1–10^5 mg m^{-2} day^{-1} over 10^4-m^2 [1.07×10^5-ft^2] areas, at least) and produce significant CH_4–H_2S enrichments in the atmosphere up to 1 m (3.3 ft) above the soil.

The gas seeps are caused by salt tectonics producing zones of weakness and faults along which CH_4–H_2S migrate upward. The distribution and depth of the hypocenters in the Katakolo zone suggest that the thrusting faults in the pierced crust might be seismogenic. If so, the seismicity of western Greece could have two components: microseismicity by salt tectonics and macroseismicity by Ionian plate subduction. Accordingly,

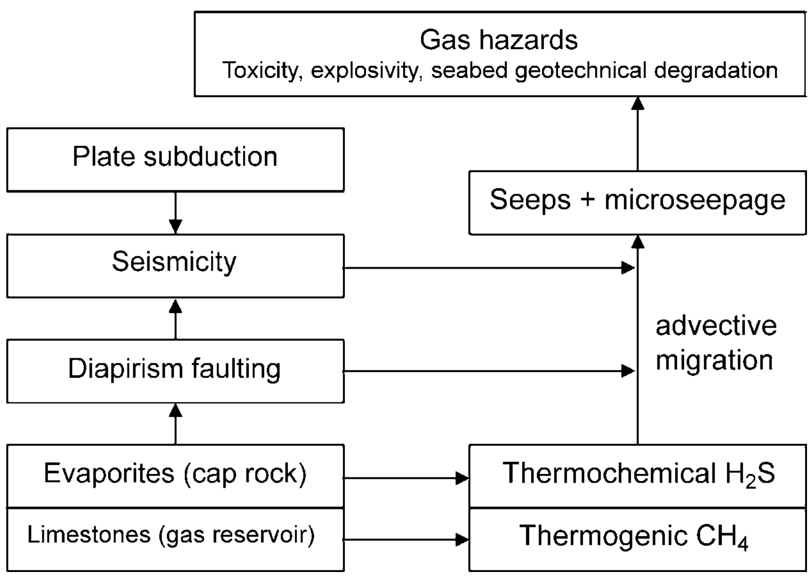

Figure 6. Model summarizing the origin, tectonics, and hazards of the gas seeps by linking geological factors (left column) and their related effects (right column).

gas migration and seepage might respond mainly to the diapirism-linked seismicity because the stress-strain field is closer to the gas accumulations and may easily perturb the fluid-pressure gradients and the gas-bearing property of the faults.

The gas seeps produce severe geohazards for people, buildings, and construction facilities because of the explosive and toxicological properties of methane and hydrogen sulfide, respectively. Gas-charged sediments are also hazardous for offshore structures.

Further studies should focus on the analysis of $\delta^{34}S$ of H_2S and anhydrite to confirm the TSR origin and on the links between salt tectonics and seismicity. Finally, a monitoring program will be necessary to follow the evolution of the seepage and to assess possible precursor signals of enhanced degassing, blowouts, or explosions related to seismicity and underground gas-pressure buildup.

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