The geological links of the ancient Delphic Oracle (Greece): A reappraisal of natural gas occurrence and origin

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ABSTRACT

Recent studies have speculated that the prophetic powers of Pythia, the woman of the Delphic Oracle, at the Temple of Apollo in Greece, were induced by hydrocarbon vapors, specifically ethylene, rising from bedrock fissures at the intersection of the E-W Delphi fault with the NNW-SSE Kerna fault, and producing neurotoxic effects, including trance and delirium. New surveys including gas flux from soil, gas in groundwater, and isotopic analyses of spring scales, provide the experimental confirmation of the gas release in the Delphi area. Presently, methane, ethane, and carbon dioxide are being released from a thermogenic (catagenetic) hydrocarbon-prone environment. This environment is not prone to biogenic production of ethylene in amounts inducing neurotoxic effects (hundreds or thousands of ppmv). A WNW-ESE–trending subsidiary fault within the Delphi fault zone, extending for ~2 km, passes under the Temple of Apollo and shrine of Athena. The Temple of Apollo, located above this fault, may have been the site of enhanced degassing in the past. If gas-linked neurotoxic effects upon Pythia need to be invoked, they should be sought in the possibility of oxygen depletion due to CO_2-CH_4 exhalation in the indoor temple. Alternatively, a plausible geological explanation behind the natural presence of sweet scents could be the occurrence of aromatic hydrocarbons, such as benzene, dissolved in the groundwater spring.

Keywords: Delphi, gas, seeps, fault, methane, ethylene.

INTRODUCTION

The Delphi Sanctuary, located in central Greece, is considered the most important religious location of the ancient Greek world. The sanctuary was the pole of attraction for pilgrims for ~11 centuries, between 700 B.C. and A.D. 400. Pythia, a Delphic woman, was seated upon a tripod placed over a chasm in the *Adyton* (an inaccessible place inside the temple). Plutarch, who served as a priest in the oracle for many years, wrote that intoxicating vapors were released from the chasm and induced in Pythia a mantic state that enabled her to be the intermediary of the prophet god (Holland, 1933).

Two articles published in *Geology* (Piccardi, 2000; De Boer et al., 2001) proposed a link between faults, gas occurrence, and the prophetic properties in the Temple of Apollo. Piccardi (2000) suggested that the vapor-bearing chasm was related to the Delphi fault, an E-W normal tectonic dislocation of regional importance in the Gulf of Corinth Rift crossing precisely the shrine of Athena located ~500 m east of the Temple of Apollo. De Boer et al. (2001) suggested that the Temple of Apollo is located exactly above the intersection of the Delphi fault with a NNW-SSE fault (Kerna fault), and upon analyzing the local Kerna spring water detected small amounts of ethylene. They concluded that ethylene was likely the gas inducing the neurotoxic effects, trance and delirium, in the woman sitting in the *Adyton*. Moreover, Piccardi (2000) mentioned that gas emissions and the local travertine deposits may indicate hydrothermal activity.

In order to better understand the gas-bearing properties of the Delphi rocks and faults, and the nature of the gas discharged, a more complete gas-geochemical study was performed in 2004 and 2005, including the search of gas seepage sites by investigating methane concentrations at the ground-air interface, by measuring the methane flux from soil, and by analyzing the local spring waters and scales. Location and orientation of the fault traces have been reviewed. The potential of hydrothermalism or hydrocarbon generation in the Delphi area has been reexamined.

TECTONICS

The Delphi Sanctuary is located above the E-W–trending normal Delphi fault zone, which dips to the south and is the most prominent of the active antithetic structures of the Gulf of Corinth Rift (Fig. 1) (Mariolakos et al., 1991). This rift is one of the most seismically active and rapidly extending areas of the world (Stefatos et al., 2002).

Piccardi (2000) showed that the shrine of Athena was built upon an active fault within a fault zone many meters wide consisting of the Delphi fault and a few parallel subsidiary faults. De Boer et al. (2001) suggest that the Temple of Apollo was built over the intersection of two faults: the E-W Delphi fault and the NNW-SSE Kerna fault. According to De Boer et al. (2001), the Kerna fault was observed at the mountainside above Delphi and continues southeastward below the Temple of Apollo, based on a more or less linear sequence of five springs.

We have reexamined the positions of the five springs. They constitute a NW-SE linear structure almost parallel to the faults, which have been considered as subsidiary of the main Delphi fault by Piccardi (2000) (Fig. 1). Although it is difficult to interpret a linear sequence of springs as a fault, the location of the sequence may suggest that this structure could be considered as the western end of the subsidiary fault that passes below the shrine of Athena (Fig. 1). In that case, a WNW-ESE–trending 2-km-long subsidiary fault within the Delphi fault zone, passing under the Temple of Apollo and shrine of Athena, could be associated with the mythological oracular chasm of the Temple of Apollo. The existence of subsidiary faults within the Delphi fault zone has been also documented by Mariolakos et al. (1991) and Piccardi (2000). The Kerna fault was detected at the mountainside above Delphi, but the southeastward continuation under the Temple of Apollo as proposed by De Boer et al. (2001) is not proved in this survey. However, the Delphic Oracle is located in an area that is characterized by a dynamic geological regime due to the E-W–trending extensional structures and the pre-existing constructional NNW-SSE structures (Kokkalas et al., 2005). As a result, the Mesozoic limestone beneath the ancient oracular site is expected to be heavily fractured and highly permeable to groundwater and gas.

POTENTIAL OF GAS OCCURRENCE

Piccardi (2000) reported that gas emissions described by Fontenrose (1981) and travertine deposits are an indication of hydrothermal activity. De Boer et al. (2001) suggested hydrocarbon generation from bituminous rocks. Both conditions are, however, incompatible with ethylene generation.

Ethylene (C_2H_4) is an olefin hydrocarbon, produced by bacterial fermentation in the diagenic phase (low temperature and pressure) of kerogen-to-hydrocarbon maturation (Hunt, 1996). It is only present in

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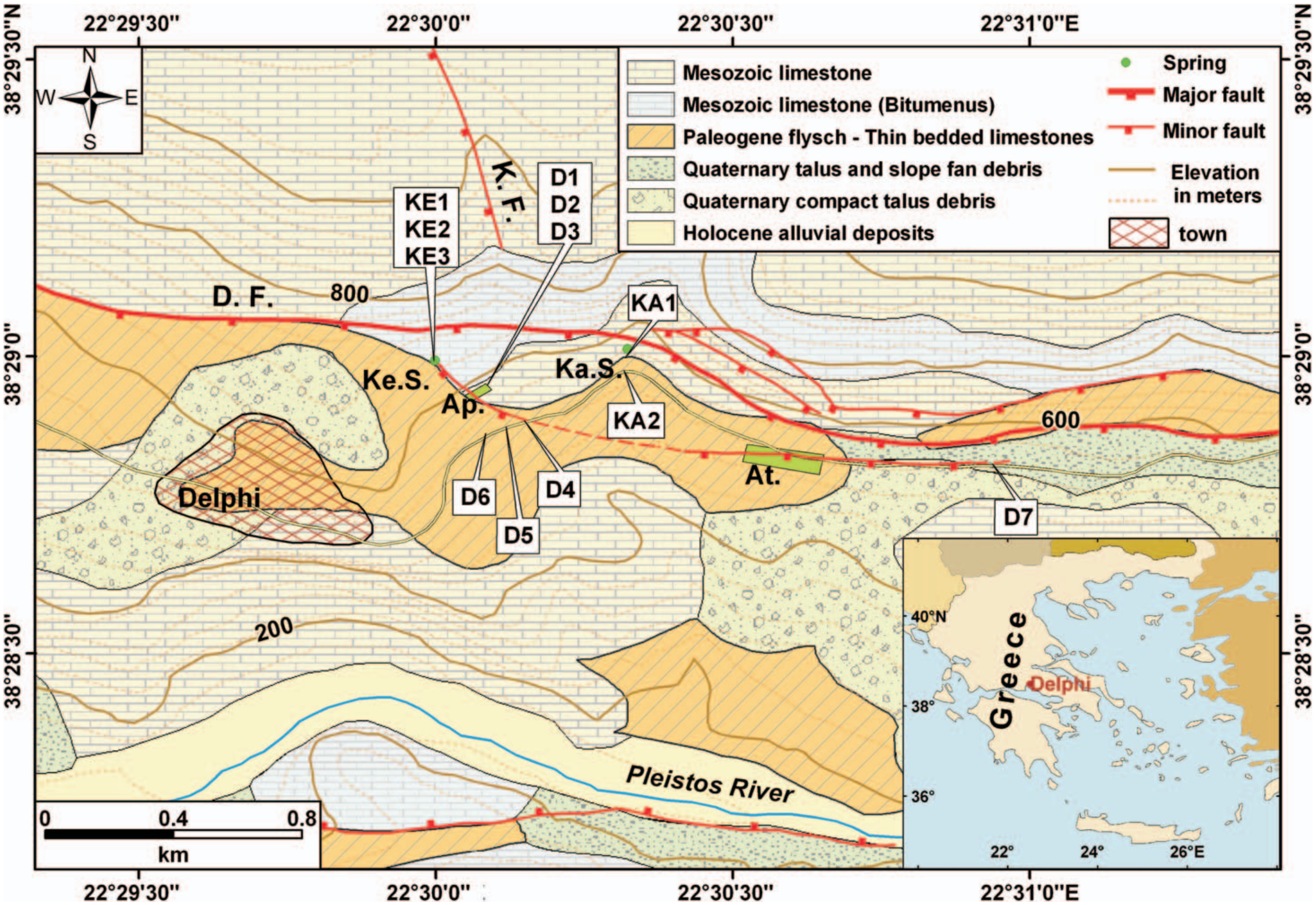

Figure 1. Geologic map of the Delphi area (modified from Zachos, 1964), with fault position and orientation (modified from Piccardi, 2000). KE1–KE3 (Kerna spring), D1–D3 (Temple of Apollo, Adyton), D4–D7 (WNW-ESE–trending subsidiary fault), and KA1–KA2 (Kastalia spring) are the gas sampling and flux measurement points (see also Tables 1 and 2). D.F.—Delphi fault; K.F.—Kerna fault; Ke.S.—Kerna spring; Ka.S.—Kastalia spring; Ap.—Temple of Apollo; At.—shrine of Athena.

natural biogenic gases in very low amounts: Marine sediments typically have 0.5 ppmv (max. 3 ppmv; B. Bernard, 2005, personal commun.). Ethylene cannot persist for enough time to accumulate, as it is readily reduced to paraffin by hydrogen. Even large biogenic gas pockets that may produce seepage out of the sediments do not have more than a few ppmv of ethylene. On average, ~2–6 ppmv (up to 23 ppmv) of ethylene are reported to be found in the soil over biogenic gas reservoirs (Gole and Butt, 1985). The gas reservoir has a lower ethylene concentration, and the enrichment in the soil is due to microbiologic activity, not to gas migration from depth. At the thermogenic phase (high temperature and pressure) any ethylene molecule gets destroyed to form heavier hydrocarbons. For the same reasons, ethylene can be found in geothermal fluids only at ppb levels (e.g., Capaccioni et al., 2004).

If the sweet smell of the vapors described by Plutarch was due to the presence of ethylene (De Boer et al., 2001), its concentration should have been above the odor threshold, which is 290 ppmv (Amoore and Hautala, 1983).

Delphi lies in the Parnassus-Ghiona tectonic unit of the Hellenides (Avramidis et al., 2002). The heat flow of this sector is 80 mW/m^2; it is too low to produce hydrothermal circulation, and in any case no warm springs occur in the Parnassus zone. The heat flow is, however, higher than that of other petroliferous zones of Greece (e.g., Ionian zone: 30–40 mW/m^2; Mesohellenic basin: 40–50 mW/m^2); this relatively high thermal regime accelerates the maturation and destruction of microbial gases (such as ethylene) and is coherent with the presence of bituminous limestones, which are the products of advanced thermal maturation of sapropelic kerogen.

The Mesozoic (Upper Cretaceous) limestone with a high petrochemical content is the rock from which ethylene was produced, as is claimed by De Boer et al. (2001). De Boer et al. (2001) reported, as evidence for ethylene occurrence, the gas analyses in two Delphi springs (Kerna and Kastalia) and two springs located in Zakinthos, an island hundreds of km west of Delphi, in a completely different geological context: Zakinthos lies in the petroliferous productive zone of the Ionian tectonic unit of the Hellenides, while Delphi is part of a more internal Parnassus-Ghiona tectonic unit, which has no gas-oil prospects. At Delphi, 0.3 n*M* (or 7 nL/L) of ethylene was detected by De Boer et al. (2001) only in the Kerna spring. This is a negligible amount: Light hydrocarbons in atmosphere-equilibrium waters are normally in the range of a few units of nanoliter/liter, in the absence of local microenvironment with bacterial activity.

GAS SURVEYS

Looking for Macroscopic Methane Emissions

A portable laser sensor (Lasermethane^{TM} SA3C06A, Tokyo Gas Engineering and Anritsu Corp.), based on infrared laser beam and wavelength modulation absorption spectroscopy, has been used to detect methane anomalies in the air (>2 ppmv) a few centimeters above the ground (lower detection limit of 1.3 ppm × m). The laser scanned the area from distances of 1 m to dozens of meters, using retroreflectors, in the Adyton site, below the floor level of the temple and out-

Figure 2. View of the Temple of Apollo and the site of the measurements in the Adyton (left); gas flux measurement by closed chamber on the soil inside the temple (right).

doors, around the temple, in correspondence with the fault traces, the travertine deposits, and the Kerna and Kastalia springs. No signals of significant methane seepage have been detected; at present, the area does not show macroscopic gas emissions.

Weaker Gas Exhalations

The existence of weak and diffuse exhalations of methane from the soil, which do not necessarily lead to methane anomalies in the atmosphere, has been investigated by using the closed-chamber method (Fig. 2), a technique widely employed in microseepage studies in petroliferous areas and in the study of biological fluxes of CH_4 in wetlands and drylands (e.g., Etiope et al., 2004). Twelve methane flux measurements were performed at the Temple of Apollo area, in the *Adyton* and around the Kerna and Kastalia springs. The air extracted from the chamber was analyzed in duplicate for methane by gas chromatograph with FID detector (Autofim II, Telegan; detection limit 0.1 ppmv; accuracy 4%–5%). Flux measurement reproducibility is within 15%. In normal conditions (dry soil), methane flux from the soil is generally from 0 down to -5 mg m^{-2} d^{-1}, due to methanotrophic consumption. In areas with microseepage from natural gas reservoirs, the flux can be positive, reaching values of tens and hundreds of mg m^{-2} d^{-1}.

These measurements did not show high gas emissions, but some positive fluxes were detected at three sites along the WNW-ESE–trending subsidiary fault (Table 1; Fig. 1). One is in the floor of the Temple of Apollo, assumed to be the *Adyton*, and showed up to 65 mg CH_4 m^{-2} d^{-1}; the foot of the scarp at the Kerna spring showed the highest fluxes, up to 145 mg CH_4 m^{-2} d^{-1} (Fig. 3). Far from the WNW-ESE fault trace, no positive methane signals were detected.

TABLE 1. METHANE FLUX FROM THE SOIL

Location	Position	Microseepage (mg m^{-2} d^{-1})
Temple of Apollo	D1-Adyton 1	5
	D2-Adyton 2	65
	D3-Adyton 3	−3
Kerna spring	KE1-3 m from spring	10
	KE2-Fault base	145
	KE3-Fault base	90
Delphi fault zone	D4-Main road (at WNW-ESE–trending Fault trace)	105
	D5-Main road (50 n from WNW-ESE–trending Fault trace)	0
	D6-Main road (100 m from WNW-ESE–trending Fault trace)	−5
	D7-Main road (1.5 km from Temple of Apollo)	0
Kastalia spring	KA1-30 m from spring	0
	KA2-Main road	−5

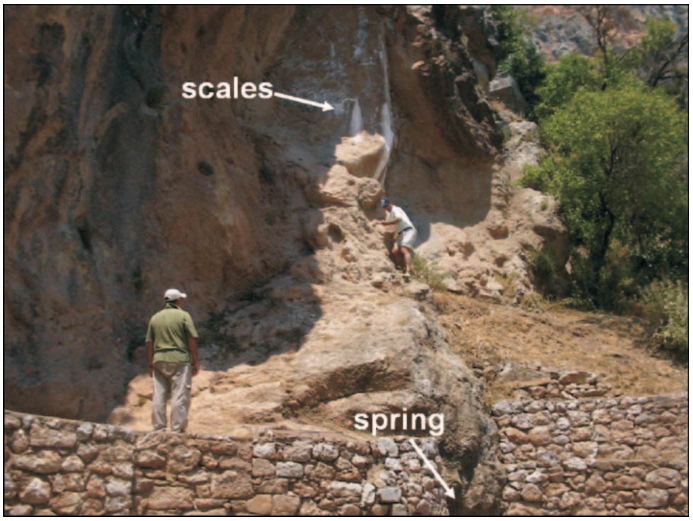

Figure 3. Tectonic scarp along the Delphi fault, in correspondence with the Kerna spring. The highest methane microseepage flux occurs at the base of this scarp.

Gas Dissolved in Spring Waters

A wide screening of gas dissolved in water samples from Kerna and Kastalia springs was performed. The samples were analyzed for C_1, C_2, C_2H_4, C_3, iC_4, nC_4, iC_5, nC_5, C_6+, He, H_2, Ar, O_2, CO_2, CO, and H_2S by gas chromatography (Carle AGC 100–400 TCD-FID GC; detection limit of CO_2, N_2, Ar, and O_2: 40 ppmv; H_2S: 150 ppmv; He and HC: 10 ppmv; accuracy 2%) and mass spectrometry (Finnigan Delta Plus XL) at Isotech Labs (Illinois, USA). On-site analyses were also made for CH_4 and C_2H_6 by the portable GC-FID used for microseepage (with Rivoira calibration standards, ±2%) and for H_2S by RAE colorimetric tubes and sampling pump (detection limit 0.2 ppmv; accuracy <10%).

The results are shown in Table 2. The main feature is the occurrence of relatively high carbon dioxide (CO_2: 1.86 m*M,* equivalent to 4.1% v/v in the dissolved air) in the Kerna spring water and the presence of methane and ethane with a very low C_1/C_2 ratio (30). Ethylene and other hydrocarbons are below the detection limit. $C_1/C_2 < 100$ is generally an indicator of thermogenic gas (a similar value was reported also by De Boer et al., 2001). Kastalia spring does not show any significant gas anomaly, with values close to the equilibrium with the atmosphere.

There is no indication of hydrothermal or low-enthalpy fluids, as also suggested by a low temperature of the spring water. The CO_2 concentration of Kerna spring is much lower than typical geothermal waters, but sufficient to explain the deposition of travertine at discharge.

The amount of methane in solution was too small to perform carbon and hydrogen isotopic analyses, essential to understand its origin. However, the association of low C_1/C_2 (<100) and the significant amount of CO_2 is coherent with an advanced stage of kerogen matu-

TABLE 2. GAS CONCENTRATION IN SPRING WATERS

Location	CH_4 nmol/l	C_2H_6 nmol/l	C_2H_4 nmol/l	CO_2 nmol/l	O_2 nmol/l	Ar nmol/l
Kerna spring	73.2	2.2	N.D.	1.86	0.44	0.02
Kastalia spring	12.3	N.D.	N.D.	0.7	0.26	0.01

N.D. = not detected (value below detection limit).

ration, or catagenesis, where thermogenic processes at $T > 90$ °C produce C_1 and C_{2+} hydrocarbons, with CO_2 due to thermal destruction of carbonates and/or methane oxidation (Hunt, 1996). The geothermal gradient of the Delphi area, 4–5 °C per hundred meters would suggest temperatures above 90 °C at depths below 1500 m. This frame is wholly compatible with the sapropelic (marine) matter of the carbonate source rocks.

Calcite Scales Analyses

Analysis by X-ray diffractometry of the scales occurring at the Kerna spring indicates pure $CaCO_3$ in hexagonal structure. Two sets of calcite samples have been analyzed for $\delta^{13}C$ in two different laboratories, using mass spectrometric methods (Analytical Precision AP 2003 and Finnigan MAT 253). $\delta^{13}C$ is $-18.4‰$ (PDB) for one sample, and $-15.9‰$ to $-18.4‰$ (PDB) for a second sample set. These values indicate that the carbonate was only partially precipitated (or altered) from meteoric water and was mainly formed by oxidation of hydrocarbons to CO_2, dissolution in water to form bicarbonate, and then precipitation of calcite. Values lower than $-16‰$ are thus often an indication of methane oxidation in seepage areas and are therefore used as a hydrocarbon prospecting tool (Schumacher, 1996).

CONCLUSIONS

We confirm the basic hypothesis of hydrocarbon exhalation in the Delphi Temple of Apollo, suggested by De Boer et al. (2001). However, the possibility of significant ethylene emissions is not obvious. Ethylene could not be produced, neither in the present nor in the past, in the deep carbonate rocks of Delphi in a sufficient amount (hundreds of ppmv) to produce a noticeable odor. Ethylene can be found in very low amounts (a few ppmv), only in shallow clastic sediments with biogenic gas, and there is no known way of forming hundreds of ppmv of ethylene seeping from accumulations in the subsurface.

The geological framework of Delphi is characterized by a carbonate platform with a relatively high thermal regime, which caused advanced maturation (catagenetic) of sapropelic kerogen. Methane (not microbial), ethane, their ratio $C_1/C_2 \ll 100$, and bitumens are all typical products of this environment. The CH_4 and CO_2 release must have been much greater thousands of years ago as indicated by the formation of travertine, the analysis of which suggests CO_2 precipitation originating from CH_4 oxidation.

Weak exhalations of CH_4 occur from the soil at three sites along a WNW-ESE–trending subsidiary fault within the Delphi fault zone. The Temple of Apollo, located above this fault, could have been the site of enhanced degassing in the past.

If any gas-linked neurotoxic effect of Pythia needs to be invoked, as suggested by historical tradition, it could be searched for in the possibility of oxygen depletion due to CO_2-CH_4 exhalation in the enclosed and nonaerated *Adyton* (possibly accelerated by the use of a coal burner with essential oils, perfumes, or drugs, leading to production of carbon monoxide). Should archaeologists require a reason for the natural presence of sweet odors, an alternative geological explanation could be the occurrence of aromatic hydrocarbons, such as benzene, dissolved in the groundwater spring. Benzene is common in catagenetic hydrocarbons and bitumens; it can be transported for long distances by groundwater advection or petroleum seepage without significant decomposition (Davis, 1967), and its vapors can be released from springs (Zhang et al., 2005). Slaine and Barker (1990) reported the presence of naturally occurring benzene in groundwater, up to 500 μg/L, which may have been leached from bituminous rocks (similar to those of Delphi). In petroleum seepage areas, benzene vapor concentration in soil can be higher than the odor threshold, which is only 12 ppmv, and can be used as an indicator of subsurface petroleum reservoirs (Calhoun and Hawkins, 1998). Short-term exposure to tens of ppmv of benzene leads to shortness of breath, diminished mental alertness, impaired vision, flawed judgment, emotional instability, and unconsciousness; long-term exposure may produce various diseases, including a weakening of the immune system and leukemia.

Thus, the ‘‘benzene’’ hypothesis would imply the existence of an oil seep or, at least, a spring of groundwater in the temple that strongly interacted with the bituminous rocks or underground petroleum brines. Although this is not a common phenomenon, theoretically it is not in contrast with Delphi's geological/geochemical environment. Specific investigations (e.g., laboratory tests on interaction of water with Delphi's bituminous rocks) are required to further support this hypothesis.

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