

GEOCHEMISTRY OF THE GAS MANIFESTATIONS OF GREECE: METHANE AND LIGHT HYDROCARBONS

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Abstract

Greece has a very complex geodynamic setting deriving from a long and complicated geological history being characterized by intense seismic activity and enhanced geothermal gradient. This activity, with the contribution of an active volcanic arc, favours the existence of many gas manifestations. Depending on the prevailing gas species, the latter can be subdivided in three main groups: CO₂-, N₂- and CH₄-dominated. In the present work, we focus on methane and light hydrocarbons (C₂-C₆) to define their origin. CH₄ concentrations (<2 to 915,200 μmol/mol) and isotopic ratios (δ¹³C -79.8 to +16.9 ‰, δD -298 to +264‰) cover a wide range of values indicating different origins and/or secondary post-genetic processes. Samples from gas discharged along the Ionian coast and in northern Aegean Sea have a prevailing microbial origin. Cold and thermal gas manifestations of central and northern Greece display a prevalent thermogenic origin. Methane in gases released along the active volcanic arc is prevailingly abiogenic, although thermogenic contributions cannot be excluded. Gases collected in the geothermal areas of Sperchios basin and northern Euboea are likely affected by strong secondary oxidation processes, as suggested by their highly positive C and H isotopic values (up to +16.9‰ and +264‰ respectively) and low C₁/(C₂+C₃) ratios.

Keywords: Hellenic territory, hydrothermal gases, cold gas emissions, origin of hydrocarbon gases.

Περίληψη

Το σύνθετο γεωδυναμικό καθεστώς της Ελλάδας πηγάζει από την πολύπλοκη γεωλογική της ιστορία, η οποία χαρακτηρίζεται από έντονη σεισμική δραστηριότητα και ενισχυμένη γεωθερμική βαθμίδα. Αυτή η δραστηριότητα σε συνδυασμό με το ενεργό

ηφαιστειακό τόξο, ευνοεί την ύπαρξη πολλών εκπομπών αερίων, με αποτέλεσμα την κατηγοριοποίηση σε CO₂-, N₂- και CH₄- αέρια, ανάλογα με το επικρατών είδος. Η παρούσα εργασία επικεντρώνεται στο μεθάνιο και τους ελαφρούς υδρογονάνθρακες (C₂-C₆) με σκοπό τον προσδιορισμό της προέλευσής τους. Οι συγκεντρώσεις του CH₄ (<2 έως 915,200 μmol/mol) και η ισοτοπική του αναλογία (δ¹³C -79.8 έως +16.9 ‰, δD -298 έως +264‰) καλύπτουν ένα ευρύ φάσμα τιμών, που υποδεικνύει διαφορετικές προελεύσεις ή/και δευτερογενείς μεταγενετικές διεργασίες. Δείγματα εκφορτισμένων αερίων που συλλέχθηκαν στις ακτές του Ιονίου Πελάγους και στο Βόρειο Αιγαίο, δείχνουν να επικρατεί η μικροβιακή προέλευση ενώ στις ψυχρές και θερμές εκπομπές αερίων της κεντρικής και βόρειας Ελλάδας η θερμογενετική. Το μεθάνιο που απελευθερώνεται από τα αέρια του ηφαιστειακού τόξου είναι κυρίως αβιογενές, αν και οι θερμογενετικές συνθήκες δεν μπορούν να εξαιρεθούν. Τα συλλεγμένα αέρια των περιοχών της κεντρικής Ελλάδας (λεκάνη Σπερχειού και βόρεια Εύβοια) πιθανά επηρεάστηκαν από έντονες δευτερογενετικές οξειδωτικές διεργασίες, όπως φαίνεται από τις υψηλές θετικές ισοτοπικές τιμές των C και H (έως +16.9‰ και +264‰ αντίστοιχα) και από τις χαμηλές αναλογίες των C₁/(C₂+C₃).

Λέξεις κλειδιά: Ελληνική περιοχή, υδροθερμικά αέρια, εκπομπές ψυχρών αερίων, προέλευση υδρογονανθράκων.

1. Introduction

The Hellenic territory has a complex geodynamic setting deriving from a long and complicated geological history. Due to this specific geological background, conditions for the formation of many thermal springs were favoured (D'Alessandro *et al.*, 2006, 2008, 2010, 2011; Kyriakopoulos *et al.*, 2010). The major geodynamic activity in macroscale gave rise to a geological evolution which is expressed in volcanism, orogenic processes and active tectonics. Widespread volcanic activity in the Aegean Sea started in the Oligocene and continues to the present. Two major phases took place. The first one was developed in the North Aegean area from the Oligocene to the Middle Miocene and the second started in the Pliocene forming the active South Aegean Volcanic Arc. During the Oligocene – Miocene volcanic phase the volcanic activity occurred in an East to West oriented zone from Thrace to the Central Aegean. Many places of the Aegean region (North Euboea, Tinos, Sikinos, Patmos and Samos Islands) were affected by this activity. Chemical- physical conditions related to the recent volcanism, coupled with the major faults were the fundamental causes for the warming and uplift of deep thermal waters, resulting in this discharge at the surface thermal springs (Fytikas *et al.*, 1984; Pe-Piper *et al.*, 1989).

Geochemical studies based on the isotopic composition of carbon and hydrogen, along with helium isotopic ratios have become a good indicator of the origin of the gas. The isotopic ratio ¹³C/¹²C of CO₂ expressed in δ ¹³C (‰), may provide important information about the amount of CO₂ released from the Earth's crust or mantle. Carbon and hydrogen isotopic compositions and C₁/(C₂+C₃) hydrocarbon ratios can characterize the origin of methane. In sedimentary environments, CH₄ is primarily produced by 1) processes related to metabolic and biosynthetic activity of biological organisms (biogenesis), and 2) decomposition of organic matter buried in sediments at T>150 °C (thermogenesis) (Schoell, 1980, 1988; Whiticar *et al.*, 1986; Galimov, 1988; Welhan, 1988; Whiticar and Suess, 1990; Whiticar, 1999). Helium isotopic ratios provide additional information about crustal or mantle origin of the gas.

This study is focusing on methane and light hydrocarbons and is having as an aim the identification and the characterization of methane's origin and the identification of post-genetic processes affecting hydrocarbon gases.

2. Geodynamic setting and volcanism of Greece

The Hellenides are the result of the collision of several microcontinental fragments with the margin of Eurasia through the Cretaceous and Paleogene (van Hinsbergen *et al.*, 2005). After the collision, the Hellenides have been characterized by widespread extension, particularly since the Miocene, as a result of subduction rollback from the oceanic crust of the African plate. The modern fault pattern is a result of the westward and southwestward motion of the Aegean-Anatolian microplate with respect to the Eurasian plate.

The Paleogene Hellenide orogeny of Greece and its eastward continuation into western Turkey resulted from the collision of the Apulian microcontinental fragment in the Eocene to Oligocene with the Pelagonian, Rhodope, and Serbo-Macedonian fragments, which had previously accreted to the southern margin of Eurasia in the Cretaceous. Subsequent extension in the Aegean was rapid, likely due to subduction rollback over residual oceanic crust of the African plate, whereas Anatolia had been bounded by African continental crust south of Cyprus since the Early Miocene. This regional extension and the thermal effects of asthenospheric upwelling, related to changes in the geometry of subducting slabs, have been interpreted as causing magma genesis principally within the lithospheric mantle (Pe- Piper and Piper, 2002).

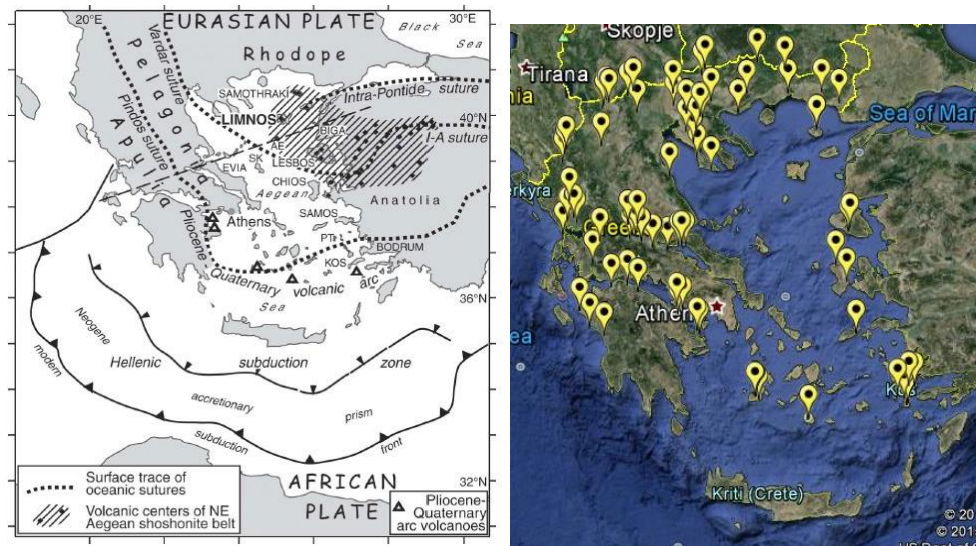


Figure 1 – a) Map that shows the plate boundaries and the geodynamic pattern of Greece and the Ionian and Aegean Seas (Pe-Piper, 2006). This map was the criteria used for the categorization of the samples collected in the Hellenic territory as seen in Figure b.

At the south Aegean Volcanic Arc the activity started during the Upper Pliocene (Fytikas *et al.*, 1986) and is currently active at solfataric stage. The calc-alkaline volcanic activity of Southern Aegean region developed in various volcanic centers from Sousaki to Nisyros through Methana-Poros, Milos and Santorini. The volcanic products are dominated by lava domes and lava flows with associated minor pyroclastic breccias and felsic ignimbritic covers (Mitropoulos *et al.*, 1987). The final activity of this orogenic cycle is characterized by the presence of K-rich shoshonites and latites with ultrapotassic character.

On the basis of the previous description of the Hellenic geodynamic setting, the whole territory has been subdivided into 5 homogeneous areas (see map of fig. 1a): Apulia, Pelagonia, Rhodope, North Aegean and South Aegean active volcanic arc. The results of the present study will be discussed in the light of such subdivision.

3. Fluid emissions in Greece

Greece, like many other Mediterranean countries (e.g. Italy and Turkey) has a significant geothermal potential, since most areas of the country are geodynamically active as a result of the movement of the African plate towards the Eurasian plate. Heat flow higher than 80 m/Wm² characterize several regions, mainly in the internal Hellenides and the Aegean Sea. Such an intense volcanotectonic activity caused the geological conditions for accumulation of heat energy, as testified by the occurrence of low-medium and high enthalpy hydrothermal systems. The most important high-enthalpy geothermal fields are located in the Southern Aegean, along the active volcanic arc (Milos, Nisyros), whereas medium and low enthalpy reservoirs are mostly associated with grabens (Central Aegean) and post-orogenic sedimentary molassic basins (southern boundaries of the Rhodope and Servo-Macedonian Massifs) (Fytikas *et al.*, 2005).

4. Materials and Methods

Bubbling gases were sampled using an inverted funnel positioned above the bubbles, whereas soil gases were collected by inserting a pipe in the soil and driving the gas by a syringe and a 3-way valve. Gases were collected in 12 ml Exetainer® vials (only for hydrocarbons) and glass sampling bottles equipped with two vacuum stopcocks.

In the laboratory, samples were analysed for He, H₂, O₂, N₂, CH₄ and CO₂ by gas-chromatography (Perkin Elmer Clarus500 equipped with a double Carboxen 1000 columns, TCD-FID detectors) using argon as the carrier gas. Analytical uncertainties were ± 5%. Hydrocarbon analysis, were performed with a Shimadzu 14a gas-chromatograph equipped with a Flame Ionization Detector (FID) using helium as the carrier gas. The analytical error was ≤5%. The ¹³C/¹²C ratios of CO₂ (expressed as δ¹³C-CO₂‰ V-PDB) were measured with a Finnigan Delta S mass spectrometer after purification of the gas mixture by standard procedures using cryogenic traps (precisions ±0.1‰). Carbon and hydrogen isotopic compositions of CH₄ were measured using a Thermo TRACE GC and a Thermo GC/C III interfaced to a Delta Plus XP gas source mass spectrometer. ¹³C/¹²C ratios are reported here as δ¹³C values (±0.2 ‰) with respect to the V-PDB standard. H/D ratios are reported here as δD values (±2 ‰) with respect to the V-SMOW standard.

5. Results and discussion

The gas samples collected in the Hellenic territory (Fig 1b) display a large variability in the chemical composition. Helium ranges from 0.10 to 3372 ppm and shows a fair positive correlation with N₂. Almost 112 samples out of 399 have detectable H₂ (>2 ppm) concentrations ranging from 3.50 up to 149,100 ppm. O₂ concentrations range from below the detection limit (<200 ppm - 45 samples) up to 192,700. The concentrations of N₂, CH₄ and CO₂ range from 600 up to 995,100 ppm, from less than 2 up to 915,200 ppm and from less than 50 up to 999,900 ppm. The last three species represent always the main gas component and all the samples can be subdivided in N₂-, CH₄- or CO₂- dominated gases.

The O₂- N₂- CO₂ triangular graph (Fig. 2a) reveals that only few samples plot close to the point representing atmospheric air excluding important contaminations for most of the samples. The majority of the gases display N₂/O₂ ratios less than air or Air Saturated Waters (ASW), which is indicating that the atmospheric component of meteoric water has been modified by redox reactions that took place either in the subsoil or in the aquifers. Furthermore, most of the samples show a strong contribution of helium deriving either from a crustal or mantle sources.

As shown by the CH₄- N₂- CO₂ triangular plot (Fig 2b), only few samples, mostly from Apulia, display a CH₄- dominated composition. In general, the collected samples can also be subdivided in 3 groups:

- a) CO₂- dominated, consisted of the samples collected in the Volcanic Arc and a part of Pelagonia and Aegean,
- b) N₂- dominated, consisted of a part of the samples collected in Pelagonia and Rhodope
- c) CH₄- dominated, consisted of the samples mainly collected in Apulia (Fig 2a, 2b).

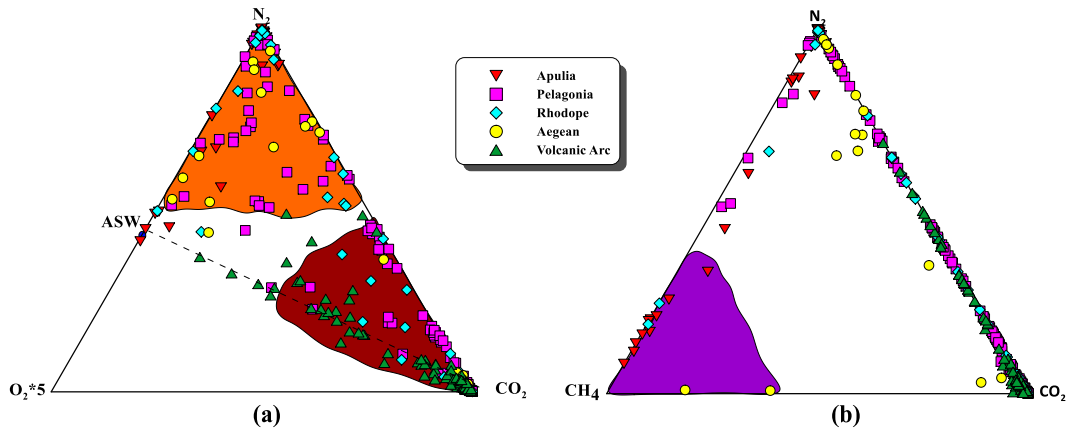


Figure 2 - Ternary plots of a) O₂- N₂- CO₂, b) CH₄- N₂- CO₂ in which are plotted the samples divided by geographic areas. The polygons represent the dominant gas: CO₂- dominated, red, N₂- dominated, orange, CH₄- dominated, purple.

He isotopic values, expressed as ³He/⁴He ratio, normalized to the atmospheric one (Ra=1.386*10⁻⁶), range from 0.03 to 6.70 R/Ra. Measured values corrected for the atmospheric contamination of the sample on the base of its ⁴He/²⁰Ne ratio (Sano and Wakita, 1985) display a similar range (Rc/Ra 0.02 – 6.73). Such a wide range is indicative of different sources for He in the studied gases.

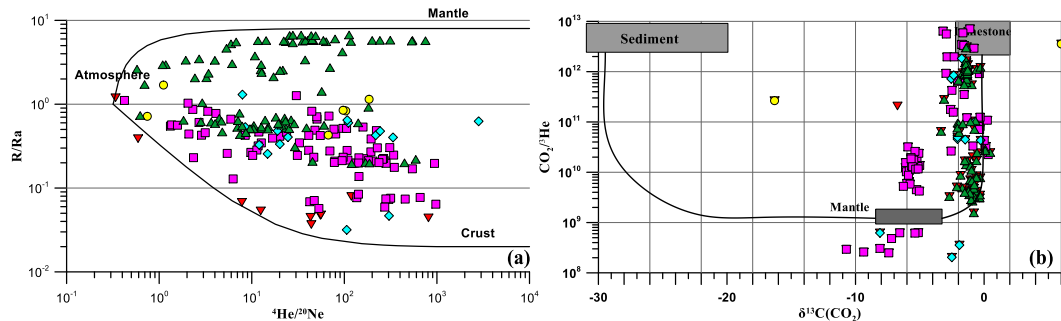


Figure 3 - a) Binary plot of R/Ra vs. ⁴He/²⁰Ne of the natural gas manifestations of Greece. Atmosphere, Mantle and Crust represent three possible end-members: atmospheric air, MORB-like mantle and crust. The mixing lines between Atmosphere and Mantle and between Atmosphere and Crust are also plotted, b) Binary plot of CO₂/³He vs. δ¹³C(CO₂) of natural gas manifestations of Greece. The end-member compositions for Sediments, MORB-like Mantle and Limestones are δ¹³C(CO₂) = -30‰, -5‰ and 0‰ and CO₂/³He = 1*10¹³, 2*10⁹ and 1*10¹³, respectively (Sano and Marty, 1995).

On Fig. 3a, the measured values of R/Ra are plotted against the ⁴He/²⁰Ne ratio. Only few samples plot close to the atmospheric end member, confirming that the atmospheric contribution is negligible. The majority of the samples collected in the Volcanic Arc display high contributions of mantle component, as shown by the highest Rc/Ra ratios (up to 6.73) found at the islands of Kos and Nisyros. Samples collected in Apulia show a prevailing crustal component with Rc/Ra ratios <0.1. The

remaining samples (Pelagonia, Rhodope, Aegean) show a mixed mantle-crustal composition with Rc/Ra ratios up to 2.15.

The carbon isotopic composition of CO₂ of the free gas samples displays a wide range from -16.5 to +6.0‰ (vs. V-PDB) although the majority falls in a narrower range (from -6.0 to +0.0 δ¹³C(CO₂) ‰). By taking into account the δ¹³C(CO₂) values and the CO₂/³He ratios (Fig. 3b), it is noticed that the majority of the collected samples is a mixture of mantle and limestone end-members, whereas the contribution of the sedimentary organic member to the fluids deriving from the descending slab is considered to be insignificant. However, a small contribution from organic sediments can be detected in the CO₂-dominated gases of Apulia deriving from crustal sources. On the contrary, CH₄ and N₂-dominated gases display sometimes a strong organic contribution and low CO₂/³He ratios (samples collected in Pelagonia and Rhodope) probably due to CO₂-depleting processes (CO₂ dissolution in groundwater, carbonate precipitation, CO₂ reduction, etc.).

Thermogenic CH₄ has been reported to exhibit δ¹³C(CH₄) values ranging from -50 up to -30‰ V-PDB, whereas microbial CH₄ usually has δ¹³C(CH₄) values <-50‰ V-PDB (e.g., Whiticar, 1999; McCollom and Seewald, 2007). However, these limit values may vary depending on processes occurring during gas migration, such as isotopic fractionation by diffusion (Prinzhofer and Battani, 2003), secondary methanogenesis and anaerobic biodegradation (Dimitrakopoulos and Muehlenbachs, 1987; Pallasser, 2000; Etiope *et al.*, 2009). Gases produced by the decay of organic matter at T > 150 °C (thermogenic gases) are commonly characterized by CH₄/(C₂H₆+C₃H₈) concentration ratios (the so called “Bernard parameter”) <100, whereas higher ratios (>1000) are expected when hydrocarbon production derives exclusively from microbial activity (Whiticar and Suess, 1990; Jenden *et al.*, 1993). As previously pointed out, concentrations of CH₄ as well as its isotopic composition cover a wide range (<2 to 915.200 μmol/mol and δ¹³C from -79.8 ‰ to +16.9 ‰, δD from -298 ‰ to +264 ‰ respectively) indicating different origins and/or secondary post-genetic processes. On Fig. 4a and 4b, it is shown that samples from gas discharge located in Apulia and North Aegean likely have a microbial origin, as suggested by the low δ¹³C(CH₄) values (down to -79.8 ‰ for Apulia and down to -45.9 ‰ for Aegean) and high C₁/(C₂+C₃) ratios (highest values reaching up to 9000). The cold and thermal manifestations of Rhodope and a part of Apulia and Pelagonia seem to display a thermogenic origin. CH₄ released along the Volcanic Arc, seems to be prevalently abiogenic (Fiebig *et al.*, 2009; Tassi *et al.*, 2012, 2012) according to the high δ¹³C(CH₄) values (> -25‰) and high C₁/(C₂+C₃) ratios (up to 16,000), although thermogenic contribution cannot be excluded. Some of the remaining gases of Apulia and Pelagonia are affected by secondary oxidation processes, as highlighted by their high isotopic values of H and C (up to +16.9 ‰ and +264 ‰ respectively) and their low C₁/(C₂+C₃) ratios. Incubation experiments on waters and sediments of some of these springs, showed that the oxidation of CH₄ is generally microbially driven.

As shown in Fig. 5, the CH₄/C₂H₆ concentration ratios of the studied gases vary by more than three orders of magnitude, whereas the ratios between the light hydrocarbons (C₂H₆, C₃H₈ and C₆H₆) vary by less than two orders of magnitude. As far as this evidence is concerned, the redox processes between CO₂ (CO) and CH₄, which likely controls the CH₄ abundance in volcanic-hydrothermal fluids, does not affect the higher alkanes whose origin could be entirely related to thermal degradation of organic matter. At the same time, the residual methane seems to retain its primary carbon isotopic composition due to the possible low degree of polymerization. This could also explain why there is no significant correlation between the carbon isotopic composition of methane and the CH₄/(C₂H₆+C₃H₈) values for gases from volcanic environments (Fig. 5a and 5b), whose δ¹³C (CH₄) seems to be controlled by δ¹³C (CO₂) and temperature. In addition, methane polymerization may explain why volcanic-hydrothermal gas emissions exhibit a spread to much lower CH₄/(C₂H₆+C₃H₈) concentration ratios than the geothermal discharges.

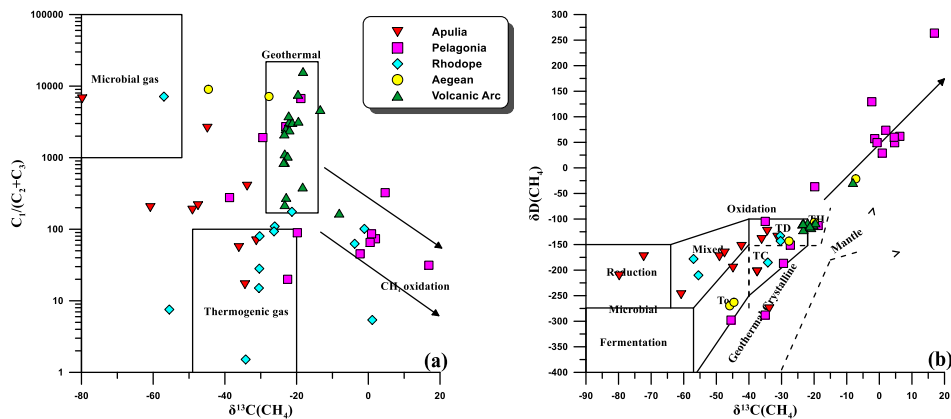


Figure 4 – a) $C_1/(C_2+C_3)$ vs $\delta^{13}C(CH_4)$ and b) $\delta D(CH_4)$ vs $\delta^{13}C(CH_4)$ diagrams for the Hellenic gas discharges.

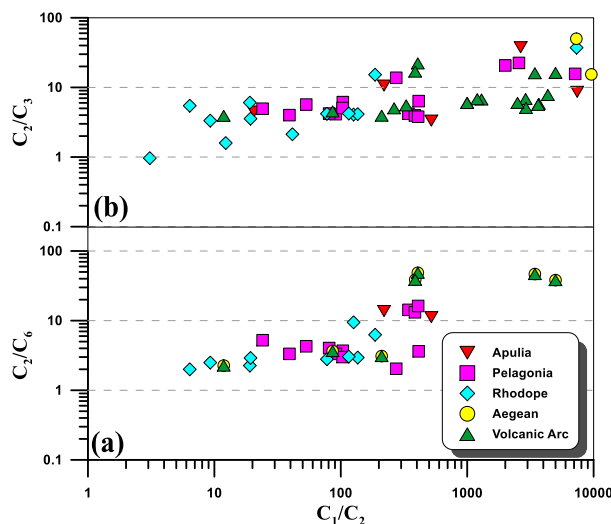


Figure 5 – a) CH_4/C_2H_6 vs. C_2H_6/C_3H_8 and b) CH_4/C_2H_6 vs. C_2H_6/C_6H_6 binary plots for the Greek gas discharges.

6. Conclusions

The chemical and isotopic compositions of CH_4 indicate that this gas has different primary sources and is significantly affected by secondary post-genetic processes (oxidation). The preliminary results of this study show that the Hellenic territory can be subdivided in 4 groups according to the gas compounds dominating the chemical composition of gas emissions (Fig. 6) as follows:

- along the Volcanic arc, gases are CO_2 -dominated, with CH_4 showing a hydrothermal origin (abiotic and / or thermogenic) and a prevailing mantle component for He and CO_2 .
- the Apulia region shows N_2 - CH_4 - dominated gases with a biogenic origin for CH_4 and a dominant crustal component for He.
- Pelagonia, Rhodope and Aegean regions show variable composition (CO_2 , CH_4 and N_2 -dominated) with a mixed crustal component for He, whereas CH_4 is mainly thermogenic.

- d) in the Sperchios Basin and northern Evia area (Pelagonia), the CH₄ is strongly affected by oxidation processes probably microbial driven.

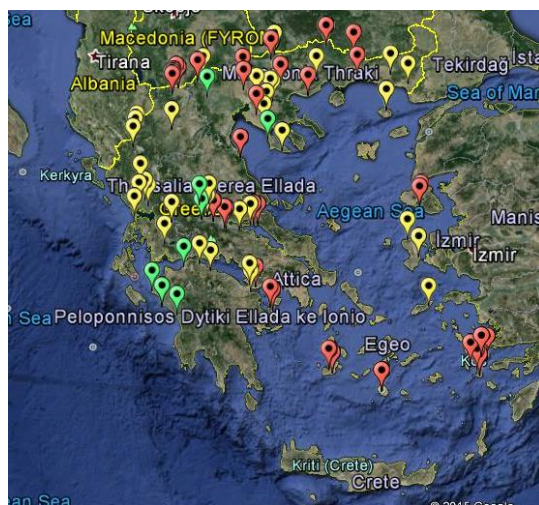


Figure 6 – Map of the Hellenic territory with the dominated gases in the sampled regions, with red color are shown the CO₂ dominated sampling points, with yellow the N₂ and with green the CH₄.

7. References

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