Origin of methane and light hydrocarbons in the gas manifestations of Greece

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The geologic emissions of greenhouse gases (CO_2 and CH_4) give an important natural contribution to the global carbon budget. However, the contribution of these emissions to the global carbon cycle and their possible role on the climate change remain still poorly quantified (Guliyev and Feizullayev, 1997; Milkov, 2000; Etiope et al., 2015 and references therein). Methane, the most abundant organic compound in Earth's atmosphere, may be created either from existing organic matter or synthesized from inorganic molecules. Accordingly, it can be differentiated in two main classes: a) biotic (either microbial or thermogenic) and b) abiotic.

For this study, 115 gas samples of fumarolic, thermal and cold discharges from all over the Hellenic territory were collected and both chemical (CO_2, H_2S, CH_4, N_2, O_2, Ar, H_2 and light hydrocarbons) and isotopic ($\delta^{13}C$-CO_2, $\delta^{13}C$-CH_4, δD-CH_4) analyses were performed, in order to investigate the genetic processes that produced CH_4 in fluids related with the complex geodynamic setting of Greece. On the basis of the spatial distribution of the gas discharges and their type of emission, the whole dataset was subdivided into 3 main "domains", as follows: 1) Volcanic Arc (VA) - 34 samples; 2) External Hellenides (EH) - 23 samples of cold emissions and of hyperalkaline aqueous solutions; 3) Internal Hellenides (IH) - 62 samples of cold and geothermal emissions. Almost each group is characterized, as long as subdivided in 3 groups based on the type of emission (on-land free or dissolved gases and subaqueous gases) and a 4th group includes literature data.

Samples collected from cold manifestations in the internal Hellenides and the Volcanic Arc mostly have CO_2 as the main species, whereas gases associated with hyperalkaline waters are N_2 dominated sometimes with significant CH_4 contributions. In the cold manifestations collected from the external Hellenides the prevailing gas is CH_4. The remaining gas samples collected from the geothermal emissions that occur in the Hellenic territory are showing a mixed N_2 - CO_2 composition (Figure 1).

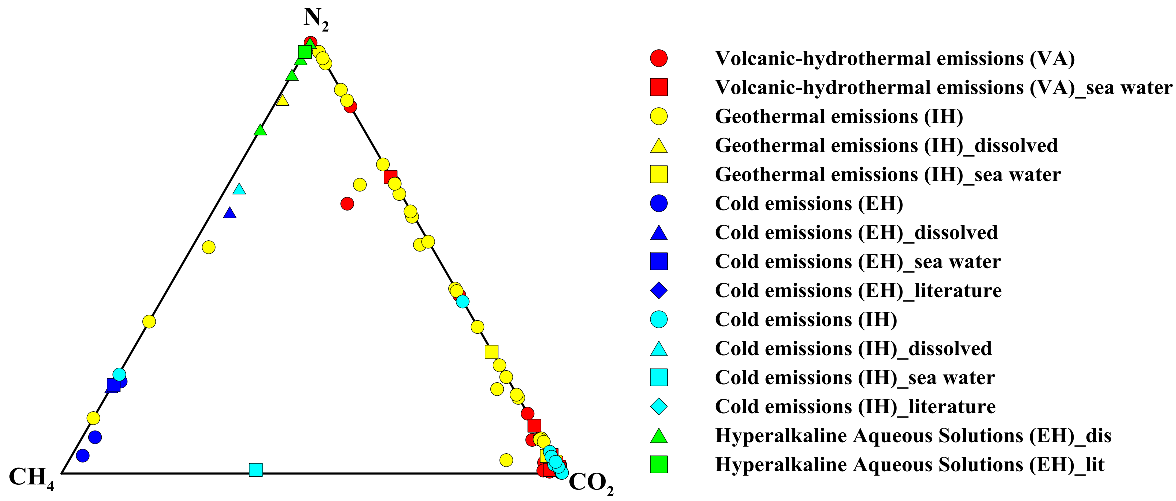

Figure 1: Chemical composition of the gas manifestations in Greece. VA = volcanic arc; IH = internal Hellenides; EH = external Hellenides

The present study highlights a widespread continental and underwater degassing activity along the Hellenic territory. Both chemical and isotopic compositions of CH_4 underscore the different primary sources and the secondary post-generic processes (oxidation) that can significantly affect the origin of this gas compound (Figure 2a, 2b). Hydrocarbons in the CH_4-dominated gases from the external Hellenides are showing a clear biotic origin. In particular, those collected in the Gavrovo-Tripolis zone are showing a dominating thermogenic origin, whereas it is also noticeable that some of the samples of the Ionian zone are produced by both microbial activity and thermal maturation of sedimentary organic matter. The CO_2-dominated gas discharges from the main geothermal systems of the Internal Hellenides and from the Volcanic Arc most likely predominantly contain abiogenic CH_4 deriving from CO_2 reduction. This process seems to have a lower effectiveness in producing higher hydrocarbons, such as C_2H_6, C_3H_8 and C_6H_6. However, some of the CO_2-rich gas discharges of the geothermal and volcanic-hydrothermal systems located in the sedimentary Pelagonian and the Gavrovo-Tripolis zones, seem to exhibit significant contributions from thermogenic sources. This is likely due to 1) low temperatures of the fluid reservoirs, i.e. too low to promote an efficient CO_2 to CH_4 conversion, and 2) the large amounts of organic matter that were buried in the sedimentary formations and that is available for thermal degradation processes. The presence of abiotic methane was also recognized in the hyperalkaline aqueous solutions that are issuing from the ophiolites of Othrys and Argolida (Etiope et al., 2013; D'Alessandro et al., 2017).

Most of the geothermal gases of central Greece (internal Hellenides) and some of the volcanic-hydrothermal ones show lower Bernard ratios ($CH_4/[C_2H_6+C_3H_8]$ – Fig. 2a) and strongly positive isotopic ratios of CH_4 ($\delta^{13}C$ up to +45‰ and δD up to 301‰ – Fig. 2). Such chemical and isotopic features can be explained by microbial oxidation of CH_4. In these environments microbes obtain energy from aerobic or anaerobic CH_4 oxidation (Murrell and Jetten, 2009), preferentially consuming CH_4 with respect to higher hydrocarbons and preferring light isotopes. This results in a noticeable decrease in the Bernard ratio and a progressive enrichment in heavy isotopes (both ^{13}C and D) in the residual CH_4.

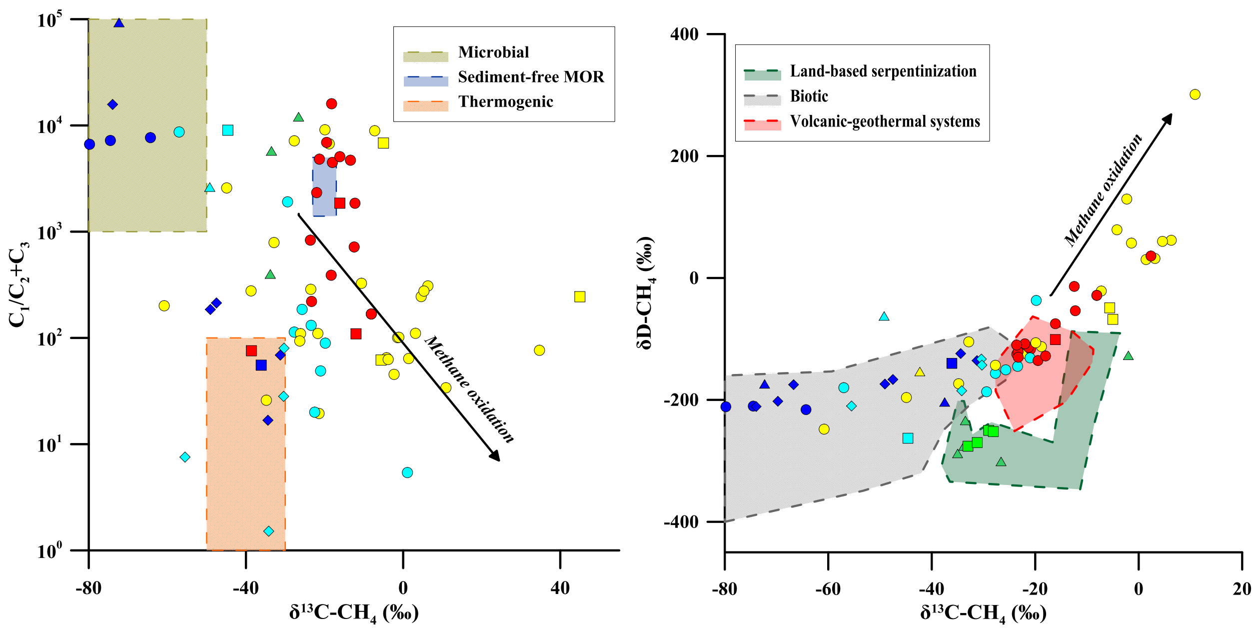

Figure 2: a) Bernard classification diagram (Bernard et al., 1978) that is correlating the $CH_4/(C_2H_6+C_3H_8)$ concentration ratios with the $\delta^{13}C-CH_4$ ratios for the Hellenic gas discharges. Values for gases of biogenic origin (microbial and thermogenic) and from unsedimented mid-oceanic ridges are reported (McCollom and Seewald, 2007, and references therein) for comparison; **b)** Schoell binary diagram (Etiope and Schoell, 2014) which is correlating $\delta D-CH_4$ with $\delta^{13}C-CH_4$ ratio for the Hellenic gas discharges.

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