Light hydrocarbons as a proxy to identify the origin of the gas manifestations in Greece

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The geologic emissions of greenhouse gases (CO_2 and CH_4) have an important natural contribution in the global carbon budget. Tectonics, through faults in geothermal and oil producing areas, play a significant role in the release of C-gases in many non-volcanic regions of the Earth. Methane, the most abundant organic compound in Earth's atmosphere, has a potential global warming that is 28 times higher than that of CO_2 on a 100-year time horizon. In this study, $\delta^{13}C$-CH_4, $\delta^{2}H$-CH_4 and light hydrocarbon (alkane: CH_4, C_2H_6, C_3H_8, C_3H_6, i-C_4H_{10}, n-C_4H_{10}; alkene C_3H_6, i-C_4H_8; and aromatic C_6H_6) gas concentration data of 119 gas samples (103 unpublished data and 16 literature data) from volcanic-hydrothermal, geothermal and cold discharges are used to shed light on the genetic processes that have formed CH_4 in 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 4 main "domains", as follows: 1) Volcanic Arc (VA); 2) External Hellenides (EH); 3) Internal Hellenides (IH); 4) Hellenic Hinterland (HH). 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 submarine gases) and a 4th group includes literature data. Concentrations of CH_4 range from < 2 to 925,200 µmol/mol and its isotopic ratios cover a wide range ($\delta^{13}C$ from -79.8 ‰ to +45 ‰; $\delta^{2}H$ from -311 ‰ to +301 ‰) indicating the different primary sources and the secondary post-genetic processes (oxidation) that can significantly affect the origin of this gas compound. Hydrocarbons in the CH_4-dominated gases discharged from the EH are showing a clear biotic origin. In particular, those collected in the Gavrovo-Tripolis zone are showing a dominating biotic origin, whereas it is also noticeable that some gas 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 IH and from the VA most likely predominantly contain abiogenic CH_4 deriving from CO_2 reduction. However, some of the gas discharges of the geothermal and volcanic-hydrothermal systems located in the neritic sedimentary Pelagonian, Gavrovo-Tripolis and Attico-cycladic zones (IH) and in Rhodope massif (HH), seem to exhibit significant contributions from thermogenic sources. The presence of abiotic methane was also recognized in the hyperalkaline aqueous solutions that are issuing from the ophiolites of Othrys and Argolida (Pindos zone (EH)). Most of the geothermal gases of Subpelagonian and Vardar/Axios zones (IH), the cold manifestations of the Rhodope massif (HH) and some of the volcanic-hydrothermal ones of the Attico-cycladic zone (VA) are presenting a microbial oxidation of CH_4.