



Origins of methane in volcanic and hydrothermal gas discharges as inferred from the chemical and isotopic signature of n-alkanes

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The origin of hydrocarbons, including methane, in hydrothermal fluids is commonly ascribed to various thermogenic degradation processes acting on pre-existing organic material at temperatures higher than 120-150 °C. At lower temperatures, hydrocarbon production is basically driven by bacteria. Carbon and hydrogen isotopic signatures can provide indications on these two different sources. Apart from microbial and thermogenic production, abiogenic generation of methane and heavier hydrocarbons in hydrothermal-volcanic systems is still a matter of debate. Fluids discharging from serpentinite-hosted hydrothermal systems, such as Lost City and Socorro Island, have relevant concentrations of methane and light alkanes. They were considered to be abiogenic in origin, mainly because of the occurrence of an isotopic inverse trend of the C1-C4 series and C1/C2+ ratios >1000. Effective production of abiogenic methane was also proposed to occur in continental-hydrothermal systems characterized by relatively oxidizing redox conditions.

In this study we present concentration and isotopic data of hydrocarbons in fluid emissions discharging in central and southern Italy. The peri-Tyrrhenian sector of peninsular Italy is characterized by the presence of a large number of CO₂-rich discharges where CH₄ rarely exceeds 1 % by vol. On the contrary CH₄-rich fluids are typically emitted on the Adriatic side. Measured d¹³C-CO₂ values do not show any preferential spatial distribution and indicate that this gas has a deep origin, likely related to thermometamorphic processes and mantle degassing. Conversely, the isotopic signatures of methane as well as distribution ratios of n-alkanes show significant variations. According to these, it can be distinguished between 5 different types of natural systems: 1) fluid discharges from the Campanian active volcanoes (Phlegrean Fields and Vesuvio), whose reservoir temperatures were estimated at 400-500 °C, are characterized by high d¹³C- and dD-CH₄ values and medium-to-high C1/C2+ ratios. These values are almost always higher than those typical for thermogenic methane; 2) hydrothermal systems with temperatures in the range of 250-400 °C (Mt. Amiata, Larderello, Latera, Manziana and Pantelleria) have high C1/C2+ ratios, but d¹³C- and dD-CH₄ values slightly more negative than those of the active volcanic emissions; 3) fluids emitted from discharges located between the main hydrothermal-volcanic systems and the western slope of the Apennine chain, where temperatures at the fluid source does not exceed 200 °C, show thermogenic d¹³C- and dD-CH₄ values and relatively low C1/C2+ ratios; 4) CH₄-rich gas discharges seeping out from the innermost eastern slope of the peninsula have thermogenic d¹³C- and dD-CH₄ values and C1/C2+ ratios as high as those of the volcanic gases; 5) CH₄-rich gas discharges of the Po Valley have extremely negative d¹³C- and dD-CH₄ as well as high C1/C2+ ratios, approaching those values typical for biogenic methane. The spatial distribution pattern of chemical and isotopic signatures suggests that methane contribution from abiogenic CO₂-reduction (Sabatier type reaction) becomes relevant at relatively high temperatures. At lower temperatures, thermogenic methane tends to prevail. Everywhere, where the fluid source is shallow and temperatures are lower than 120 °C, biogenesis is the dominating methane genetic process. This implies that in high temperature fluids methane and its higher chain homologues have distinct origins. The former depends on CO₂(CO)-CH₄ reactions, whereas the latter are mainly produced by thermal decomposition of organic matter. Isotopic and chemical data from several hydrothermal and volcanic areas, i.e. Nisyros, Yellowstone, Taiwan, El Tatio, Kizildere, are consistent with the proposed geochemical model.