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Stable carbon and hydrogen isotopes in CH_4 and light alkanes in magmatic and hydrothermal emissions from Vulcano Island (southern Italy)

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Vulcano Island, whose last eruption dates back to 1888-1890, is the southernmost island of the Aeolian Archipelago (southern Italy), a subduction-related volcanic arc in the Southern Tyrrhenian Sea. The active volcanic cone, namely La Fossa, displays an intense fumarolic activity, mostly occurring in its north-western sector. The fumaroles are characterized by outlet temperatures up to $\sim$400 ˚C, and a typical magmatic composition with relatively high concentrations of HCl, HF and SO_2. A second fumarolic area in the island occurs at Baia di Levante, the bay delimiting the eastern side of a flat isthmus that connects Vulcano to Vulcanello. In this area, low temperature ($\leq$ 100˚C) fumaroles and bubbling gases are discharged, displaying the typical hydrothermal-type composition, i.e. being characterized by relatively high contents of H_2S and hydrocarbons and by the absence of acid gas constituents. We have investigated the chemical and isotopic (δ^{13}C and δD) compositions of CH_4 and light alkanes (C_2H_6, C_3H_8, C_4H_{10}) of the fumaroles venting from both the crater and the bay area. To the best of our knowledge, the isotopic data of CH_4 from La Fossa crater presented in this work are the first ones on terrestrial high-temperature fumaroles ever reported. The main aim is to use these geochemical parameters to identify the fluid source(s) and the processes controlling the isotopic composition of the hydrocarbons. Our analytical results highlight that the δD–CH_4 values of gases from La Fossa crater are extremely depleted in deuterium (down to -657‰ vs. V-SMOW), whereas those of the beach fumaroles range from -100‰ to -85‰ vs. V-SMOW. The $^{13}C/^{12}C$ ratios of CH_4 and C_{2+} n-alkanes in the crater fumaroles also strongly differ from the isotopic signature measured in the hydrothermal gases, with the carbon isotopic composition of the low-temperature gases occurring significantly enriched in ^{13}C relative to the magmatic gases. Assuming a deep source for light hydrocarbon common to both the crater and the beach fumaroles, these preliminary data suggest the occurrence of not well defined secondary processes able to strongly modify their primary isotopic signature. Alternatively, two distinct hydrocarbon sources characterized by dramatically different δ^{13}C and δD values, feeding the magmatic and the hydrothermal emissions, respectively, are to be invoked to explain the observed data.