

Isotopic constraints on the origin of hydrocarbons in volcanic-hydrothermal emissions

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Hydrocarbon occurrences were identified as being abiogenic in origin, mainly based on a carbon isotope reversal between methane and ethane [1,2]. We have analyzed the carbon and hydrogen isotopic composition of methane as well as the carbon isotopic composition of ethane and propane contained in subaerial hydrothermal emissions from mafic and more evolved volcanic systems. These systems may provide all the prerequisites necessary for abiogenic hydrocarbon production. Sampled locations include Krafla, Namafjall, Reykjanes (all Iceland), Furnas and Fogo (Azores), Nisyros and Santorini (Greece), Vesuvio, Campi Flegrei, Ischia, Vulcano, Pantelleria (all Italy), Copahue (Argentina), Teide (Spain), Mageik and Trident (USA). Overall, $\delta^{13}\text{C}-\text{CH}_4$ varies over a large range from -5‰ to -70‰. Methane strongly depleted in ^{13}C and presumably of a microbial origin is even encountered in emissions exhibiting vent temperatures as high as 97°C. In contrast to methane, the carbon isotopic composition of propane varies in a relatively narrow range of 15‰ only, coinciding with the range characteristic for terrestrial and marine organic matter. There is a strong correlation between the carbon isotopic compositions of ethane and propane, but none between methane and its higher chain homologues. For some systems, carbon isotope reversals between methane and ethane are observed. However, even in these cases the close proximity of $\delta^{13}\text{C}-\text{C}_{2+}$ to the carbon isotopic composition of common terrestrial and marine organic matter may point to the importance of high-temperature pyrolysis of organic matter followed by open system degassing in controlling the carbon isotopic composition of the discharged hydrocarbons.

[1] Sherwood Lollar et al. (2002), *Nature* 416, 522-524

[2] Proskurowski et al. (2008), *Science* 319, 604-607