Extreme isotope fractionation of hydrothermal methane due to oxidation processes in hot springs of Central Greece

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The Greek territory belongs to the geodynamically active Alpine-Himalayan orogenic belt. As such, it shows intense seismic activity, active volcanic systems and areas of enhanced geothermal fluxes. One of these areas is the Sperchios basin and the northern part of Evia island in central Greece, which present widespread thermal manifestations [1]. Five of them with temperatures from 33 to 80°C present bubbling gases whose dominating species are either CO_2 or N_2. All gases contain from 27 to 4000 ppm of CH_4. The isotopic composition of CH_4 in these gases covers a wide range with $\delta^{13}C$ values ranging from -21.7 to +16.9‰ and $\delta^{2}H$ values ranging from -124 to +301‰.

The hottest manifestation displays the lowest isotopic values within the typical range of volcanic and geothermal systems. All the remaining samples fit a methane oxidation trend reaching very positive values. If we consider the lowest values as the deep hydrothermal marker the obtained $\Delta H/\Delta C$ values range between 5 and 13 which are close to those typical of microbially driven oxidation [2].

Although the outlet temperature of the hottest manifestations is at the upper limit for methanotrophic microrganisms [3], we can hypothesize that environmental conditions are not favorable for their survival at this site while they can thrive in the other strongly consuming methane and producing very positive isotopic values.

[1] D'Alessandro et al. (2014), *Mar. Petrol. Geol.* 55, 295-308; [2] Kinnaman et al. (2007), *Geochim. Cosmochim. Acta* 71, 271-283; [3] Sharp et al. (2014), *Environ. Microbiol.* 16, 1867-1878