

# Identifying and Quantifying Biological Consumption Processes of Subsurface Propane using Position-Specific Isotope Analysis

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Understanding the sources and sinks of natural gas hydrocarbons in the subsurface is of key importance for investigations of atmospheric chemistry, energy resources, and the global C-cycle [1]. Stable isotopes of carbon and hydrogen are widely used to identify the sources and sinks of hydrocarbons, but do not always lead to unique interpretations, let alone quantification of the processes involved.

We have developed a method to measure <sup>13</sup>C isotope composition of each position in propane [2]. The data from several gas fields shows a strong <sup>13</sup>C-enrichment on the central position of propane, with differences between the two positions of propane ( $D_{\text{central}} = d_{\text{central}} - d_{\text{Terminal}}$ ) as high as 50 ‰ [3]. This strong <sup>13</sup>C-enrichment has been linked to the biodegradation of propane by BuS5 bacteria [4], which degrades propane through an activation at the central position, hence the strong isotope fractionation ( $e_{\text{Terminal}} = -2.8$  ‰;  $e_{\text{central}} = -33$  ‰; [3]). However, the fractionation factors obtained in natural samples are lower compared with those obtained from pure bacterial incubations, suggesting additional processes are at play. Here, we report position-specific isotope fractionation factors for the recently isolated propane-degrading archaea (Laso-Perez et al. 2016) which culture experiments show lower isotope fractionation factor compared with bacteria ( $e_{\text{Terminal}} = -1.3$  ‰;  $e_{\text{central}} = -4.9$  ‰).

Applied to natural gas samples from Canada, USA, Australia and mud volcanoes in Japan [6], we show that between 60 % and 90 % of propane is degraded by archaea, the rest being degraded by bacteria. The approach presented here is useful to quantify cycling of hydrocarbons in the subsurface, in particular when linked to methane production from hydrocarbon biodegradation, a process that is still difficult to quantify [7].

[1] Etiope & Ciccioli **2009** *Science*, v323, 478

[2] Gilbert et al. **2016** *Geochim. Cosmochim. Acta* v177, 205

[3] Gilbert et al. **2019** *Proc. Natl. Acad. Sci.*, v116, 6653

[4] Kinemeyer et al. **2007** *Nature* v449, 898

[5] Laso-Pérez **2016** *Nature* v539, 396

[6] Etiope et al. **2011** *Appl. Geochem.* v26, 348

[7] Milkov **2011** *Org. Geochem.* v42, 184