Thermogenic and microbial methane in Southwest Ontario: Insights from $^{13}CH_3D$ and $^{12}CH_2D_2$

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Recent developments in high-resolution gas-source mass spectrometry[1] allow the measurement of rare methane isotopologues $^{13}CH_3D$ and $^{12}CH_2D_2$. When these two doubly-substituted species are consistent with internal equilibrium, they provide a reliable formation temperature for methane. Alternatively, where signatures are not consistent with equilibrium, they may provide information on kinetic effects critical to discriminating between different mechanisms and/or the rate of methane production[2,3].

We investigated hydrocarbon gases from the lower Paleozoic strata of Southwest Ontario (SWO) in order to test the applicability of these new tools in a geological context where the origin and the source of methane reflects a contribution from both thermogenic and microbial methane end-members. SWO lies between the Michigan and the Appalachian Basins on the Algonquin arch. Gas is predominantly composed of CH_4 (>70% in volume) with significant amounts of higher hydrocarbons (C_2+>5%). Positive correlations between $\delta^{13}C$ and δD for methane have been interpreted as resulting from different degrees of thermal maturation and/or from mixing between thermogenic and microbial endmembers [4].

We show that methane from Cambrian and Ordovician strata are all near internal equilibrium for $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ values, with formation temperature estimates from 120 - 200°C. Bulk D/H measurements for methane and co-existing waters also seem to be in hydrogen isotope equilibrium for the calculated temperatures, suggesting these gases remained in association with their formation waters.

In contrast, methane from Silurian strata are inconsistent with thermodynamic equilibrium. We report the lowest $\Delta^{12}CH_2D_2$ value (-20 ‰) measured so far in a natural environment. We show that Silurian strata are likely affected by the presence of microbial methane, although the concentrations of C_2+ support mixing with thermogenic components as well.

[1]Young et al., (2015). [2]Wang et al., (2015) [3]Young et al., (2016). [4]Sherwood Lollar et al., (1994)