

## Near equilibrium, non-thermogenic, methane in sedimentary systems: the unrecognized role of Anaerobic Oxidation of Methane?

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In continental sedimentary systems, methane originates from either the thermogenic cracking of organic matter and/or microbial methanogenesis. Typically microbial gas is considered to be rich in methane compared to the light hydrocarbon gases ( $C_1/C_{2+} > 1000$ ), and the methane to be relatively depleted in heavy isotopologues ( $^{13}CH_4$ ,  $^{12}CH_3D$ ,  $^{13}CH_3D$  and  $^{12}CH_2D_2$ ), reflecting Kinetic Isotope Effects (KIE) associated with microbial methanogenesis [1, 2, 3].

Using traditional ( $\delta^{13}C$ ,  $\delta D$  and  $C_1/C_{2+}$ ) and non-traditional ( $\Delta^{13}CH_3D$  and  $\Delta^{12}CH_2D_2$ ) systematics, we investigate two sedimentary systems where microbial methanogenesis has been proposed to be a significant contributor to the methane pool [4, 5]. In the Silurian units from Southwest Ontario containing saline porewaters, methane isotopologues reflect the dominance of KIE, consistent with an origin via microbial methanogenesis, although the relatively low  $C_1/C_{2+}$  (~10) indicates additional contribution from thermogenic gases. By contrast, in the Devonian Antrim Shale from the Michigan Basin where freshwater incursion is significant, gases exhibit elevated  $C_1/C_{2+}$  (>1000) and methane appears to fall along a line close to equilibrium in clumped isotope space. A recent study on the Antrim Shale [2] proposed that nearly-equilibrated microbial methane may result from significant reversibility of microbial methanogenesis under low substrate availability. However, such reversibility is not typically observed in laboratory cultures [3]. Instead, we suggest that nearly-equilibrated signatures result from the re-processing of the methane pool during Anaerobic Oxidation of Methane, and that elevated  $C_1/C_{2+}$  reflect the overall preferential *in situ* oxidation of methane, ethane and propane [5], rather than net production of methane.

[1] Wang et al., (2015) *Science*, 348 (6233), 428-431. [2] Stolper et al., (2015) *GCA*, 161, 219-247. [3] Young et al., (2017) *GCA*, 203, 235-264. [4] Sherwood Lollar et al., (1994) *BCEG*, 42(3), 283-295. [5] Martini et al., (1996) *Nature*, 383(6596), 155.