The potential of methane clumped isotopes to constrain formational environments of natural gas deposits

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Constraining the source and thermal maturity of hydrocarbon gases (C_{1-5} alkanes) in petroleum systems is often accomplished using measurements of $^{13}C/^{12}C$ and D/H ratios and molecular compositions [1]. Though a key starting point, these measurements do not directly yield quantitative insights into a gas's formational environment. Measurements of CH_4 clumped isotopologues appear, in many environments relevant to petroleum exploration, to reflect CH_4 formation temperatures [2-5]. Consequently 'clumped-isotope temperatures' (T_{CI}) have the potential to add new, quantitative constraints on gas formation conditions in hydrocarbon systems. First we will highlight and review the to-date measurements on samples from marine biogenic seeps (T_{CI}=6-16°C), mixed biogenic-thermogenic deposits (T_{CI}=34-115°C), conventional and migrated gas accumulations (T_{CI}=100-220°C), and 'unconventional' shale-gas reservoirs (T_{CI} =150-205°C).

Following initial work done in [3], we will then explore the meaning of these temperatures in the context of quantitative models of gas formation that combine basin thermal histories with oil/gas formation kinetics. Problematically, different kinetic models of thermogenic gas formation predict non-overlapping temperature ranges for methane formation using the same thermal history and organic source type. For example, the published models examined (n=14) predict average methane formation temperatures from 155-230°C. This model disagreement demonstrates the potential for T_{CI} measurements to add new insights to and independently test models of gas formation. Finally, we will incorporate T_{CI} measurements into gas formation models and will demonstrate that T_{CI} measurements add distinctive constraints to the thermal and petroleum generation histories of sedimentary basins.

[1] Whiticar (1999) *Chemical Geology*; [2] Stolper et al. (2014) *GCA*; [3] Stolper et al. (2014) *Science*; [4] Ono et al. (2014) *Analytical Chemistry*; [5] Wang et al., (in press) *Science*.