Clumped isotopes of methane: applications to both low and high temperature natural systems

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Methane (CH_4) is a key component of the carbon cycle forming from microbes at low temperatures (<80°C) and thermal maturation of organic carbon at elevated temperatures (>80°C). Distinguishing between the sources of CH_4 in nature can be difficult due to the migration and mixing of gases and overlapping chemical and isotopic signatures of various formational processes [1]. In contrast, formation temperatures clearly differentiate biogenic from thermogenic CH_4 and also CH_4 formed during different stages of hydrocarbon cracking. To this end, we developed a way to measure the abundances of CH_4 clumped isotopologues, which, for isotopically equilibrated systems, can be used as a geothermometer [2]. We present here 'clumped temperatures' from experiments and natural thermogenic and biogenic gases.

Measurements of clumped temperatures for shale gases (170-210°C) with contrasting thermal histories agree with independently modeled formation temperatures. CH_4 from pyrolysis experiments at 360 and 600°C yield clumped temperatures within error of experimental temperatures. We interpret these results to indicate that clumped temperatures reflect thermogenic CH_4 formation temperatures. Additionally, analyses of gases from a migrated hydrocarbon system where formation temperatures are not known yield clumped temperatures (155-220°C) that help discriminate among various interpretative frameworks.

Finally, measurements of biogenic CH_4 from natural systems yield clumped temperatures consistent with their low temperature environmental settings. In contrast, pure-culture experiments can exhibit kinetic isotope effects for clumped temperatures. Combined, these results suggest that methane clumped isotopes can be used for geothermometry in a broad variety of natural settings.

[1] Whiticar (1999), *Chemical Geology*. [2] Stolper *et al* (2014), GCA.