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Tracking origin and evolution of natural methane with clumped isotopologues

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Methane is the primary component of natural gas and the second most influential greenhouse gas in the atmosphere. Natural occurring methane has multiple origins, including thermal breakdown of larger organic compounds and macromolecular materials, microbial methanogenesis, and abiotic reactions; this diversity of origins complicates source identification and quantitative apportionment. Conventional stable isotope methods for methane forensic assignment are based on empirical observations and often lead to ambiguous results due to overlapping compositions of end members. The emerging studies of clumped isotopes of methane complement these conventional methods and improve both apportionment and detailed interpretations of conditions and mechanisms of methane formation.

Advances in high resolution sector IRMS have permitted measurements of the relative abundances of doubly-substituted methane isotopologues ($^{13}CH_3D$ and $^{12}CH_2D_2$). Large datasets of clumped isotopes for methanes from various sources have been established. Thermodynamic equilibrium with respect to clumped isotope reactions is common in thermogenic gases, particularly at higher thermal maturities, demonstrating the utility of 'methane clumped isotope thermometry'. Exceptions include oil-associated gases at early maturation, which have $\delta^{12}CH_2D_2$ lower than equilibrium, but approaching equilibrium with increasing maturity. Similarly, we found large depletion in $\delta^{12}CH_2D_2$ from laboratory pyrolysis of alkane. These findings indicate that the immediate cracking of hydrocarbons expresses kinetic isotope effects that can be subsequently erased by equilibration. $\delta^{12}CH_2D_2$ and $\delta^{13}CH_3D$ values of thermogenic gases evolve through a defined trajectory, demonstrating a pattern of transitioning from kinetic control to thermodynamic control in catagenesis.

Microbial methane in the environment and laboratory exhibits large ranges in both clumped isotopologues. Biogenic Methanes from marine environments have nearly equilibrated $\delta^{13}CH_3D$ and $\delta^{12}CH_2D_2$ or lower $\delta^{12}CH_2D_2$, whereas freshwater methane tends to be anomalously low in both. It is suggested that low H_2 concentration and methanogenesis rates promote reversibility that lead to equilibration. Furthermore, methane from methylotrophy tends to be have lower $\delta^{13}CH_3D$ and $\delta^{12}CH_2D_2$ than that from CO_2 reduction, and there is evidence that anaerobic oxidation drives methane to equilibrium post formation.