EGU22-4029
https://doi.org/10.5194/egusphere-egu22-4029
EGU General Assembly 2022

Isotopic characterization of methane: insights from clumped isotope ($^{13}CDH_3$ and CD_2H_2) measurements

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Atmospheric methane is an important greenhouse gas, and various methods are used to identify and quantify its sources. The measurement of bulk isotopic composition ($\delta^{13}C$ and δD) is a widely used characterization technique, but due to the overlap of source signatures, it is often difficult to distinguish between thermogenic, microbial, and other sources. With the advancement of high-resolution mass spectrometry, it is now possible to measure the rare clumped isotopologues of methane $^{13}CDH_3$ and CD_2H_2.

This novel method can give additional information to help constrain methane sources and processes. The clumping anomaly is temperature-dependent and can thus be used to calculate the formation or equilibration temperature when methane is in thermodynamic equilibrium. In case of thermodynamic disequilibrium, the clumped signatures can be exploited to identify various kinetic gas formation and fractionation (mixing, diffusion, etc.) processes.

We have developed a technique to extract pure methane from air and water samples and to measure the clumped isotope signatures ($\Delta^{13}CDH_3$ and ΔCD_2H_2) with high precision and reproducibility, using the Thermo Ultra mass spectrometer. We will present the current capabilities of this setup, and the results of the first sets of samples measured from different natural environments.