

## Applying dual isotopic fractionation of methane as sensitive tracers for microbial oxidation

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The dual (carbon and hydrogen) isotopic compositions in methane have provided important information regarding their sources, transportations, and reactions in the environments. Recently, a highly sensitive continuous-flow IRMS (CF-IRMS) method was developed to analyze the carbon and hydrogen isotope compositions of methane in atmosphere and environment with enriched methane. They have reduced the required sample size drastically. However, they have room for improvement. Applying methods to various environmental samples has been difficult, especially for those with depleted levels of methane.

We developed a rapid, sensitive, and automated analytical system to determine carbon and hydrogen isotope compositions of methane in nmol quantities in natural waters by using continuous-flow isotope ratio mass spectrometry (CF-IRMS).

The analytical system consisted of a purging line to extract dissolved methane in waters, a gas chromatograph for further purification of methane, a thermal furnace to decompose methane to molecular hydrogen, and a CF-IRMS system. In addition, we used pneumatic valves and pneumatic actuators in the system so that we could operate the system automatically based on timing software on a personal computer. The analytical precision was better than 4 per mil for hydrogen isotopic analysis with more than 2 nmol methane injections for a single measurement.

We determined the dual isotopic compositions of methane in Lake Towada in September in 2011. We found distinct carbon and hydrogen isotopic fractionation of methane during microbial oxidation in hydrothermal plume.

Keywords: methane, hydrothermal plume, hydrogen isotope fractionation, carbon isotope fractionation, dual isotopic compositions