# Experimental calibration of methane-$H_2$-$H_2O$ hydrogen isotope fractionation factor from 4-160°C

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Methane is an important greenhouse gas, energy resource, and microbial metabolite. Methane carbon and hydrogen stable isotopic compositions (given by $\delta^{13}C$ and $\delta D$ values) are commonly used to constrain gas origins (e.g., biogenic vs. thermogenic; Whiticar, 1999). Based on methane clumped isotopic studies, it has been recently proposed that both biogenic and thermogenic methane may form in or later attain hydrogen isotopic equilibrium with water at temperatures <200°C (Stolper et al., 2014; Wang et al., 2015; Giunta et al., 2019).

To evaluate this requires knowledge of the hydrogen isotopic fractionation factor between methane and liquid water ($\alpha_{CH4\text{-}H2O,l}$) at temperatures relevant to biogenic and thermogenic gas formation (typically <200°C). One experimentally based calibration exists between 200-500°C (Horibe and Craig, 1995). Theoretical calculations between $CH_4$ and $H_2O$ vapor vary by as much as 170‰ at 0°C (Richet et al., 1977 vs. Bottinga, 1969). Such uncertainty is carried into calculations of $\alpha_{CH4\text{-}H2O,l}$ based on theory. Consequently, knowledge of $\alpha_{CH4\text{-}H2O,l}$ below 200°C is uncertain.

Here, we present an experimentally based calibration of $\alpha_{CH4\text{-}H2O,l}$ from 4-160°C. Specifically, we equilibrated $CH_4$ and $H_2$ in the laboratory with catalysts and used independent knowledge of $\alpha_{H2\text{-}H2O,l}$ to create an $\alpha_{CH4\text{-}H2O,l}$ calibration. Attainment of equilibrium was verified by bracketing experiments: Some experiments were started with an $\alpha_{CH4\text{-}H2}$ of 1.1 and increased to values of 2 to 3.7. Other experiments were initialized with elevated $\alpha_{CH4\text{-}H2}$ values of 3.3 to 5.1 by pre-equilibrating in refrigerators or freezers. Bracketed $\alpha_{CH4\text{-}H2}$ values agree within 3‰ in all cases (i.e., within analytical precision).

With this calibration, we compare measured $\delta D_{CH4}$ and $\delta D_{H2O}$ values from a variety of environments with known sampling temperatures. We show that equilibrium appears to be commonly attained in some (but not all) biogenic systems. Based on this data compilation, we will discuss how methane's hydrogen isotopic composition reflects its formational mechanisms.