Experimental calibration of methane-H₂-H₂O 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 δ¹³C and δD 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 (αCH₄-H₂O) 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 CH₄ and H₂O vapor vary by as much as 170‰ at 0°C (Richet et al., 1977 vs. Bottinga, 1969). Such uncertainty is carried into calculations of αCH₄-H₂O based on theory. Consequently, knowledge of αCH₄-H₂O below 200°C is uncertain.

Here, we present an experimentally based calibration of αCH₄-H₂O from 4-160°C. Specifically, we equilibrated CH₄ and H₂ in the laboratory with catalysts and used independent knowledge of αH₂-H₂O to create an αCH₄-H₂O calibration. Attainment of equilibrium was verified by bracketing experiments: Some experiments were started with an αCH₄-H₂O of 1.1 and increased to values of 2 to 3.7. Other experiments were initialized with elevated αCH₄-H₂O values of 3.3 to 5.1 by pre-equilibrating in refrigerators or freezers. Bracketed αCH₄-H₂O values agree within 3‰ in all cases (i.e., within analytical precision).

With this calibration, we compare measured δD(CH₄) and δD(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.