

Absence of Memory Effects in Shale Maturation Experiments with 'Heavy Water' $^2\text{H}_2\text{O}$

MS. KELSEY E DOIRON¹, ARNDT SCHIMMELMANN¹,
MARIA MASTALERZ², PETER E SAUER¹ AND SIMON C
BRASSELL¹

¹Indiana University

²Indiana University, Indiana Geological & Water Survey

Presenting Author: kedoiron@indiana.edu

Laboratory experiments examining the role of water during hydrocarbon generation have often utilized hydrogen isotopes as critical tracers [1-8]. This approach has helped in evaluating the yield and isotopic composition of gases produced from shale during heating experiments at a range of maturities, especially when the low temperatures employed are insufficient for gas generation by catagenesis (i.e., thermal cleavage of C-C bonds, termed cracking). Building on these data, a further suite of long-term (12-38 months), low-temperature heating experiments (80 or 100 °C) with samples from the Second White Specks Formation and New Albany Shale employed waters with different abundances of ^2H , i.e., unlabeled water (L; $\delta^2\text{H} = -137\text{‰}$) and labeled waters with 0.2 or 1 mL of ~99 wt. % 'heavy water' $^2\text{H}_2\text{O}$ (H), or a mix (H+L) of the two (Fig. 1). Measurements of the $\delta^2\text{H}$ isotope ratio of the methane generated yielded values as high as +169,000 ‰, confirming the role of water in methane formation under these experimental conditions. Employing ~99 wt. % deuterated water produced methane with $\delta^2\text{H}$ values far beyond the normal analytical range of the mass spectrometer and outside the availability of reference materials for accurate calibration. At times, samples exceeded the range of the detector and yet no memory effects were observed when standards were analyzed immediately after each sample, which confirms the lack of isotopic exchange between H from methane and other forms of H within the analytical system, as well as limited adsorption of methane on solid surfaces. These promising results suggest that future heating experiments can employ $^2\text{H}_2\text{O}$ without the concern that memory effects will compromise isotopic measurements, provided appropriate precautions are used. Moreover, the $\delta^2\text{H}$ values measured for generated methane enables estimation of the proportion that was derived from water, which for these experiments is less than 8 %.

References

- [1] Hoering (1984) [https://doi.org/10.1016/0146-6380\(84\)90014-7](https://doi.org/10.1016/0146-6380(84)90014-7)
- [2] Lewan (1997) [https://doi.org/10.1016/S0016-7037\(97\)00176-2](https://doi.org/10.1016/S0016-7037(97)00176-2)
- [3] Schimmelmann et al. (1999) [https://doi.org/10.1016/S0016-7037\(99\)00221-5](https://doi.org/10.1016/S0016-7037(99)00221-5)
- [4] Sessions et al. (2004) <https://doi.org/10.1016/j.gca.2003.06.004>
- [5] Schimmelmann et al. (2006) <https://doi.org/10.1146/annurev.earth.34.031405.125011>

- [6] Wei et al. (2018) <https://doi.org/10.1016/j.gca.2018.04.012>
- [7] Wei et al. (2019) <https://doi.org/10.1016/j.orggeochem.2018.12.004>
- [8] Ma et al. (2021) <https://doi.org/10.1016/j.orggeochem.2021.104224>

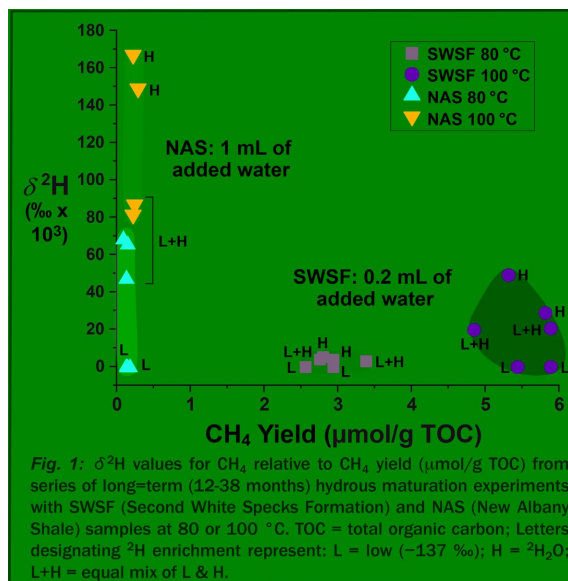


Fig. 1: $\delta^2\text{H}$ values for CH_4 relative to CH_4 yield ($\mu\text{mol/g TOC}$) from series of long-term (12-38 months) hydrous maturation experiments with SWSF (Second White Specks Formation) and NAS (New Albany Shale) samples at 80 or 100 °C. TOC = total organic carbon; Letters designating ^2H enrichment represent: L = low (-137‰); H = $^2\text{H}_2\text{O}$; L+H = equal mix of L & H.