

CH₄ clumped isotope signatures in an Ordovician aquiclude: insight into methanogenic *n*-alkanes degradation

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Previous geochemical investigations of a low-permeability ($K_f \leq 10^{-13}$ m.s⁻¹) and high-salinity (5.8 M Cl⁻) aquiclude, situated in the Upper Ordovician of the Michigan Basin, suggest a microbial origin for porewater CH₄ and CO₂ based on their stable isotope values. Furthermore, compound specific isotope analysis on *n*-alkanes showed a biodegradation overprint of their expected maturation isotopic signatures, stratigraphically linked to the biogenic CH₄. This suggested that *n*-alkane biodegradation at least partially fueled methanogenesis in this aquiclude as a late diagenetic process. To further constrain the link between *n*-alkanes biodegradation and CH₄ formation, and to investigate the temperature of CH₄ formation or isotopic equilibration, we performed CH₄ clumped isotope measurements over the entire depth profile of this aquiclude.

The clumped isotope analyses indicated CH₄ internal equilibration temperatures (15-120°C), confirming both a biogenic and a thermogenic component. Moreover, re-evaluation of the bulk $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of CH₄, CO₂, H₂O and *n*-alkanes revealed an apparent H-isotopic disequilibrium between CH₄ and H₂O, in contrast to apparent C-isotopic equilibrium between CH₄ and CO₂ and internal isotopic equilibrium based on Δ_{18} values. However, apparent H- and C-fractionation factors between non-gaseous *n*-alkanes and CH₄ seem to have reached thermodynamic equilibrium consistent with apparent CH₄ clumped isotope equilibrium between 15-35°C. We explore the hypothesis that this shale gas formation analogue could have hosted methanogenic alkane degradation that did not induce full equilibration of H-isotopes between H₂O and CH₄.