**Appendix of**

The evolution of intra- and inter-molecular isotope equilibria in natural gases with thermal maturation

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4. **Kinetic parameters and kinetic isotope effects (KIE) used in methane generation-exchange modeling**

|  |  |  |  |
| --- | --- | --- | --- |
| Type | Parameter | Value | Note |
| KIE | α13CH3 | 0.978 | Tang et al. (2000) |
| α12CH2D | 0.7 | Ni et al. (2011) |
| α13CH2D | γ13CH2D\*α13CH3 \*α12CH2D | # |
| α12CHD2 | γ12CHD2(α12CH2D)2 | # |
| αcap | 0.33 | Extrapolation to (Wang et al., 2009) |
| Precursor composition | δ13Cpre | -27‰ | Eldrett et al. (2014) |
| δDpre | -100‰ | Assumption |
| Δ13CH2Dpre | 2‰ | Assumption (equilibrium) |
| Δ12CHD2pre | 6‰ | Assumption (equilibrium) |
| δDpre-cap | -100‰ | Assumption |
| Exchange kinetics | A | 2.45×1010 s-1 | Experimental results from Koepp (1978) |
| Ea | 200 kJ/mol | Experimental results from Koepp (1978); Adjusted for catalysis |

# γ13CH2D and γ12CHD2 represent additional KIE resulted from clumped isotope effect (a.k.a. clumped isotope KIE). We ran the model with combinations of a few extreme values in the figure below, indicated by numbers in the parenthesis, with the order of (γ13CH2D, γ12CHD2). We found that results are generally insensitive to changes in γ13CH2D and γ12CHD2. Therefore, we set both to 1.



1. **Basin modeling of selective wells in the Eagle Ford Shale**

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1. **List of publications and reports with compound-specific hydrogen isotope data of C1, C2 and C3**

|  |  |
| --- | --- |
| Reference | Note |
| Krouse (1983) | Partially excluded – data with well depth shallower than 1700m are excluded due to microbial activity  |
| Prinzhofer and Huc (1995) | Included |
| Rich et al. (1995) | Excluded due to biogenic methane |
| Hulston et al. (2001) | Included |
| Strapoć et al. (2007) | Excluded due to biogenic methane |
| Boreham and Edwards (2008) | Excluded due to biodegradation |
| Liu et al. (2008) | Excluded due to thermochemical sulfate reduction (TSR) |
| Jin et al. (2009) | Excluded due to the possibility of abiotic origin |
| Burruss and Laughrey (2010) | Included |
| Rodriguez and Paul Philp, (2010) | Included |
| Dai et al. (2012) | Included |
| Dai et al. (2014) | Partially excluded – some samples from the Sichuan Basin have the sample ID as Dai et al., (2012) |
| Ni et al. (2015) | Included |
| Wang et al. (2015) | Partially excluded to avoid over-representation of the Sichuan Basin, Ordos Basin and Turpan-Hami Basin (as they have been presented in earlier studies) |
| Meng et al. (2017) | Excluded due to biodegradation |
| Thiagarajan et al., (2020) | Partially excluded; samples from Jen-Olla and Genesis are biogenic. |
| Geoscience Australia, ’ORGCHEM’ database | Samples from the Browse Basin and Otway Basin. |

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