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Position-specific distribution of hydrogen isotopes in natural propane: effects of thermal cracking, equilibration and biodegradation

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Abstract

Intramolecular isotope distributions, including isotope clumping and position specific fractionation, can provide proxies for the formation temperature and formation and destruction pathways of molecules. In this study, we explore the position-specific hydrogen isotope distribution in propane. We analyzed propane samples from 10 different petroleum systems with

high-resolution molecular mass spectrometry. Our results show that the hydrogen isotope fractionation between central and terminal positions of natural propanes ranges from -102‰ to +205‰, a much larger range than that expected for thermodynamic equilibrium at their source and reservoir temperatures (36–63‰). Based on these findings, we propose that the hydrogen isotope structure of catagenic propane is largely controlled by irreversible processes, expressing kinetic isotope effects (KIEs). Kinetic control on hydrogen isotope composition of the products of thermal cracking is supported by a hydrous pyrolysis experiment using the Woodford Shale as substrate, in which we observed isotopic disequilibrium in the early stage of pyrolysis. We make a more general prediction of KIE signatures associated with kerogen cracking by simulating this chemistry in a kinetic Monte Carlo model for different types of kerogens. In contrast, unconventional shale fluids or hot conventional reservoirs contain propane with an isotopic structure close to equilibrium, presumably reflecting internal and/or heterogeneous exchange during high temperature storage (ca. 100–150 °C). In relatively cold (<100 °C) conventional gas accumulations, propane can discharge from its source to a colder reservoir, rapidly enough to preserve disequilibrium signatures even if the source rock thermal maturity is high. These findings imply that long times at elevated temperatures are required to equilibrate the hydrogen isotopic structure of propane in natural gas host rocks and reservoirs. We further defined the kinetics of propane equilibration through hydrogen isotope exchange experiments under hydrous conditions; these experiments show that hydrogen in propane is exchangeable over laboratory timescales when exposed to clay minerals such as kaolinite. This implies rather rapid transfer of propane from sources to cold reservoirs in some of the conventional petroleum systems. Propane is also susceptible to microbial degradation in both oxic and anoxic environments. Biodegradation of propane in the Hadrian and Diana Hoover oil fields (Gulf of Mexico) results

in strong increases in central-terminal hydrogen isotope fractionation. This reflects preferential attack on the central position, consistent with previous studies.

1. Introduction

Natural propane and other volatile hydrocarbons in the subsurface are of great economic value and environmental significance. Compositional and stable isotope properties of these gases have been widely used to help trace their origins and fates (e.g., Berner and Faber, 1996; Whiticar, 1999). Recent studies of the intramolecular isotope structures of these gaseous compounds bring novel constraints to these processes (Stolper et al., 2014a; Wang et al., 2015; Young et al., 2017; Eiler et al., 2018; Piasecki et al., 2018; Clog et al., 2018; Xia and Gao, 2019). These new methods are revealing fundamental geochemical processes that control the geological distributions of hydrocarbons.

Propane (C_3H_8 , or $\text{CH}_3\text{—CH}_2\text{—CH}_3$) has two chemically nonequivalent sets of atomic sites: the central CH_2 group and the terminal CH_3 groups. The carbon and/or hydrogen isotope differences between these two positions have been analyzed by GC-pyrolysis-GC-IRMS (gas chromatography isotope ratio mass spectrometry) (Gilbert et al., 2016; Li et al., 2018), biochemical degradation with GC-IRMS (Gao et al., 2016), high-resolution direct molecular mass spectrometry (Piasecki et al., 2016a; Xie et al., 2018) and nuclear magnetic resonance (Liu et al., 2018). It has been shown that site-specific isotopic measurements are able to differentiate abiotic propane sources from common thermogenic propane (Suda et al., 2017), track thermal maturation (Piasecki et al., 2018; Liu et al., 2019; Julien et al., 2020), and identify residues of subsurface microbial degradation (Gilbert et al., 2019). Position-specific hydrogen isotopes are especially interesting because hydrogen may undergo isotopic exchange at the conditions of

some gas reservoirs, potentially driving propane to intramolecular hydrogen isotope equilibrium. The temperature dependence of equilibrium isotope fractionation between the central and terminal hydrogen positions has been theoretically predicted (Webb and Miller, 2014; Piasecki et al., 2016b) and experimentally calibrated (Xie et al., 2018). Therefore, position-specific hydrogen isotope distribution in propane can potentially work as a ‘geothermometer’ that could track the equilibration temperature at which propane has been generated and/or stored. And, because the approach to equilibrium may be time dependent, it is possible that site specific hydrogen isotope fractionation may serve as a kind of ‘geospeedometer’ for evaluating gas reservoir storage times. This kinetic property in the carbonate geothermometer has been shown to have significant value for constraining thermal histories of rock samples (e.g., Passey and Henkes, 2012; Shenton et al., 2015; Stolper and Eiler, 2015; Lawson et al., 2018; Mangenot et al., 2019; Ingalls, 2019). If such a property were demonstrated in propane, it would provide an opportunity to assess the thermal histories of fluids that migrate within sedimentary systems.

In this study, we explore what controls the position-specific hydrogen isotope distribution in propane via natural observations and laboratory experiments. We present a dataset of measurements of propane from produced natural gases in 10 different, globally distributed petroleum systems. In addition, we report isotope exchange experiments and hydrous pyrolysis experiments designed to investigate the timescales and mechanisms of isotope exchange and the position-specific isotope effects of thermal cracking. Finally, we construct a model of the position-specific isotopic fractionations associated with kerogen cracking as a means of interpreting and extrapolating from laboratory cracking experiments. We show that the geochemistry of the source rock determines the primary position-specific hydrogen isotope signature in propane immediately after formation by kerogen cracking, that exchange in

relatively hot reservoirs brings the position-specific hydrogen isotope structure of propane close to equilibrium, and that biodegradation in shallow reservoirs leads to distinctive central-terminal hydrogen isotope fractionations.

2. Samples

We examined natural gas samples from 18 different wells belonging to the following 10 petroleum fields: Diana Hoover (U.S. Gulf of Mexico), Galveston 209 (U.S. Gulf of Mexico), Genesis (U.S. Gulf of Mexico), Hadrian North and South (U.S. Gulf of Mexico), Hogsback (Wyoming, USA), Eagle Ford (Texas, USA), Briggs (Texas, USA), Santa Ynez Unit (SYU) (California, USA), Sleipner Vest (North Sea, Europe), and Potiguar Basin (Brazil). Sampled well depths range from 1880 to 4618 m with reservoir temperatures ranging from 42°C to 143°C.

All the gas samples come from conventional reservoirs (where gas migrated from the source rock is trapped in permeable formation) except those from the Eagle Ford Shale (where gas is retained in the low permeability source rock). One of the samples from Eagle Ford (Las Raices 22H) and samples from Sleipner Vest and Hogsback are non-associated gases (free gas not dissolved in oil). The rest of our samples are oil-associated solution gases.

3. Methods

3.1 Nomenclature

The hydrogen isotope fractionation between central and terminal positions of propane (or, the ‘central-terminal fractionation’) can be expressed by the epsilon notation:

$$\epsilon D_{C-T} = 1000 * \left(\frac{\left(\frac{D}{H} \right)_C}{\left(\frac{D}{H} \right)_T} - 1 \right) \quad \#(1)$$

where $\left(\frac{D}{H}\right)_C$ and $\left(\frac{D}{H}\right)_T$ are the hydrogen isotope ratios of the central and terminal positions, respectively. Neglecting the non-statistical distribution of multiply deuterated propane (a trivial contribution to overall D abundance in natural samples; e.g., a 10 ‰ enrichment in the doubly deuterated propane would only increase $\epsilon_{D_{C-T}}$ by 0.005‰), the above nomenclature is equivalent to the following function based on the concentrations of specific singly deuterated isotopomers:

$$\epsilon_{D_{C-T}} = 1000 * \left(\frac{3[CH_3CHDCH_3]}{[CH_2DCH_2CH_3]} - 1 \right) \quad \#(2)$$

where 3 is the symmetry number ratio between CH_3CHDCH_3 and $CH_2DCH_2CH_3$. Note that D/H is synonymous to the $^2H/^1H$ nomenclature suggested by IUPAC (Dukov, 2007). We opt to use D instead of 2H throughout this paper for consistency with our previous publications.

3.2 Sample purification

Propane is generally a minor component (<5%) of natural gases and needs to be isolated prior to mass spectrometric analysis. We perform an initial purification via cryogenic distillation using a vacuum line consisting of calibrated volumes, cryogenic traps, and a liquid-helium-cooled cryostat (CTI-Cryogenics and Janis Research Co.). Using a previously described protocol of cryostat cooling and warming cycles (Stolper et al., 2014b; Piasecki et al., 2016a), H_2 , He, and N_2 are pumped away and pure fractions of CH_4 , and C_2H_6 are isolated. The residual fraction containing CO_2 and the series of $\geq C_3$ alkanes is transferred into a second glass vacuum line where CO_2 is removed by adsorption to an Ascarite II (NaOH-coated-silica) trap as described by Piasecki et al. (2016a). This refined gas fraction is collected in a pre-evacuated glass U-tube with a valve and polytetrafluoroethylene (PTFE) septum.

The final sample preparation step uses gas chromatography with cryogenic fraction collection to isolate propane from the remaining $\geq C_4$ alkanes. Samples for this study are prepared on a HP 5890 gas chromatograph instrument equipped with a Restek ShinCarbon packed column (ST 80/100, 2 mm ID, 1/8" OD, 2 m length). The gas sample is transferred from the glass u-tube into the GC injector (splitless) via gas-tight syringe (15-20 ml injections). Pure He at 30 ml/min is used as the carrier gas and the GC oven was kept isothermal at 40 °C for 90 min. Under these conditions, the retention time for propane is 24.4 min. From 22–26 min after the sample injection, all column gas flow is diverted into a LN₂ trap to collect the purified propane. The LN₂ trap is then connected to the glass vacuum line and the propane transferred into a flame-sealed glass tube.

Piasecki et al. (2016a) tested the cryogenic separation and Ascarite II cleanup with artificial mixtures of propane, ethane and CO₂. They concluded that both procedures are highly efficient (>97% recovery) and observed no carbon isotope fractionation of the purified propane when compared to the starting propane. We carried out additional tests using a laboratory reference gas mixture simulating a natural gas composition (80% C₁, 10% C₂, 5% C₃, and 5% CO₂) and found that the cryogenic separation and CO₂ adsorption procedures together have a recovery efficiency for propane of 93–103%. We observed no significant difference in molecular hydrogen isotope ratio between the starting propane and the final propane isolate. We conclude that this propane purification procedure is effectively quantitative and isotopically non-fractionating.

Upon analysis, each sample is carefully examined for contamination via a wide-range mass scan on a double focusing sector mass spectrometer (the Thermo Scientific DFS described below).

The most common contaminants are butane (C₄H₁₀⁺ at m/z=58.0777), ethane (C₂H₆⁺ at m/z=30.03017), and CO₂ (m/z=43.98943). We consider a propane sample gas to be clean when

ion beams corresponding to each of the contaminants is less than 1% of that for propane, which has been tested in Piasecki et al. (2016a). In cases where severe contamination is identified, we either repeat the cryogenic and CO₂ cleanup procedures (above) until the gas is nominally pure or discarded the sample.

3.3 Measurements

3.3.1 Position-specific hydrogen isotope analysis

We analyze purified propane samples for their position-specific hydrogen isotope ratios on the Thermo Scientific Double Focusing Sector (DFS) mass spectrometer. Propane gases are introduced to the ion source through the bellows and metal capillaries of a dual-inlet system adapted from a Thermo Scientific Delta Plus IRMS. All sample measurements are made by sample/standard bracketing, referenced to an intra-laboratory working gas, CITP-1. CITP-1 has a δD of -179‰ and ϵD_{C-T} of -26‰ (Xie et al., 2018). The DFS can render very high mass-resolution ($M/\Delta M \sim 80\text{-}100,000$), though we operate it at resolutions of 35,000 (full-width half-maximum definition) for propane analysis.

Each sample measurement examines two isotopologue ratios— $[C_2H_4D]/[C_2H_5]$ (i.e., the D/H ratio of the C₂H₅ fragment ion) and $[C_3H_7D]/[C_3H_8]$ (the D/H ratio of the full molecular ion)—to constrain position-specific hydrogen isotope distribution. Each isotope ratio measurement is made using either of two mass-spectrometric methods: electric scan or multiple ion detection (MID). In an electric scan analysis, we vary the accelerating voltage across a narrow range to rapidly scan the isotopologue ions of interest across the single detector. We derive the peak areas of each isotopic species by fitting the shape and height of the resulting mass spectra (i.e., a plot of intensity vs. mass) and use them to calculate isotopologue ratios. In a MID analysis, the magnet current is repeatedly jumped to translate two or more ion beams into positions where

they intercept the detector, and the intensity ratios of these measurements constrain the abundance ratios of the species of interest. Both $[C_2H_4D]/[C_2H_5]$ and $[C_3H_7D]/[C_3H_8]$ ratios can be determined directly by this method.

Because an electric scan examines only a narrow mass range (~ 0.1 AMU), it is capable of constraining $[C_2H_4D]/[^{13}C^{12}CH_5]$ but not $[C_2H_4D]/[C_2H_5]$, and similarly constrains $[C_3H_7D]/[^{13}C^{12}C_2H_8]$ but not $[C_3H_7D]/[C_3H_8]$. For this reason, electric-scan data can be interpreted as constraints on the site-specific hydrogen isotope structure only when combined with independent constraints on the ratios: $[^{13}C^{12}CH_5]/[C_2H_5]$ and $[^{13}C^{12}C_2H_8]/[C_3H_8]$. In two samples, we combined $[C_2H_4D]/[^{13}C^{12}CH_5]$ and/or $[C_3H_7D]/[^{13}C^{12}C_2H_8]$ ratios measured by electric scan with $[^{13}C^{12}CH_5]/[C_2H_5]$ and/or $[^{13}C^{12}C_2H_8]/[C_3H_8]$ ratios measured for the same gases from Piasecki et al. (2018). In another four samples, we combined $[C_2H_4D]/[^{13}C^{12}CH_5]$ and $[C_3H_7D]/[^{13}C^{12}C_2H_8]$ ratios measured by electric scan with $[^{13}C^{12}CH_5]/[C_2H_5]$ and $[^{13}C^{12}C_2H_8]/[C_3H_8]$ ratios measured by MID method (above). Data for the rest of the samples are acquired by MID method directly. Specific methods for data acquisition of each sample are labeled in Table 1.

Regardless of the mass spectrometric method used, we typically prepare 50 μmol of propane for each sample. Acquisition of either $[C_2H_4D]/[C_2H_5]$ and $[C_3H_7D]/[C_3H_8]$ ratios lasts 1 hour, achieving a standard error of around 1‰ (Table 1). ϵD_{C-T} is calculated from constraints on $[C_2H_4D]/[C_2H_5]$ and $[C_3H_7D]/[C_3H_8]$ ratios using the data processing methods detailed in Xie et al. (2018).

3.3.2 Gas compositional analysis and compound-specific isotope analysis

A separate split of each gas sample was sent to Stratum Reservoir Services (formerly Isotech Laboratories) in Champaign, Illinois, for both molecular compositional analysis and compound-specific isotope analysis ($\delta^{13}\text{C}$ and δD). For molecular compositional analysis, gas samples were injected into a GC system equipped with both thermal conductivity detector and flame ionization detector. Relative precision was typically $\pm 5\%$ relative for $\text{C}_1\text{-C}_3$ hydrocarbon abundance and $\pm 10\%$ relative for $\text{C}_4\text{-C}_5$ hydrocarbon abundance.

A gas chromatography pyrolysis isotope-ratio mass spectrometer (GC-P-IRMS) system was used for δD analysis. In a GC-P-IRMS, gas mixtures were separated by the GC and pyrolyzed to H_2 for D/H ratio measurement with an IRMS. Typical precision for these analyses is $\pm 5\text{‰}$. We report δD values vs. the Vienna Standard Mean Ocean Water (VSMOW) standard. A gas chromatography combustion isotope-ratio mass spectrometer (GC-C-IRMS) system was used for $\delta^{13}\text{C}$ analysis. The GC system separates the individual hydrocarbons that are then combusted by a cupric oxide furnace into CO_2 for $^{13}\text{C}/^{12}\text{C}$ ratio measurement with an IRMS. Typical precision for these analyses is $\pm 0.3\text{‰}$. We report $\delta^{13}\text{C}$ values vs. the Vienna Pee Dee Belemnite (VPDB) standard.

3.3.3 Methane clumped isotope analysis

For each gas sample, a separate aliquot is taken and cryogenically purified to recover methane, which was then measured for Δ_{18} on the prototype 253 Ultra at Caltech (Eiler et al., 2013). Gas purification and handling protocols, mass spectrometry methods and protocols for data standardization follow Stolper et al. (2014b).

3.3.4 Well temperature measurements

A borehole temperature is measured at each natural gas well using standard petroleum-industry methods. However, the measured temperature is usually colder than actual formation temperature, due to invasion of drilling fluid. After drilling, the borehole temperature reaches steady state in which cooling effects of the drilling fluid are balanced by the heat flow from the surrounding warmer formation. Therefore, we apply the Horner correction (Dowdle and Cobb, 1975) to raw measured borehole temperatures, or a 10°C increase when the Horner correction is not available.

3.4 Pyrolysis experiments

Hydrous pyrolysis can simulate formation of petroleum from source rock as well as effects of maturation and expulsion (Lewan et al., 1979; Lewan, 1985; Lewan, 1997; Lewan and Ruble, 2002; Spigolon et al., 2015). In this study, hydrous pyrolysis experiments were done at the U.S. Geological Survey in Denver, Colorado. The experimental equipment, starting materials, and protocols have been previously described in detail by Stolper et al. (2014a) and Piasecki et al. (2018). Briefly, an organic rich sample from the Woodford Shale was heated under a helium environment. The shale was heated stepwise at 330, 360, 390 and 415°C for 72 hours at each temperature to simulate maturation. Mixed gases were sampled at each temperature. Experimental procedures followed Lewan (1997). We extracted and analyzed propane from these mixed gas samples with the same methods in sections 3.2. and 3.3.1.

3.5 Isotope exchange experiments

In isotope exchange experiments, we incubated propane (CITP-1) with a deuterium source that is either deuterated water (diluted to $\delta D = 11419 \pm 31$ ‰) or $CH_3CD_2CH_3$ ('propane 2,2-D₂, 98%' from Cambridge isotope laboratory) in the presence of one of three catalytic substrates described below. In the hydrous experiments, we prepared 50–70 μ mol of propane, 500–600 μ mol of D₂O, and 40–60 μ g of catalysts in each 1–2 ml Pyrex® tube. In the anhydrous experiments, the deuterated water is replaced with pre-mixed 170 ppmv of $CH_3CD_2CH_3$ into CITP-1. The three catalytic substrates were kaolinite (from Wards Natural Science Establishment Inc.), montmorillonite (from Clay Minerals Society, University of Missouri; detailed in Sessions et al. (2004)) or pulverized Green River Formation powder. Prior to each experiment, the substrate clay minerals were heated by torch flame (est. 500–600 °C) under vacuum for 10 min to remove any adsorbed gas. The organic-rich shale powder was heated only with a heat gun at 100–150 °C under vacuum to prevent thermal degradation of organic matter. Each sealed Pyrex tube containing propane $\pm$ water + catalyst was then heated at a constant temperature (160 or 200 °C) in a resistance-heated furnace, for hours to weeks. After incubation, tubes were quenched in liquid nitrogen and then thawed and opened to a glass vacuum gas line. Propane was passed through a dry ice-ethanol trap (-72 °C) to remove remaining water vapor and then condensed in a second glass tube at -196 °C (immersed in liquid N₂). This second tube was then analyzed on the DFS mass spectrometer as described above.

4. Results

Table 1 lists the position-specific hydrogen isotope compositions and Table 2 lists other geochemical data for the studied propane samples. $\delta^{13}C$ values of propane range from -34.8 to -22.7‰ and δD values of propane from -169 to -74‰. Gas dry ratios ($C_1/(C_2+C_3)$) range from 1.4

to 76. These relatively wide ranges in composition reflect the diverse source kerogens and maturities of these gases. Note that we report two independent measurements of molecular-average δD : one based on our direct mass spectrometric measurement of the molecular ion and one based on compound-specific GC-P-IRMS. These data are consistent with one another within their respective external errors (Figure A1). The $\delta^{13}C$ and δD values of methane in the sample gases indicate that most are thermogenic in origin (Figure 1). Exceptions are gases from the Diana Hoover, Hadrian, and Genesis wells (all from the U.S. Gulf of Mexico), which might contain a component of microbial methane (see supporting data and discussions in Thiagarajan et al., 2020a, b). These samples' compound-specific carbon isotope patterns of C1–C5 alkanes (i.e., methane through pentanes) show negative anomalies of methane's $\delta^{13}C$, which also support contribution of microbial methane (Figure A2).

The central-terminal hydrogen isotope fractionation in propane from subsurface reservoirs displays a very wide range, from -102 to +205‰. This is 11 times larger than the range of equilibrium isotope effects at the temperatures of gas generation and storage in conventional reservoirs (estimated central-terminal fractionations of +36 to +63‰; Webb and Miller, 2014, Xie et al., 2018). The observed range is also much greater than previously studied gases from the Woodford Shale, Eagle Ford Shale, and Spraberry Formation of the Permian Basin (Liu et al., 2018; Liu et al., 2019; Zhao et al., 2020). Samples from the U.S. Gulf of Mexico (Diana Hoover, Hadrian North and South, Genesis, and Galveston) have the most positive central-terminal hydrogen isotope fractionations, whereas a sample from the Potiguar Basin has the most negative central-terminal hydrogen isotope fractionation.

5. Discussion

5.1 Magnitude of fractionation

The wide range of central-terminal hydrogen isotope fractionation in propane indicates that isotope effects associated with irreversible, kinetically (rather than thermodynamically) controlled processes are common influences on propane hydrogen isotope distribution and site-specific structure. Plausible contributing processes include thermal ‘cracking’ of propane precursors, destruction of propane during secondary cracking or biological consumption, transport (e.g., by diffusion), or phase transformations (e.g., ‘flashing’ of dissolved gases). Transport is not likely the key source of this signal because gas phase diffusion has been shown to fractionate carbon isotopes with no positional preference (Piasecki et al., 2016a), hence not changing ϵ values. This does not rule out condensed phase position-specific diffusive fractionations and hydrogen isotope effects (either in the vapor or condensed phase), but suggests that these processes are very unlikely to explain much, if any, of the several 100 ‰ range in site specific fractionation we observe. Phase change is also unlikely the cause for such a strong signature because D/H vapor-pressure isotope effects (VPIE) of similar hydrocarbon gases tend to be small. For example, D/H VPIE of ethane is only 10‰ at -73°C (Van Hook, 1966) and that of neopentane is only 7‰ at 9°C (Höpfner, 1969). We suspect that the VPIE for propane at reservoir temperatures will be smaller than these, making it negligible.

Despite the large observed range in position specific D/H ratio and diverse processes that may have contributed to it, subsets of the samples examined in this and previous studies are at or close to thermodynamic equilibrium with respect to their central-terminal hydrogen isotope fractionations (Figure 2). In some cases, this may be fortuitous, but this finding is sufficiently common and correlated with reservoir temperature (below) that we think it is also plausible that

it reflects equilibration through intra- or intermolecular hydrogen isotope exchange. The following sections further detail the role of each of several processes we hypothesize have contributed to observed position-specific hydrogen isotope fractionations in our sample set.

5.2 Effects of catagenic formation of propane

With exception of the occurrence of Fischer-Tropsch type ('FTT') synthesis of hydrocarbons in hydrothermal systems (e.g., Charlou et al., 2000; Proskurowski et al., 2008) and rare reports of anaerobic microbial production of ethane and propane in pore water (Hinrichs et al., 2006), it is accepted that subsurface hydrocarbon molecules larger than methane are generally derived from the thermal alteration of sedimentary organic matter under catagenic conditions (Peters et al., 2004). The isotopic structure of propane formed in this manner must reflect the intramolecular isotopic patterns of the parent molecules superposed by kinetic isotope effects associated with catagenic reactions (at least, immediately after formation and prior to any subsequent exchange or secondary 'cracking').

The formation of thermogenic hydrocarbons is believed to begin with thermally activated rupture of carbon-carbon and carbon-hydrogen bonds in macromolecular kerogen or higher order hydrocarbons (Ungerer, 1990; Savage, 2000; Xiao, 2001). In this scenario, the D/H ratios of hydrogen atoms adjacent to the carbon or carbons that participated in this bond-cleaving event will be lower, on average, than those in the unreacted precursor due to kinetic isotope effects (i.e., assuming the chemical kinetics involved follows patterns of 'normal' kinetic isotope effects rather than inverse isotope effects, such as those associated with sp^3 - sp^2 reactions). Most earlier studies of the isotopic effect associated with catagenic gas generation (Chung et al., 1988; Tang et al., 2000) assume that cleavage of an *n*-alkane precursor (or, equivalently, an *n*-alkyl chain in

macromolecules) dominates small alkane generation, leading to isotopic depletion in the terminal position of the product propane relative to the central position. However, macromolecular substrates (kerogen or bitumen) can have a large variety of structural components, such as hetero-atoms (N, O and S;), branched and cross-linked chains, aromatic and non-aromatic rings with alkyl chains connected to them (Burlingame and Simoneit, 1968; Curry and Simpler, 1988; Kelemen et al., 2007; Vandenbroucke and Largeau, 2007; Gao et al., 2017). In the cleavage of isoprenoid structures of kerogen, it can be speculated that propane could potentially be generated via bond breaking at the central position (i.e., forming an isopropyl radical), making the central position of the product ^{13}C and D depleted. Such patterns have also been observed, both in this work and past studies (Piasecki et al., 2018; Liu et al., 2019).

It is challenging to make quantitative predictions of the intramolecular isotope fractionations associated with propane formation by catagenesis of kerogen. One of the biggest hurdles is defining the diverse possible elementary reaction steps, reaction pathways and intermediate products. Peterson et al. (2018) introduced the kinetic Monte Carlo (kMC) method to approach a simplified version of this problem—homolytic cleavage of C-C bonds in initially isotopically homogeneous n-C₂₀ alkane. Here, we present a conceptually similar but more complex kMC model to describe the position-specific isotope distribution in propane produced from various types of macromolecular kerogens and oil mixtures. The parent substrates we considered include two sets of model kerogens: One set includes Type I, Type II, and Type III kerogens (Ungerer et al., 2015) where each is described by a relatively small and structurally simple unit cell (200–350 carbon atoms each). It also includes four type II kerogen models of different maturity levels. The second set of model kerogens was created to describe the source kerogens of specific economically significant petroleum systems, including the Eagle Ford Shale, the Marcellus Shale

and a shale from the Middle East (Bousige et al., 2016). These latter models have 4000–9000 carbon atoms per kerogen unit cell. In addition to these model kerogens, we also created models that describe catagenic cracking of *n*-alkanes and branched alkanes, which were mixed to mimic crude oil, and a molecular model of pure pristane to represent an isoprenoid endmember. Models of these simple molecules illuminate the relationships between molecular structure of reactants and isotopic structures of products.

We constructed a kMC model for each model substrate. Each model simulates an idealized reaction network that results from the thermal breakdown of precursors, as well as further breakdown of intermediate products (i.e., we describe both primary catagenesis of bonds in the initial precursor and secondary catagenesis of the primary products). Each simulation starts with many units of the parent molecule, such that the model system contains more than 100,000 C atoms. Isotope substitution (^{13}C and D) is randomly populated across these molecules. In doing so, we assume that each position of the precursors has uniform stable isotope ratios. However, this might not be realistic, and the possible implications of this assumption are discussed later in this section. The system then goes through a multi-step bond cleavage process. In each step, the model randomly chooses one of bonds that are enabled to react (here, we consider only homolytic cleavage of single bonds: C-C, C-N, C-O and C-S). The probability of choosing a given bond for cleavage is given by the rate for that particular bond (based on its structural position and the isotope effect if a ^{13}C or D is present) normalized by the sum of all events' rates. The rate of a bond-rupture event is based on the chemical type of the bond, determined for each using similar types of reactions that have been calculated by the Python version of the Reaction Mechanism Generator (RMG-Py) rate rules (Gao et al., 2016). In the next step, we modify the reaction rates of bonds influenced by ^{13}C and/or D with KIEs. We use KIE values from previous

ab initio calculations (Tang et al., 2000; Tang et al., 2005). We neglect tertiary or higher order KIEs for carbon and quaternary or higher order KIEs for hydrogen. The temperature of simulation is set at 180°C. The referenced values of KIEs are tabulated in Table A1. The reaction process is propagated until 20% of the original single bonds are broken. During this process, the cleaved parts of the molecules remain in the pool for iterative bond-breaking selections, therefore ‘secondary cracking’ of the intermediate products is allowed. At the end of each simulation, we count the number of produced propane molecules and assess the proportions of its isotopomers. The precision of each isotope ratio increases with the number of the repetitions of the simulation. Typically, we run 10,000 to 200,000 simulations on each parent (depending on when the results converge to within 0.5 ‰ standard error in the D/H ratio of each site of product propane). The computer codes are written in Python and MATLAB and executed on the Caltech High Performance Cluster located in Pasadena, California. This model is open source, available at <https://github.com/1995123xh/kMC>.

To simplify the chemistry and lower the computational demand, it is assumed that each radical formed by single bond dissociation is quenched by capping with an H atom immediately after the bond-breaking step. The isotopic signature of this H atom is set to be the average D/H produced by breaking the C-H bonds in the substrate, considering the primary KIE associated with C-H scission. This KIE is set equal to the reduced partition function ratio of the C-H bond (Wang et al., 2009). This is a substantial simplification of the real radical chemistry happening in organic matter, recognizing that there are also other reactions, such as radical propagation reactions, radical decomposition reactions, and radical termination reactions without H radicals. We note that such simplifications could cause errors such as unrealistically high $\delta^{13}\text{C}$ values of C_2^+

alkanes at high conversion ratios (Peterson et al., 2018). These other reactions might affect the carbon and hydrogen isotope composition of propane and need to be further explored.

In each simulation, we initiated precursors with uniform probability of isotope substitution across molecules. However, it has been widely expected and observed that biomolecules have non-stochastic intramolecular carbon and hydrogen isotope distribution (Abelson and Hoering, 1961; Monson and Hayes, 1982; Rossmann et al., 1991; Gilbert et al., 2012; Romek et al., 2015; Ehlers et al., 2015; Robins et al., 2017). Therefore, sedimentary organic matter likely would have similarly non-even hydrogen isotope distributions. However, to our knowledge, there is no sufficiently complete description of isotope distributions in organic structures of the size and complexity of kerogens. It is also questionable how much of this signature of the starting material can be transferred to the products (like propane), as the radical chemistry of thermal cracking involves random dissociation and re-combinations that tend to erase such biases. In order to explore the inheritance effects of isotopic structure, we experimented with an odd-even alternative pattern in *n*-alkanes that has been suggested to originate from biosynthesis of fatty acids (Monson and Hayes, 1982; Hayes, 2001; Gilbert et al., 2013). We initiated *n*-heptadecane with the even-numbered positions (2, 4, 6, ..., 16) more enriched in D than the odd-number positions (1, 3, 5, ..., 17) by 100 ‰. The propane product from cracking of *n*-heptadecane with this odd-even effect has ϵ_{D-C-T} value of 439‰, comparing to 392‰ when cracking *n*-heptadecane with homogeneously distributed D in molecules. The difference is greater than the statistical error of simulations and resolvable by our current instrumental precision. However, it is still second-order compared to the large effect of cracking reactions. In this example, the KIEs associated with radical initiation still dominates the position-specific hydrogen isotope signal in

propane (though it remains true that inheritance of isotopic structures of precursors byproducts is a high priority for future study).

The propane produced by these simulations encompasses the range in position-specific hydrogen isotope structures we observe in natural samples (Figure 3 and Table 3). Overall, the central-terminal difference in δD in propane is predicted to be positive for most source substrates, except for that sourced from pristane or the over-mature Type II kerogen model from Ungerer et al. (2015). Propane from pristane cracking is the most D-depleted in the central position. Propane from the oil cracking model is very D-enriched in the central position. Since oil in this model has a high abundance of *n*-alkanes, this contrast most likely reflects the difference between breaking straight chains and methyl-branched chains (isoprenoid structures). The cleavage of straight chains to generate propyl radicals always happens at a C-C bond that will place one of the reacted C sites (and its attached hydrogens) at the terminal position, but methyl-branched chains can often cleave in such a way that the reacted C site ends up in the central position of a propyl product. The model thus shows that molecular structure of the parent material exerts an important influence over the intramolecular isotope distribution of its products. A plausible way of generating propane with D-depletion in the central position is by cracking precursors enriched in methyl-branched aliphatic chain structures.

Propane hydrogen isotope structures predicted by most of the kerogen models (8 of 9) are higher in ϵD_{C-T} than natural samples observed, in most cases by 200‰ or more. We consider several possible explanations for these discrepancies. First, they could be attributed to potential deficiencies of the kerogen models, such as under representation of branched aliphatic structures. For example, a previous study simulated infrared spectra of all the larger kerogen models and the Type I and Type II smaller kerogen models used in this study and found that the computed

spectra are all in major disagreement with direct Fourier transform infrared spectroscopy (FTIR) observations of the kerogens from the Mancos, Woodford, and Marcellus Shales (directly described by one of the larger models) (Weck et al., 2017). The mismatch is likely attributable to inaccurate construction of functional groups or carbon backbones in the theoretical models. Second, isotopic discrepancies might reflect limitation of the model treatment of catagenetic chemistry. For example, it was suggested that beta-scission rather than homolytic cleavage can play an important role in hydrocarbon decomposition (Xiao, 2001). Besides thermal cracking, alternative mechanisms such as transition-metal catalysis (Mango et al., 2010) or sulfur radical catalysis (Lewan, 1998) have also been proposed to be responsible for short-chain hydrocarbon generation. These mechanisms could have isotope fractionations that differ from those of homolytic cleavage. Third, intra- or intermolecular hydrogen exchange of propane after its formation could erase the primary KIE signature. It is possible that propane in most natural gases is subject to some level of hydrogen isotope exchange. Finally, yet importantly, the discrepancy might be due to sampling bias in our selection of kerogen model structures. We are limited by both the number of molecular models that exist and the sizes of those models, which are to some extent limited by computational resources. Future work exploring this technique needs to address these issues.

On the other hand, natural gas accumulations often represent a mixture of gas from multiple stages of charging, which might originate from different types of source kerogen and different thermal maturities. Unlike the clumped isotope signatures that show a nonlinear anomaly associated with mixing isotopically distinct endmembers (Eiler, 2007), site-preference signatures tend to mix linearly (e.g., Piasecki et al., 2016a). Therefore, the position-specific hydrogen isotope composition of propane is expected to reflect a weighted average value of the

accumulated gas; in some cases, this could significantly impact the interpretation of gas measurements; .e.g., if a gas is a mixture of two end members, one from Type II kerogen and one from Type III kerogens (e.g., Dai et al., 2004), as these end members might differ in propane hydrogen isotope site preference.

5.3 Exchange and equilibration

It has previously been suggested that alkyl hydrogen can be susceptible to isotopic exchange over geological timescales under natural conditions (e.g., Sessions et al., 2004; Schimmelmann et al., 2006). Isotope exchange for both positions of propane with some common pool, such as H₂O or other hydrocarbons should drive intramolecular hydrogen isotope fractionation towards thermodynamic equilibrium. Alternatively, propane may equilibrate its hydrogen isotope structure by intramolecular exchange between the CH₂ and CH₃ groups.

Previous studies have shown that certain reduced metals (e.g., Ni, Pd, Pt) and activated metal oxides such as Al₂O₃ can catalyze hydrogen isotope exchange of propane with or without D₂ gas with apparent activation energies in the range of 30–90 kJ/mol (Sattler, 2018; Xie et al., 2018). And, in the absence of such solid catalysts, radical chain reactions, such as H-transfer reactions (e.g., Ungerer, 1990), could promote hydrogen exchange among coexisting alkanes at relatively high thermal maturation. But there is very little knowledge of the rates and conditions of hydrogen isotope exchange for propane, especially when water is present. To better quantify the exchangeability of hydrogen in natural propane, we conducted both hydrous and anhydrous hydrogen isotope exchange experiments on several substrates, including kaolinite, montmorillonite and pulverized shale powder of the Green River Formation (Table 4)

In the hydrous exchange experiments with labeled water as a deuterium source, some level of hydrogen isotope exchange between propane and water was observed on laboratory timescales at 200 °C. Experiments conducted in the presence of kaolinite exhibited the most significant exchange ($P < 0.05$), whereas lower rates of exchange were observed in the presence of montmorillonite and shale powder. The shale powder catalyzed experiments did not produce statistically significant ($> 2\sigma$) evidence of exchange. In the anhydrous experiments with montmorillonite substrate and $\text{CH}_3\text{CD}_2\text{CH}_3$ as a deuterium source, exchange happened much faster, with expected completion time of 500 days (5 half-lives). Hence, naturally occurring clay minerals can catalyze hydrogen isotope exchange both between water and propane and within propane (i.e., intermolecularly and/or between the central and terminal sites), at geological temperatures and timescales (Table 4). We suspect the slower rates of our hydrous experiments are more representative of natural behavior, as water is generally present in shallow crustal settings.

When the conditions are adequate for hydrogen exchange of propane (high enough temperature, presence of natural catalysts, and long enough time at temperature), this exchange will tend to drive propane toward a site-specific hydrogen isotope structure consistent with equilibrium. Several suites of samples examined in this study are apparently at thermodynamic equilibrium at their current storage temperature (Figure 4). They include samples from Eagle Ford, Sleipner Vest, Briggs, and one sample from Hadrian field. The Eagle Ford Shale data presented are also consistent with previously published nuclear magnetic resonance (NMR) measurements of site-specific hydrogen isotope structures of samples from the Eagle Ford system (Liu et al., 2018; Zhao et al., 2020). Most of the conventional gases that closely approach equilibrium reside in relatively hotter reservoirs (> 100 °C) and none of our gas samples that come from reservoirs this

hot contain propane significantly out of equilibrium. We conclude that hydrogen exchange of propane drives it to an equilibrium isotopic structure in geological conditions at temperatures greater than 100 °C and timescales similar to the residence of gas in reservoirs from the studied systems (for example, $>10^7$ years for the equilibrated Eagle Ford Shale gas). In contrast, propanes sampled from reservoirs colder than 100 °C are frequently out of isotopic equilibrium, leading us to suggest that below this temperature threshold hydrogen isotope exchange is too slow to equilibrate intramolecular D/H of propane readily on relevant geological timescales. (Below, we consider the quantitative constraints on just what these timescales might be.)

Gases from unconventional reservoirs provide a natural field test of the role of hydrogen exchange in controlling propane isotopic structure, because these gases are retained in their source rocks with residence times that are long and relatively predictable based on sequence stratigraphic and thermal histories of a basin. Fluid sampled from unconventional systems also may represent a more integrated composition as it doesn't migrate long distances. In these systems, thermal maturation of the gas can be determined via source shale analysis and molecular maturity evaluation of the fluids. We examined the response of the $\epsilon_{D_{C-T}}$ value for two unconventional reservoirs at a range of thermal maturity (based primarily on previous vitrinite reflectance data; Figure 5). The thermal maturity for the Eagle Ford samples shown here is based on molecular maturity indicators of biomarkers from co-produced oil or condensate (e.g., C_{29} sterane $20S/(20S+20R)$ and $\beta\beta/(\beta\beta+\alpha\alpha)$; Peters et al., 2004). In the case of the Irvin Minerals gas from the Eagle Ford Shale, this estimate is also consistent with observation of vitrinite reflectance at the depth of production. Both the Eagle Ford Shale (this study) and the Woodford Shale (Liu et al., 2019) produce propane in disequilibrium at the early thermal maturation stage. As maturity increases, the $\epsilon_{D_{C-T}}$ value for both formations also increases, eventually reaching

equilibrium values at $R_0 > 1.5$. This is consistent with the conclusion that hydrogen isotopic exchange of propane is greater at higher storage temperatures and times. We suggest a value of $\%R_0 > 1.5$ may provide a good threshold for the integrated time at temperature required for propane to equilibrate its isotopic structure in confined rock pore spaces and natural settings.

The equilibration trend of propane from unconventional reservoirs occurs at maturation stages similar to equilibration of methane clumped isotopologues in similar samples (Xie et al., 2019). This could reflect similarities between methane and propane in the mechanisms and kinetics of carbon-bound hydrogen equilibration. This could reflect the ability of both to undergo catalyst-mediated exchange or that they are both participants in radical chain reactions that allow interconversion of molecules and radicals and exchange of atoms (Xia and Gao, 2018; Thiagarajan et al., 2020b).

Samples at $\%R_0 < 1.5$ from both the Eagle Ford and Woodford Shales have ϵD_{C-T} lower than equilibrium, possibly related to the fact that they are sourced from Type II kerogens; it may also be relevant that some fraction of gas in these systems migrated out of the source rocks—i.e., we are looking at a residual fraction of partial loss (e.g., Zumberge et al., 2016). Isotope fractionation due to transport-related processes have been modeled and experimentally calibrated to be relatively small (Schloemer and Krooss, 2004; Xia and Tang, 2012) and should be negligible in the Eagle Ford Shale, because it is estimated to have retained 40%–80% of hydrocarbons (Byrne et al., 2018). Additionally, transport processes such as molecular diffusion are also unlikely to have large positional preference in isotopic fractionations, as discussed earlier in the section.

Residual fluids in petroleum source rocks under partial expulsion may evolve in their molecular composition, meaning the source organic structures subjected to cracking differ between low and

high maturities. Figure 3 illustrates that this factor may impact the isotope composition of propane, particularly as secondary cracking becomes a significant propane source (see a fuller discussion of this issue below). However, source maturity is not correlated with the hydrogen isotopic structures of propanes from conventional reservoirs (Figure 5), where source rock thermal maturity or ‘Equivalent %R₀’ was estimated from the $\delta^{13}\text{C}$ values of ethane or propane (Whiticar, 1990). Many samples at higher maturity (Equivalent %R₀>1.5) are still above equilibrium in position-specific D/H ratio of propane. We suggest this reflects preservation of the primary KIE signal associated with catagenic formation of propane, followed by relatively rapid discharge of gas to cool (<100 °C) reservoirs. This interpretation is supported by data from the Briggs fields, where the colder wells with higher maturity gas are out of hydrogen isotope equilibrium whereas nearby hotter wells filled with lower maturity gases are at equilibrium. That is, the critical determinant of propane isotopic equilibration is long-term storage temperature, not generation temperature, suggesting hydrogen isotope exchange (with or without heterogeneous catalysts) controls the rate of approach to equilibrium.

This interpretation raises the possibility that the hydrogen isotopic structure of propane may provide a means of separately constraining temperature-time histories of fluids and their sources. The re-equilibration experiments we present provide a means of making initial estimates of the gas migration timescales implied by this interpretation. Our exchange experiments found that the timescale to reach equilibrium is likely short (Table 4), which limits the longest average time of these gases residing in the source rock (not the time of charging the reservoir). At 200°C, the time required to erase disequilibrium signals (5 halftime) is $10^2\sim 10^4$ years. Since 200°C is near the high-end of the gas window (Hunt, 1996), longer timescales can be expected for colder environments. For instance, if source rock temperature is 150°C and assuming a typical

activation energy of 70kJ/mol (experimentally determined for natural existing materials such as Al_2O_3 ; Sattler, 2018) and first-order kinetics, we estimate an exchange halftime that is about 8 times longer, implying a timescale of generation and expulsion of $10^3\sim 10^5$ years. Either way, in these systems, our laboratory exchange experiments imply that gas expulsion was geologically rapid compared to the timescales of source rock thermal evolution ($10^6\text{--}10^7$ years). This suggests that conventional gases that are found to be in disequilibrium (from Briggs, Galveston, Potiguar, SYU) were generated and expelled from their respective source rocks at those short timescales. It is worth noting that the source rock of the Potiguar gas (which is farthest away from equilibrium) is deposited during the Neocomian–Aptian rift phase of the basin evolution, when the heat flow increases very rapidly, allowing faster generation and expulsion (Trindade et al., 1992). We recognize that these estimations are based on the premise that clay minerals or other naturally occurring catalytic materials are available and as accessible to and catalytically active as those present in our experiments. If these assumptions are not true in the natural shale setting, then expulsion timescales could have been longer.

Exchange rates also can be estimated by modeling exchange equilibration of propane in unconventional natural gas reservoirs. Liu et al. (2019) presented position-specific hydrogen isotope compositions of propane from the Woodford Shale in the Arkoma basin, collected from source rocks spanning a range of thermal maturation. Assuming that the change of $\epsilon_{\text{D}_{\text{C-T}}}$ with increasing thermal maturation is controlled by hydrogen exchange, we created a numeric model to reconstruct the position-specific hydrogen isotope composition of propane as a function of temperature and time and fit that model to the data of Liu et al. We used a gas accumulation model determined with PetroMod (Higley et al., 2014) and thermal curves adapted from the burial and uplifting model of the Arkoma basin from Byrnes and Lawyer (1999). In this model,

propane is generated and exchanged continuously, with first-order exchange kinetics (Sessions et al., 2004; Xie et al., 2018). We used a Monte Carlo method to constrain the key kinetic parameters for hydrogen isotope exchange on the central position of propane (i.e., the activation energy, E_a , and pre-exponential frequency factor), obtaining a range of possible combinations of their distributions that are consistent with these data and the hydrogen-exchange hypothesis. The best fit of those parameters ($E_a=114$ kJ/mol and $A=4.9e5$ yr⁻¹) accurately captures the measured values (Figure 5).

The posterior range of exchange halftime at 200°C from the Monte Carlo simulation is 4.9–17 My (Figure 6). This is longer than those values obtained from clay-catalyzed experiments (10^2 – 10^4 years). This large discrepancy could be due to the lack of those minerals and/or inhibition to the catalytic surfaces. Kaolinite appears as a minor mineral in the Woodford Shale (Lewan, 1985), but natural shale conditions are unlikely to possess such high surface area/gas ratios as we created in the laboratory. Nevertheless, we compared the Monte Carlo outcome of possible rates with kinetic data of laboratory experiments on a few other relevant processes (Figure 6). First of all, it was found that the predicted values are broadly consistent with (though a little slower than) exchange experiments between methane/hexane and water without catalysts (Koepp, 1978; Sessions et al., 2004). Secondly, the chemistry of either oil cracking (Ungerer et al., 1988) or hydrous pyrolysis (Lewan, 1985) would be faster than exchange processes if we extrapolate their high-temperature experiments to the temperatures of natural gas formation. This implies that the kinetic fractionation signatures of propane generation are not equilibrated over geologically brief times (i.e., less than a million years), explaining why such signals are preserved in so many conventional reservoirs with a wide range of source maturation. Lastly, the self-cracking kinetics of propane (Laidler et al., 1962), when extrapolated to gas window temperatures, would be

slower than hydrogen exchange. Taken together, this suggests that during propane loss (transformation from wet gas to dry gas) propane should stay at intramolecular hydrogen isotope equilibrium.

When propane is equilibrated, $\epsilon_{D_{C-T}}$ constrains the equilibration temperature of the environment where isotope exchange happened. Unfortunately, the analytical precision of the NMR and DFS methods from this and previous studies is insufficient to usefully constrain this apparent temperature. However, the recently developed multi-collector high-resolution gas source isotope ratio mass spectrometers (Eiler et al., 2013; Young et al., 2016) are capable of measuring δD of methane down to 0.05–0.1‰ precision. The application of such mass spectrometric techniques to propane site-specific D/H ratios could enable quantitatively useful geo-thermometry of gas storage. For example, a 0.05‰ error in hydrogen isotope ratios of both the ethyl fragment and molecular ion would be propagated to a 0.45‰ error in $\epsilon_{D_{C-T}}$ (for natural propane with typical hydrogen isotope composition), which could be translated to around 2°C inferred equilibrium temperature error in the relevant temperature range. The gases that yield propane in hydrogen isotope equilibrium in our study also yield methane in clumped-isotope equilibrium (Figure 7) with self-consistent (or higher) apparent temperatures of 150–220°C—generally in the gas window.

Propane from more mature fluids tends to have higher $\epsilon_{D_{C-T}}$ values in both unconventional and conventional reservoirs. It is possible that this is driven by a change in cracking source material as thermal maturation proceeds (as mentioned above). As thermal maturity increases, the organic substrate that propane and other hydrocarbons derive from vary in their chemical composition and structure. Natural gases formed by direct thermal decomposition of kerogen at earlier maturation are often categorized as ‘primary gas,’ distinguished from the ‘secondary gas’ that

results from oil cracking at later stages of maturation. For Type I/II kerogens, oil-associated gases are commonly the primary gases of kerogen cracking, whereas non-associated gases are the secondary gases from further cracking of oil. The majority of our sample set are gases derived from Type II kerogen, except for the Potiguar sample, which was generated from a lacustrine section (the Lower Cretaceous (130 Ma) Pendência Formation) mainly related to an organic-rich shale with Type I kerogen (Pestilho et al., 2018). The source origin of the non-associated Hogsback gas is unclear, though we favor an interpretation that it is a primary gas derived from a more gas-prone mixed Type II/III source rock, based on the Δ_{18} apparent temperature of its methane, compound specific $\delta^{13}\text{C}$ of methane, ethane and propane, and biomarker data (not presented here) of co-produced condensate. With our background knowledge, samples from Potiguar, Diana Hoover, Genesis, Keathley Canyon, SYU, and Irvin Minerals South of Eagle Ford Shale would be categorized as primary gas by this reasoning, and samples from Galveston, Sleipner Vest, Briggs, and Las Raices 22H of Eagle Ford Shale would be classified as secondary gases. We found that $\epsilon\text{D}_{\text{C-T}}$ of the secondary gases are observed to be higher than the equilibrium line, whereas that of the primary gases can be either higher or lower. This is consistent with the oil-cracking signature predicted by the kMC model (Figure 3), where oil as a substrate produces propane with highly positive $\epsilon\text{D}_{\text{C-T}}$. This interpretation is also consistent with observed trends of higher $\epsilon^{13}\text{C}_{\text{C-T}}$ at higher maturation in both pyrolysis experiments and natural samples (Piasecki et al., 2018; Gilbert et al., 2019). When we examine the position-specific hydrogen isotope of propane in the hydrous pyrolysis experiments of the Woodford Shale, we also observed $\epsilon\text{D}_{\text{C-T}}$ increases as experimental temperature increases and more secondary cracking is happening (Figure 8). However, this theory (i.e., change in $\epsilon\text{D}_{\text{C-T}}$ is controlled by source maturation) requires the hydrogen exchange rate to be very slow, which is

not favored by experimental results reported earlier in this section. Propane sampled from more mature unconventional gases could provide evidence as to whether cracking chemistry or hydrogen exchange have stronger influences in this signature. If the hydrogen isotope structure of propane is primarily controlled by cracking chemistry, $\epsilon_{D_{C-T}}$ values would continue to increase with maturity to $\%R_0 \sim 2$ or above, but if it is primarily controlled by hydrogen exchange, $\epsilon_{D_{C-T}}$ values would remain in hydrogen isotope equilibrium as $\%R_0$ rises to extreme values.

5.4 Propane destruction

5.4.1 Secondary cracking of propane

Secondary cracking of propane is associated with high-maturity cracking of hydrocarbons to destroy C_2 - C_5 alkanes and increase the dryness (C_1 to C_{2+} ratio) of the system. Position-specific hydrogen isotope fractionation could be changed during this process, as different isotopomers have different cracking rates. We can calculate the isotopic structure of residual propane using KIEs-associated propane cracking. We consider the homolytic cleavage of the C-C bond to be the primary mechanism that initiates secondary cracking of propane, as C-C breaking is approximately 5 orders of magnitude faster than C-H breaking at relevant temperatures (e.g., Dean, 1985). Deuterium KIEs predicted for homolytic cleavage of the C-C bond has been previously calculated using quantum chemical methods (Ni et al., 2011). It is found that this process enriches the central position in D faster than the terminal position, which could be explained by the fact that there are twice as many terminal carbons and 3x more terminal hydrogens as central ones, but an equal number of each positions is involved in C-C cracking. We predict that $\epsilon_{D_{C-T}}$ increases by 53‰ after 1 e-folding time (63% reaction progress) of propane cracking at 200°C.

Results from hydrous pyrolysis experiments support this prediction (Figure 8 and Table 5). At lower temperature, pyrolytic propane has a relatively D-depleted central position. As temperature increases, both δD and ϵD_{C-T} rises. ϵD_{C-T} reaches equilibrium values at 390°C, but continue to rise as temperature increases to 415°C. The data provide suggestive but not definitive evidence that at the maximum temperature of 415°C, ϵD_{C-T} just exceeds equilibrium isotope effects. If this is not simply a statistical anomaly (as it is just outside errors of equilibrium), it would suggest that the trend of rising ϵD_{C-T} with increasing maturity is at least influenced by kinetic isotope effects instead of (or perhaps in addition to) equilibration.

On the other hand, we do not see any natural samples from the unconventional reservoirs at higher fluid maturity with significantly elevated ϵD_{C-T} values (statistically above equilibrium). In fact, it is conceivable that H exchange, via either catalysis or other mechanisms, will play an important role in the maturation stage of gas cracking, as discussed in section 5.3. That is, perhaps H exchange reactions are faster than secondary cracking of propane, erasing any kinetic fractionations resulting from secondary cracking in natural settings. This may be because the high activation energy of secondary cracking reactions renders them ineffective compared to exchange at geological temperatures (Figure 6).

5.4.2 Biological degradation

In relatively cool (up to 80°C) reservoirs where biological activity could occur, propane is susceptible to microbial degradation both by aerobes (where suitable conditions exist) and—more commonly—anaerobes. Amongst C₂-C₅ hydrocarbons, propane is biodegraded most rapidly (Head et al., 2003). Biological consumption of propane expresses normal KIEs, leaving the residual propane more enriched in ¹³C and D. Previous deuterium labeling studies have shown that the central position is preferentially (70%) attacked in the anaerobic oxidation of

propane by a sulfate-reducing bacteria (Jaekel et al., 2014). This position preference would cause more rapid isotopic enrichment in the central position than the terminal position (both positions are enriched), such that the central-terminal difference in both carbon and hydrogen isotopes increases as biodegradation intensifies. The greater enrichment of ^{13}C at the central position has been confirmed in both lab cultures and several natural gas basins for carbon isotopes (Gilbert et al., 2019), where the central attack fraction was estimated to be 85%. It is also notable that a recent study has shown that thermophilic anaerobic methanotrophic archaea (ANME-1) can oxidize butane (and potentially propane) by methyl-CoM reductase (MCR). This mechanism attacks the terminal position, so it would lead to decrease in central-terminal difference that is opposite to bacterial degradation.

Moderately elevated $\epsilon\text{D}_{\text{C-T}}$ values in propane samples retrieved from several wells in the Diana Hoover and Hadrian (U.S. Gulf of Mexico) fields—places known to contain biogenic methane—suggest that these gases could have been biodegraded. Since these gases are sampled from deep wells (>2000 m), the potential biodegraders would be anaerobes. Several independent lines of evidence also support that these gases are biodegraded: (1) the propanes have high δD values (-120‰ to -80‰) compared to other samples from the Gulf of Mexico (-126‰ to -116‰); (2) propane concentration is relatively low for the immature gases in these formations; (3) methanogenesis is commonly associated with hydrocarbon biodegradation (sometimes referred to as ‘secondary methanogenesis’; e.g., Jones et al., 2008), and compound-specific stable isotope signatures indicate significant microbial input of methane; that is to say, δD and $\delta^{13}\text{C}$ of methane in these samples match a microbial origin in a ‘Schoell/Whiticar diagram’ (Figure 1; Whiticar, 1999), and $\delta^{13}\text{C}$ of methane has a negative anomaly (compared to $\delta^{13}\text{C}$ trend of C_2+ alkanes) in a ‘Chung plot’ (Figure A2); and (4) apparent temperatures derived from Δ_{18} -clumped

isotope measurements of methane are between 30–68 °C (Figure 7), consistent with the reservoir temperatures of these wells (42–59 °C), suggesting that these methanes were formed (or microbially recycled) *in situ* (see Thiagarajan et al., 2020a). Although microbial methane is often in clumped isotope disequilibrium (Stolper et al., 2015; Wang et al., 2015; Douglas et al., 2016; Young et al., 2017), microbial methane found in marine and/or subsurface environments is usually in or close to equilibrium. It has been proposed that slow anaerobic coupled methanogenesis and methanotrophy in nature under low thermodynamic drive (e.g., H₂ supply) could drive methane to internal isotopic equilibrium at its environmental temperature (e.g., Gruen et al., 2018; Giunta et al., 2019; Douglas et al., 2020). Besides that, microbes degrading C₂–C₄ short alkanes have been found in the Gulf of Mexico sediments (Kniemeyer et al., 2007; Laso-Pérez et al., 2016; Chen et al., 2019).

The three samples from the Hadrian field provide suggestive evidence of the hydrogen isotope signature of the biodegradation progress. Their ϵD_{C-T} values increase with molecular δD values of propane (Figure 9). Assuming that biodegradation occurs as a closed system process and that the amplitude of the KIE is similar between central and terminal uptake, we can model the position-specific propane isotopic composition with a modified Rayleigh relationship:

$$\frac{\epsilon D_{C-T} + 1000}{\epsilon D_{C-T(0)} + 1000} = F^{x_C(1-\alpha) - (1-x_C)(0.5\alpha+0.5)} \quad \#(3)$$

where x_C is the fraction of central attack and α is the primary KIE of methane binding with methane monooxygenase (MMO). Results of this model for the Hadrian field propanes are consistent with having a high central preference, with an x_C value between 80 and 90%.

6. Conclusions

We used high-resolution mass spectrometry to examine the position-specific hydrogen isotope distribution in propane from a diverse set of natural gas samples and laboratory experiments. We explored the effects of various processes of propane formation, storage, and destruction on intramolecular isotope fractionation, via both theory and experiment. The wide range of this central-terminal difference in natural samples suggests that catagenesis is dominated by kinetic fractionations and forms propane out of H-isotopic equilibrium. Kinetic Monte Carlo models reveal that structural properties of the organic precursors can control the direction and amplitude of intramolecular fractionation. Specifically, straight-chain precursors lead to center-site D enrichment, whereas branched precursors lead to terminal site D enrichment. Based on their position-specific hydrogen isotope ratios, natural propanes appear to sample branched precursors with greater frequencies than one might predict from some structural models of kerogen (Ungerer et al., 2015; Bousige et al., 2016), particularly in gases from unconventional reservoirs.

Once formed, propane can be subject to hydrogen exchange that will drive its site-specific isotopic distribution towards equilibrium. Results from laboratory isotope exchange experiments indicate that hydrogen isotope exchange can be catalyzed by clay minerals such as kaolinite. The exchange timescale estimated from these experiments can be relatively short (10^2 – 10^4 yrs) in the presence of clays at 200°C. The natural observations show that higher maturity propane in non-associated gases sitting in relatively hot reservoirs (>100 °C) are nearly equilibrated (though this may or may not reflect the role of solid catalysts such as those used in our laboratory experiments). In unconventional reservoirs, position-specific hydrogen isotopes of propane in fluids with an integrated maturity of $R_o < 1.5$ % is out of equilibrium and tend to approach equilibrium as thermal maturity increases. If this is driven by exchange equilibration, the

exchange halftime is estimated to be 5–17 My at 200 °C based on data from the Woodford Shale. In conventional reservoirs, propane can still be out of equilibrium despite having relatively high source maturity, suggesting fast ($<10^5$ years) expulsion from source formations and storage in cool (<100 °C) reservoirs. More generally, position-specific hydrogen isotope compositions of propane can be used to constrain the temperature-time histories of gas expulsion and migration. It is worth mentioning that biodegradation can also impact $\epsilon_{D_{C-T}}$ values, as observed in two relatively cold reservoirs, Hadrian North and Diana Hoover. These elevated values reflect a strong central position preference in the chemical degradation reactions during biological uptake, consistent with previously reported carbon isotope behavior. Intramolecular isotope distributions for both ^{13}C and D in propane provide a distinct signature for subsurface hydrocarbon biodegradation.

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9. Figures

Figure 1: Methane isotopic composition of the natural gases in this study. δD is on VSMOW scale and $\delta^{13}C$ is on VPDB scale. Categorization areas are based on Whiticar (1999). Errors for these analyses are typically 0.3‰ for $\delta^{13}C$ and 3-5‰ for δD .

Figure 2: Central-terminal differences of D/H in natural propanes from this study. Error bars show 2 standard error of sample analysis. The coloring scheme in this figure is consistent with other figures in this paper. GOM= Gulf of Mexico.

Figure 3: Comparison of kinetic Monte Carlo model outputs with natural propane data. Dashed lines show results of the small kerogen models (Ungerer et al., 2015), dotted lines show results of the big kerogen models (Bousige et al., 2016), and solid lines show results from pristane and oil. Propane isotope data of the Woodford Shale is from Liu et al. (2019). GOM= Gulf of Mexico.

Figure 4: Central-terminal hydrogen isotope differences of natural propanes plotted vs. their reservoir temperatures. The temperatures were measured at the wells and adjusted.

Figure 5: Left: ϵD_{C-T} plotted vs. mapped maturity (vitrinite reflectance) of the gases recovered from unconventional formations, the Eagle Ford Shale (this study) and the Woodford Shale (Liu et al., 2019). Right: ϵD_{C-T} plotted vs. gas maturity for the conventional hydrocarbon systems in this study. The solid line in the left panel represents the hydrogen exchange model with the best-fit parameters for the Woodford Shale series. The grey area shows isotope equilibrium at 50–200 °C.

Figure 6: Arrhenius plot showing the result of modeling the hydrogen exchange rate constants of propane in Woodford Shale (labeled as ‘Woodford exchange’ in the figure) compared to various processes. The simulated activation energy is between 80–180 kJ/mol. Hydrogen exchange refers to D/H exchange experiments on methane and hexane (Koepp., 1978; Sessions et al., 2004). Hydrous pyrolysis refers to hydrous pyrolysis experiments on the Woodford, Alum, Phosphoria, and Monterey Shales (Lewan and Ruble, 2002). Oil cracking refers to oil-cracking experiments on the Boscan oil and Pematang oil (Ungerer et al., 1988). Propane cracking refers to propane pyrolysis experiments (Laidler et al., 1962).

Figure 7: Position specific D/H fractionation in propane plotted vs. a measure of isotope clumping in methane. The equilibrium fractionation line and its apparent temperature (top horizontal axis) is based on ab initio calculations from Webb and Miller (2014) for propane and experimental calibration from Stolper et al. (2014b) for methane.

Figure 8: Propane isotope data for the hydrous pyrolysis experiments (horizontal axis is molecular average δD of propane). Equilibrium isotope effect at 330–415° C is extrapolated from Xie et al. (2018) and Webb and Miller (2014).

Figure 9: Isotopic constraints on the sites of propane decomposition associated with biodegradation in the Hadrian field gas samples (horizontal axis is molecular average δD of propane). Dashed lines represent modeled trends of the residual propane as biodegradation intensifies, where the numerical label notes the percentage of destroyed propane that was subject to attack at the central carbon site (x_c). Changes in the primary KIE of methane oxidation does not alter the modeled lines (assuming that KIE is closely similar for the terminal and central site mechanisms).

Figure A1: A comparison of molecular δD (VSMOW) of propane measured by DFS and in other laboratories ('external'). DFS results are based on molecular ion measurements ($[C_3H_7D^+]/[C_3H_8^+]$). External measurements were made with GC-py-IRMS, with expected 1σ error of 3–5‰.

Figure A2: Compound-specific carbon isotope data of studies natural gas samples in this study. The x-axis, $1/n$, denote reciprocal of the alkane chain length. Left panel: gases with potential microbial methane input and/or hydrocarbon consumption. (See Thiagarajan et al. (2020a) and Section 5.4.2 of this paper). Right panel: gases of thermogenic origin.

10. Table Captions

Table 1: Position-specific hydrogen isotope measurement results for natural gas samples analyzed in this study. $\delta D_{\text{molecular}}$ and δD_{ethyl} are the hydrogen isotope values of the molecular ion and the ethyl fragment, respectively, normalized to those of the reference gas (CITP-1). GOM = Gulf of Mexico; MID = multiple ion detection.

Table 2: Compound-specific isotope compositions and other geological and geochemical information of natural gases analyzed in this study.

Table 3: Results of the kinetic Monte Carlo model for various molecular model inputs.

*kia refers to the Type I kerogen model in Ungerer et al. (2015). kiia, kiib, kiic and kiid refers to the four Type II kerogen models in Ungerer et al. (2015), ordered from least to most mature. kiii refers to the Type III kerogen model in Ungerer et al. (2015).

Table 4: Results of the isotope exchange experiments in this study. $\Delta\delta D$ is isotopic change of molecular/ethyl δD relative to the starting material. The ranges of exchanged halftime were calculated following the exchange kinetics expressed in $e^{-kt} = (F_e - F_i) / (F_e - F_0)$ (Sessions et al., 2004) using $\Delta\delta D_{\text{molecular}}$. All measurements here are made with the electronic scan method.

Table 5: Results of the hydrous pyrolysis experiments in this study. All measurements here are made with the MID method.

Table in the Appendix

Table A1: Kinetic parameters for homolytic dissociation of single bonds in the kinetic Monte Carlo model. Hydrogen KIE is for hydrogen bonded to the carbon position with asterisk. Temperature is set at 180 °C.

[#]This denotes KIE of isotopically substituting the C/H position adjacent to the cracking position, which is formally secondary KIE for carbon and tertiary KIE for hydrogen. The adjacent isotope KIE is treated to be the same for all bonding environments.

Table 5: Position-specific hydrogen isotope measurement results for natural gas samples analyzed in this study. $\delta D_{\text{molecular}}$ and δD_{ethyl} are the hydrogen isotope values of the molecular ion and the ethyl fragment, respectively, normalized to those of the reference gas (CITP-1). GOM= Gulf of Mexico. MID= multiple ion detection.

Sample	Basin	Well	$\delta D_{\text{molecular}}$	error	Method	δD_{ethyl}	error	Method	$\epsilon D_{\text{C-T}}$	error
SD1	Diana Hoover-GOM	SD1	81.2	0.7	MID	106.3	1.7	MID	108.0	10.2
DB2	Diana Hoover-GOM	DB2-ST4	72.2	1.8	MID	111.6	3.0	MID	205.3	18.4
Las Raices 21H	Eagleford	Las Raices 21H	100.5	1.3	MID	118.1	1.1	MID	58.7	9.4
IS1H_R	Eagleford	Irvin South	82.1	1.1	E-scan+Piasecki	91.0	1.7	E-scan+Piasecki	6.1	11.6
GI-BD7	Galveston Island-GOM	BD7	76.3	0.7	MID	105.4	1.6	MID	135.0	9.2
GenA12_ST4_R	Genesis-GOM	5909 A12 ST4	72.9	0.6	MID	84.3	0.8	MID	22.2	5.6
GenA15_ST1	Genesis-GOM	5909 A15 ST1	64.1	0.8	MID	93.8	0.9	MID	141.5	6.4
KC919	Hadrian-GOM	Hadrian-6	78.7	0.9	MID	97.4	1.3	MID	67.5	8.6
KC5499_R	Hadrian-GOM	Hadrian-2	109.1	0.8	MID	139.6	0.6	MID	138.0	5.1
KC5500_R	Hadrian-GOM	Hadrian-2	123.1	0.7	MID	165.2	1.8	MID	209.9	9.7
H68-23	Hogsback	H68-23	7.5	1.6	MID	15.7	1.3	MID	5.6	12.1
PT-2	Potiguar		53.9	1.6	E-scan+Piasecki	45.0	1.0	E-scan+Piasecki	-	11.5
B17-T2	Spleipner Vest	15/19 B17	47.7	1.1	E-scan+MID	63.1	1.5	E-scan+MID	49.2	10.6
B14-T2	Spleipner Vest	15/19 B14	51.0	0.8	MID	69.1	2.2	E-scan+MID	66.6	13.7
B1-T1-A1r	Spleipner Vest	15/19 B1	50.7	1.3	MID	71.4	1.9	E-scan+MID	83.8	13.2
5A-5L	SYU-Pescado	HE024	23.7	1.1	MID	28.4	1.4	E-scan+MID	-17.9	10.9
Holcomb 6	Briggs	Holcomb 6	86.4	0.9	MID	101.5	1.2	MID	44.2	8.1
McGee 4_R	Briggs	Scott McGee 4	114.3	0.7	MID	141.3	0.9	MID	115.2	5.9

Table 2: Compound-specific isotope compositions and other geological and geochemical information of natural gases analyzed in this study.

Sample	Basin	Well	Well T °C	% C3	Gas type	A ₁₈	error	C1/(C2+C3)	$\delta^{13}C_{C1}$	δD_{C1}	$\delta^{13}C_{C2}$	δD_{C2}	$\delta^{13}C_{C3}$	δD_{C3}	Gas isotope maturity R ₀ %
SD1	Diana Hoover-GOM	SD1	59	2.04	Conventional oil associated	5.34	0.25	15.68	-56.6	-203.2	-28.8	-122.6	-26.6	-116	1.5
DB2	Diana Hoover-GOM	DB2-ST4	54	1.88	Conventional oil associated	4.86	0.24	17.10	-53.7	-195.0	-28.9	-	-26.5	-	1.5
Las Raices 21H	Eagleford	Las Raices	143	4.05	Unconventional non-associated	2.52	0.23	5.28	-40.7	-181	-24.6	-	-22.7	-	2.4

21H				.3									
IS1H_R	Eagleford	Irvin South	141	5.3 2	Unconventional solution gas	2.39	0.22	4.34	-47.4	-260.1	-32.2	-29.3	1.0
GI-BD7	Galveston Island-GOM	BD7	89	0.7 61	Conventional solution gas	3.59	0.39	25.45	-41.8	-164.7	-26.5	-128.9	1.9
GenA12-ST4_R	Genesis-GOM	5909 A12 ST4	79	4.4 1	Conventional solution gas	5.73	0.25	8.19	-63.2	-204.9	-33.3	-158.2	0.9
GenA15-ST1	Genesis-GOM	5909 A15 ST1	66	4.3 3	Conventional solution gas	4.09	0.25	7.12	-54.7	-209.1	-31.6	-150.0	1.1
KC919	Hadrian-GOM	Hadrian-6	64.4	7.8 8	Conventional solution gas	4.14	0.25	3.20	-55.6	-247.7	-40.5	-160.1	0.4
KC5499_R	Hadrian-GOM	Hadrian-2	48.3	0.4 71	Conventional oil associated	5.56	0.24	77.58	-58.0	-178.3	-39.7	-28.8	0.4
KC5500_R	Hadrian-GOM	Hadrian-2	42.2	1.0 67	Conventional oil associated	5.98	0.26	42.86	-60.4	-177.0	-40.4	-30.2	0.4
H68-23	Hogsback	H68-23	100	3.1 2	Conventional non-associated	3.26	0.36	9.20	-36.9	-185.7	-31.0	-178.9	1.2
PT-2	Potiguar		71	18. 2	Conventional oil associated	3.03	0.27	1.42	-48.3	-206.8	-38.0	-196.3	0.5
B17-T2	Spleipner Vest	15/19 B17	121	4.6 4	Conventional non-associated	2.64	0.25	5.57	-39.9	-217.3	-28.0	-27.0	1.6
B14-T2	Spleipner Vest	15/19 B14	123	4.2 7	Conventional non-associated	2.68	0.25	5.97	-39.8	-221.0	-28.7	-27.1	1.5
B1-T1-A1r	Spleipner Vest	15/19 B1	123	18. 2	Conventional non-associated	2.21	0.25	5.50	-40.9	-230.9	-29.1	-27.3	1.4
5A-5L	SYU-Pescado	HE024	105	4.2 3	Conventional solution gas	2.69	0.25	7.26	-38.3	-175.0	-31.3	-28.4	1.1
Holcomb 6	Briggs	Holcomb 6	120	3.6 2	Conventional non-associated	2.98	0.25	8.41	-44.0	-181.8	-27.9	-121.0	1.6
McGee 4_R	Briggs	Scott McGee 4	93	1.5 8	Conventional non-associated	3.15	0.30	14.42	-40.3	-160.6	-25.2	-110.4	2.2

Table 3: Results of the kinetic Monte Carlo model for various molecular model inputs.

precursor	source	Size(C atoms)	ϵD_{C-T}	$\epsilon^{13}C_{C-T}$
pristane		19	-193	-1.7
oil		2206	326	10.0
kiia*	Ungerer et al. (2015)	251	293	6.9
kiia	Ungerer et al. (2015)	252	417	9.9
kiib	Ungerer et al. (2015)	234	378	7.0
kiic	Ungerer et al. (2015)	242	304	7.2
kiid	Ungerer et al. (2015)	175	-31	-3.6
kiia	Ungerer et al. (2015)	233	345	10.4
Eagle Ford Shale	Bousige et al. (2016)	3849	339	8.7
Middle East Shale	Bousige et al. (2016)	3995	303	8.5
Marcellus Shale	Bousige et al. (2016)	5160	235	5.2

*kia refers to the type I kerogen model in Ungerer et al. (2015). kiia, kiib, kiic and kiid refers to the four type II kerogen models in Ungerer et al. (2015), ordered from least to most mature. kiiia refers to the type III kerogen model in Ungerer et al. (2015).

Table 6: Results of the isotope exchange experiments in this study. $\Delta\delta D$ is isotopic change of molecular/ethyl δD relative to the starting material. The ranges of exchanged halftime were calculated following the exchange kinetics expressed in $e^{-kt} = (F_e - F_t) / (F_e - F_0)$ (Sessions et al., 2004) using $\Delta\delta D_{\text{molecular}}$. All measurements here are made with the electronic scan method.

Catalysts	State	Temperature(°C)	Time(d)	$\Delta\delta D_{\text{molecular}}$	error	$\Delta\delta D_{\text{ethyl}}$	error	Estimated exchange halftime
Kaolinite	hydrous	200	7	4.0	1.6			20-83 yr
	hydrous	200	14	4.4	1.8			
	hydrous	160	21	1.8	3.0			>70 yr
Montmorillonite	hydrous	200	7	-2.3	1.7	-1.0	1.3	∞ yr
	anhydrous	200	7	14.7	1.1	34.0	0.9	100-110 d
Green River Shale	hydrous	200	7	1.6	1.7	3.4	1.3	>400 yr
	hydrous	200	21	2.3	1.3	2.6	2.0	
	hydrous	200	49	2.7	1.2	2.5	2.9	
	hydrous	200	56	0.6	0.9	1.8	1.9	

Table 5: Results of the hydrous pyrolysis experiments in this study. All measurements here are made with the MID method.

Temperature(°C)	Propane data							Compound-specific isotope data			
	$\delta D_{\text{molecula}}$ r	erro r	δD_{ethy} l	erro r	$\epsilon D_{\text{C-}}$ T	erro r	δD_{vsmo} w	$\delta^{13}\text{C}_{\text{C}}$ 1	$\delta^{13}\text{C}_{\text{C}}$ 2	$\delta^{13}\text{C}_{\text{C}}$ 3	δD_{C} 1
330	-118.6	0.7	- 122.6	0.6	-77.0	6.7	-270	-42.87	-37.96	-35.62	-340
360	-109.5	0.9	- 112.1	0.4	-66.6	6.5	-264	-44.38	-34.61	-33.51	-340
390	-76.1	1.0	-69.0	1.2	2.8	10.5	-239	-39.19	-31.9	-30.96	-336
415	-49.3	0.9	-36.5	1.4	41.3	10.8	-219	-33.11	-28.42	-25.54	-324

Table in the Appendix

Table A1: Kinetic parameters for homolytic dissociation of single bonds in the kinetic Monte-Carlo model. Hydrogen KIE is for hydrogen bonded to the carbon position with asterisk. Temperature is set at 180 °C.

Bond type	Carbon KIE($k^{12}\text{C}/k^{13}\text{C}$)			Hydrogen KIE ($k\text{H}/k\text{D}$)		
	1°	2°	3°	1°	2°	3°
C*-C(aliphatic)	1.025	1.024	1.017	1.277	1.198	1.184
C*-C(aromatic)	1.024	1.014	1.010	1.242	1.165	1.151
C*-N	N/A					
C*-O	1.024	1.018	1.014	1.339	1.257	1.242
C*-S	1.013	1.019	1.015	1.267	1.189	1.175
Adjacent [#]	1.002	1.006	1.006	1.034	0.990	0.990

[#]This denotes KIE of isotopically substituting the C/H position adjacent to the cracking position, which is formally secondary KIE for carbon and tertiary KIE for hydrogen. The adjacent isotope KIE is treated to be the same for all bonding environments.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Figure 1: Isotopic composition of methane from natural gases examined in this study. δD is on VSMOW scale and $\delta^{13}\text{C}$ is on VPDB scale. Categorization areas are based on Whiticar (1999). Errors for these analyses are typically 0.3‰ for $\delta^{13}\text{C}$ and 3–5‰ for δD .

Figure 2: Central-terminal differences of D/H in natural propanes from this study. Error bars show 2 standard error of sample analysis. The coloring scheme in this figure is consistent with other figures in this paper. GOM=Gulf of Mexico.

Figure 3: Comparison of kinetic Monte-Carlo model outputs with natural propane data. Dashed lines show results of the small kerogen models (Ungerer et al., 2015), dotted lines show results of the big kerogen models (Bousige et al., 2016) and solid lines show results from pristane and oil. Propane isotope data of the Woodford shale is from Liu et al. (2019). GOM=Gulf of Mexico.

Figure 4: Central-terminal hydrogen isotope differences of natural propanes plotted vs. their reservoir temperatures. The temperatures were measured at the wells and adjusted.

Figure 5: Left: ϵD_{C-T} plotted vs. mapped maturity (vitritine reflectance) of the gases recovered from unconventional formations, the Eagle Ford Shale (this study) and the Woodford Shale (Liu et al., 2019). Right: ϵD_{C-T} plotted vs. gas maturity for the conventional hydrocarbon systems in this study. The solid line in the left panel represents the hydrogen exchange model with the best-fit parameters for the Woodford Shale series. The grey area shows isotope equilibrium at 50–200 °C.

Figure 6: Arrhenius plot showing the result of modeling the hydrogen exchange rate constants of propane in the Woodford Shale (labeled as ‘Woodford exchange’ in the figure) compared to various processes. The simulated activation energy is between 80-180 kJ/mol. Hydrogen exchange refers to D/H exchange experiments on methane and hexane (Koepp., 1978; Sessions et al., 2004). Hydrous pyrolysis refers to hydrous pyrolysis experiments on the Woodford shale, Alum shale, Phosphoria shale and Monterey shale (Lewan and Ruble, 2002). Oil cracking refers to oil-cracking experiments on the Boscan oil and Pematang oil (Ungerer et al., 1988). Propane cracking refers to propane pyrolysis experiments (Laidler et al., 1962).

Figure 7: Position specific D/H fractionation in propane plotted vs. a measure of isotope clumping in methane. The equilibrium fractionation line and its apparent temperature (top horizontal axis) is based on ab initio calculations from Webb and Miller (2014) for propane and experimental calibration from Stolper et al. (2014b) for methane.

Figure 8: Propane isotope data for the hydrous pyrolysis experiments (horizontal axis is molecular average δD of propane). Equilibrium isotope effect at 330-415°C is extrapolated from Xie et al., (2018) and Webb and Miller (2014)

Figure 9: Isotopic constraints on the sites of propane decomposition associated with biodegradation in the Hadrian field gas samples (horizontal axis is molecular average δD of propane). Dashed lines represent modeled trends of the residual propane as biodegradation intensifies, where the numerical label notes the percentage of destroyed propane that was subject to attack at the central carbon site (x_c). Changes in the primary KIE of methane oxidation does not alter the modeled lines (assuming that KIE is closely similar for the terminal and central site mechanisms).

Figure in the Appendix:

Figure A1: A comparison of molecular δD (VSMOW) of propane measured by DFS and in other laboratories ('external'). DFS results are based on molecular ion measurements ($[C_3H_7D^+]/[C_3H_8^+]$). External measurements were made with GC-py-IRMS, with expected 1σ error of 3-5‰.

Figure A2: Compound-specific carbon isotope data of studies natural gas samples in this study. The x-axis, $1/n$, denote reciprocal of the alkane chain length. Left panel: gases with potential microbial methane input and/or hydrocarbon consumption. (See Thiagarajan et al. (2020a) and Section 5.4.2 of this paper); Right panel: gases of thermogenic origin.