



Article Unconventional Gas Geochemistry—An Emerging Concept after 20 Years of Shale Gas Development?

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Citation: Cesar, J. Unconventional Gas Geochemistry—An Emerging Concept after 20 Years of Shale Gas Development?. *Minerals* **2022**, *12*, 1188. https://doi.org/10.3390/ min12101188

Academic Editor: Leszek Marynowski

Received: 17 August 2022 Accepted: 19 September 2022 Published: 22 September 2022

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Abstract: Geochemical studies of gases from low-permeability reservoirs have raised new questions regarding the chemical and stable isotope systematics of gas hydrocarbons. For instance, the possibility of thermodynamic equilibrium is recurrently in discussion. However, it is not clear whether there is anything "unconventional" in the way these systems continue to be studied. Using molecular and stable carbon isotope data from North American unconventional and conventional reservoirs, this research has applied two parameters that well describe key transformation stages during gas generation. The δ^{13} C of ethane and the C₂/C₃ ratio increase from baseline values (<1%Ro, prominent kerogen cracking) until a first inflexion at 1.5%Ro. The same inflexion leads to ¹³C depletion of ethane and a rapidly increasing C₂/C₃ ratio as hydrocarbon cracking becomes prominent. The transition between these two stages is proposed to be a crossover from equilibrium to non-equilibrium conditions. There is no evidence for these characteristics to be limited to low-permeability reservoirs. Unconventional gas geochemistry should represent an approach that acknowledges that chemical and isotope distributions are not ruled by only one mechanism but several and at specific intervals of the thermal history.

Keywords: unconventional; gas; carbon isotopes; ethane

1. Introduction

The term "unconventional gas geochemistry" has been ambiguously mentioned in recent years, usually to refer to geochemical tools applied to study low-permeability hydrocarbon reservoirs [1–3]. However, is there anything unconventional in the way we interpret the geochemistry of such environments? That is a question we have not found a complete answer for.

Previous studies suggested that the main isotopic difference between unconventional and conventional gas resources is the carbon isotope reversal of ethane with respect to methane at thermal maturities above 2%Ro [4,5]. The reversal consists in δ^{13} C values of ethane that are more negative than the δ^{13} C values of methane from the same gas charge ($\delta^{13}C_{ethane} < \delta^{13}C_{methane}$). Recent explanations for this phenomenon include partly reversible free radical reactions for the formation of isotopically light ethane [6], diffusion fractionation due to basin uplift [7], and methane cracking with subsequent generation of ethane and propane [8].

Although less common then, isotope reversals had already been mentioned in the 1970s [9], and were proposed to result from a late increment of gas produced by its source, where previously produced gas had been lost [9]. Additionally, open pyrolysis experiments found ¹³C depletion of methane at temperatures above 600 °C, which was attributed to a second precursor pool producing lighter methane [10,11]. It was also mentioned that decreasing δ^{13} C values of methane were probably seldom observed because the ¹³C depletion is not perceived in the cumulative isotopic trend of methane in commercial gas accumulations [8–10].

A more recent study [12] reported an additional feature in the isotopic composition of low-permeability gas reservoirs that seems to be unique. Using gas isotope data from

26 reservoirs around the world, these authors showed the tendency towards an even isotopic distribution (EID) of 6‰ between methane and ethane, and between ethane and propane at a thermal maturity of 1.5%Ro. This likely universal isotopic characteristic implies that the carbon isotope distribution may shift towards equilibrium, and the same tendency is interrupted by secondary cracking of hydrocarbons at the indicated maturity level (~1.5% Ro). Around the same time, carbon isotope equilibrated gases were also identified in other global conventional and unconventional gas isotope datasets [13,14], at a thermal maturity of around 1.5%Ro.

Furthermore, pyrolysis experiments on Woodford Shale samples indicated the possibility of both, isotopic and chemical equilibrium, in gas hydrocarbons [15]. The concept of chemical equilibrium alone had been proposed by Mango et al. (2009) [16], and later applied by Cesar et al. (2021a) [17] to identify hydrocarbon plays within the Montney Formation, Western Canadian Sedimentary Basin (WCSB).

Although the findings mentioned above point towards new ways of interpreting gas geochemical data, the geochemical parameters to study low-permeability reservoirs continue to be applied in a rather traditional way (i.e., interpreted as conventional hydrocarbon systems, kinetic isotope fractionation during the entire maturation process). The concept of "unconventional gas geochemistry" as a new understanding of the molecular and isotope systematics of hydrocarbons from low-permeability reservoirs has not settled in.

In order to continue exploring different trends in the geochemistry of gas accumulations, this study proposes new graphical tools that exhibit variances in molecular and stable carbon isotope distribution of gases from low-permeability reservoirs compared to conventional accumulations. It investigates how important changes in certain molecular and isotope parameters may be attributed to key geochemical transformations during the thermal history of hydrocarbon generation. Furthermore, it shows some caveats of using an "unconventional gas geochemistry" approach, suggesting paths for improvement. The data presented in this work were obtained from public molecular and carbon isotope data of well-known North American low-permeability reservoirs.

2. Materials and Methods

Fundamental characteristics of the samples and low-permeability reservoirs included in this study can be found in Table 1 and Table S1, with their corresponding sources. The unconventional reservoirs include the Barnett Shale and the Fayetteville Shale from the USA, and the Lorraine Shale from Eastern Canada; whereas, the conventional samples originated in Kansas Midcontinent (USA). The selection of these datasets was based on the public knowledge about them, and their relatively wide thermal maturity range (0.7–3%Ro). An example from a well through Jurassic, Triassic, and Devonian strata from the Western Canadian Sedimentary Basin has also been included for discussion (Table S2).

Table 1. Low-permeability reservoirs and conventional (*) reservoirs from which molecular and carbon isotope data of gas samples was included in this study.

	Reservoir (Age)	Hydrocarbon Source	Maturity	Reference
	Barnett Shale (Mississippian)	Self-sourced	1–2%Ro	[5]
	Fayetteville Shale (Mississippian)	Self-sourced	2–3%Ro	[5]
	Lorraine Shale (Ordovician)	Self-sourced	0.6–2%Ro	[18,19]
Ν	Nemaha/Kansas * (Carboniferous)	Woodford Shale	1–1.4%Ro	[20-22]
	Sedgwick Basin * (Carboniferous)	Woodford Shale, Chattanooga Shale	0.7%Ro	[20-22]

3. Results

3.1. The δ^{13} C of Ethane and the $\Delta^{13}C_{C1-C2}$ Versus the C₂/C₃ Ratio

The significance of the molecular ratio ethane/propane (C_2/C_3) probably goes back to the work of Prinzhofer and Huc (1995) [23], who studied the thermal maturity evolution of these two compounds given the multiple origins of methane and its susceptibility

to migration. Then, methane was the only hydrocarbon gas considered to also have a microbial origin (recent studies report ¹³C depleted ethane associated with microbial methane [24,25]). The authors [23] found that in thermogenic gases, the C_2/C_3 ratio remains almost constant during kerogen cracking and increases at higher thermal maturity, specifically during hydrocarbon cracking. However, over the years, it is more common to observe gas geochemistry studies using parameters such as the Bernard ratio $C_1/[C_2 + C_3]$, and the isobutane to butane ratio $i-C_4/C_4$ (e.g., [7,26]).

Given the importance of hydrocarbon cracking for Early Triassic low-permeability reservoirs in Western Canada (because it has generated gas/condensate fluids of economic significance and lower carbon footprint), Cesar et al. (2021a) [17] reconsidered the ideas presented by Prinzhofer and Huc (1995) [23], and used the C_2/C_3 ratio to identify regional thresholds for the start of hydrocarbon cracking, which became target areas for natural gas liquids (i.e., very light condensate) within the Lower Triassic Montney Formation. Earlier, the same authors [12] had shown that changes in the C_2/C_3 ratio were also consistent with key stable carbon isotope variations in these molecules. For example, ¹³C depletion of ethane only registers during increasing C_2/C_3 ratio.

The above-mentioned provides the motivation for the application of the $\delta^{13}C$ of ethane, the $\Delta^{13}C_{C1-C2}$, and C_2/C_3 in the following subsections. The $\delta^{13}C$ of ethane is used because ethane is expected to be less affected by migration (compared to methane). Additionally, the $\delta^{13}C$ values of propane have not been included since they are less often reported due to the lower propane abundance for isotope measurements.

3.1.1. The Barnett Shale and the Fayetteville Shale

The Barnett shale (Fort Worth Basin, USA) was selected as an example of self-sourced low-permeability reservoir (e.g., [2,27]) because of the availability of data covering a thermal maturity range from 1 to 2%Ro, approximately [5]. The Barnett Shale consists of black marine shales with some limestone; its total organic carbon (TOC) content averages 2.5%–3.5% and the organic matter is primarily Type II kerogen [2]. Data from the Fayetteville Shale (Arkoma Bain, USA), also of Mississippian age, were included to cover a higher thermal maturity range (>2.5%Ro). The higher thermal maturity has obscured the original organic matter type of the Fayetteville shale, although it is estimated to be a mixture of types II and III kerogen [28]. The molecular and stable isotope characteristics of produced gas from these reservoirs can be found in the Table S1.

Figure 1a shows the variation of the δ^{13} C values of ethane as the C₂/C₃ ratio increases. For the Barnett Shale, the δ^{13} C of ethane increases from -37% to -32% with a relatively constant C₂/C₃ ratio of 2.5 (original or baseline C₂/C₃). As this ratio starts to increase, the δ^{13} C of ethane increases to a maximum of -29%, which is reached at a C₂/C₃ value of 6.6. After this section, ethane starts to deplete in ¹³C down to values as negative as -42% at C₂/C₃ values above 26. For highly mature gases (2–3%Ro), such as those from the Fayetteville Shale, δ^{13} C values of ethane are more negative (<-41%) and show the highest C₂/C₃ ratios (>40).

The $\Delta^{13}C_{C1-C2}$ difference of the original Barnett Shale ranges from -13 to -6%(Figure 1b) with a relatively constant C_2/C_3 ratio of 2.5. As the C_2/C_3 ratio increases, the $\Delta^{13}C_{C1-C2}$ difference shifts towards a value of zero, which is reached at a C_2/C_3 ratio of 25. The trend in Figure 1b confirms that the $\Delta^{13}C_{C1-C2}$ values are never above -6% when the C_2/C_3 ratio is relatively constant (original or baseline C_2/C_3). This is consistent with previous findings indicating that $\Delta^{13}C_{C1-C2} > -6\%$ values are only identified when secondary cracking of hydrocarbons is prominent as evidenced by a continuous increase in the C_2/C_3 ratio [12]. Likewise, Figure 1b allows identifying the C_2/C_3 value at which the $\Delta^{13}C_{C1-C2}$ reaches 0%. Therefore, it is now possible to detect the C_2/C_3 value at which the ethane carbon isotope reversal takes place (~26 for the Barnett Shale). The Fayetteville gases all exhibit methane–ethane isotope reversal ($\Delta^{13}C_{C1-C2} > 0$) associated with the highest C_2/C_3 ratios.



Figure 1. The relationships between the C_2/C_3 ratio and (**a**) the δ^{13} C of ethane, and (**b**) the $\Delta^{13}C_{C1-C2}$ difference; for samples from the Barnett and Fayetteville shales.

It is important to mention that although the Fayetteville gases look like a continuation of the Barnett Shale trend in Figure 1, this does not mean that less mature Fayetteville gases would necessarily follow the Barnett Shale trend in the lower maturity section of the curve. Even though they are similar in age, their original organic matter composition and thermal history cannot be expected to be identical.

3.1.2. The Lorraine Shale

This section applies the same graphical tools described above, for two examples of gases from the Lorraine Shale (Quebec, Canada). The Ordovician Lorraine Shale in the St. Lawrence Lowlands is a flysch succession dominated by mudstones and siltstones with locally thicker bedded sandstones [29]. This dataset covers a wide thermal maturity range (from ≈ 0.6 to $\approx 2.0\%$ Ro [16]); the samples correspond to mud-gas and two different profiles (<10 km apart) of the same geological formation.

Mud-gas profiles of the Lorraine Shale show similar trends to those of the Barnett Shale. In the case of the Leclercville well (Figure 2a), the δ^{13} C values of ethane start at -37% with a C₂/C₃ value of 0.6, and increase to a value of -32% at a C₂/C₃ value of 1.6. Subsequently, the ¹³C depletion starts until reaching values of -41% with a C₂/C₃ ratio above 10. Additionally, Figure 2b shows that the methane–ethane isotope reversal starts at a C₂/C₃ value of approximately 10.



Figure 2. The relationship between the C_2/C_3 ratio and (\mathbf{a},\mathbf{c}) the $\delta^{13}C$ of ethane, and (\mathbf{b},\mathbf{d}) the $\Delta^{13}C_{C1-C2}$ difference; for samples from the Fortierville (\mathbf{a},\mathbf{b}) ; circle markers) and Leclercville (\mathbf{c},\mathbf{d}) ; square markers) wells in the Lorraine Shale.

In the Fortierville well (Figure 2c), the δ^{13} C values of ethane start at -37% with a C_2/C_3 value of 0.9, and increase to a value of -34% at a C_2/C_3 value of 2.4. Subsequently, the 13 C depletion starts until reaching values of -36% with a C_2/C_3 ratio of 4. Although fewer data points are available for this well, the trend in Figure 2d suggests that the C_2/C_3 value at the start of the isotope reversal is close to 5.

It is interesting to note that although both wells cross the same geological unit and overlapping maturity ranges (higher maturity reached in Leclercville), key isotope and molecular fluctuations are not the same. This matter will be expanded in the discussion section.

3.1.3. Nemaha/Kansas Uplift and Sedgwick Basin

Data of conventionally produced gases from Nemaha/Kansas [20] have been included because they were previously used to describe secondary cracking of oil at variable C_2/C_3 ratios [23]. These gases originated in the Andarko Basin (thermally mature rocks 1–1.4%Ro) and migrated more than 160 km [20]. The specific source was later confirmed to be the Woodford Shale [21]. With respect to conventional gas from the Sedgwick Basin, these fluids are considered to originate from local source rocks of lower maturity (Chattanooga Shale, 0.7%Ro [20], Woodford shale [22]). In this way, we cover a large variety of thermal maturity levels and migration distances.

Isotopic and chemical composition trends are less clear for the conventional gas samples. In the Nemaha/Kansas gases, the δ^{13} C values of ethane increase from -38 to -34% as the C_2/C_3 ratio increases from 0.8 to 4.1 (Figure 3a), whereas the $\Delta^{13}C_{C1-C2}$ difference varies from -12 to -4% (Figure 3b). For the gases of the Sedgwick Basin, the δ^{13} C of ethane ranges between -37 and -34% as the C_2/C_3 ratio increases from 1.2 to 3.1 (Figure 3c). The $\Delta^{13}C_{C1-C2}$ varies from -11 to -5% (Figure 3d).



Figure 3. The relationship between the C_2/C_3 ratio and (a,c) the $\delta^{13}C$ of ethane, and (b,d) the $\Delta^{13}C_{C1-C2}$ difference; for samples from the Nemaha/Kansas (a,b) and Sedgwick (c,d) fields, Kansas Midcontinent.

3.2. Devonian Duvernay Formation—Well SCL HZ KAYBOB 4-16-64-20

The example used in this section corresponds to a well from the Fox Creek area in west-central Alberta. The same well lands its horizontal section within the Devonian Duvernay Formation, which is intensively developed as a low-permeability reservoir nowadays. However, enough gas for measurement was detected in the overlying Devonian Winterbum and Ireton Formations, the Lower Triassic Montney Formation, and the Jurassic Fernie Formation (including its Gordondale/Nordegg Member). The data and specific corresponding depths can be found in Table S2. Gas data from this section are included to test the applicability of the parameters described above to multiple gas sources from the same well.

Although the thermal maturity ranged from 0.8%VR_{eq} in Gordondale/Nordegg to 1.8%VR_{eq} in Duvernay [29], the isotope data in Figure 4 do not display a maturity corresponding trend. The youngest samples from the Jurassic Fernie Formation (50 m interval) have δ^{13} C values of ethane from -40 to -32%, with C₂/C₃ ratios between 2.3 and 3.4, and $\Delta^{13}C_{C1-C2}$ from -15 to -7%. Also of Jurassic age, samples from Gordondale/Nordegg (25 m interval) have δ^{13} C values of ethane around -40% with a C₂/C₃ ratio of 3.2, and a methane–ethane carbon isotope difference of -6%. The Lower Triassic Montney Formation (70 m interval) exhibits carbon isotope values of ethane from -40 to -38%, equivalent to C₂/C₃ ratios from 1.2 to 2.6 and $\Delta^{13}C_{C1-C2}$ from -9 to -5%. The Devonian Winterbum and Ireton Formations (310 m interval) have the most positive δ^{13} C of ethane (up to -30%) with a C₂/C₃ value around 3.7 and $\Delta^{13}C_{C1-C2}$ differences below -14%. In the case of the Devonian Duvernay Formation (2 km horizontal interval), most of the samples oscillate around -33% in their δ^{13} C of ethane, C₂/C₃ values of ~3.7 , and $\Delta^{13}C_{C1-C2}$ of $\sim-12\%$.



● Fernie ● Gordondale ■ Montney ◆ Winterbum ◆ Ireton ◆ Duvernay

Figure 4. The relationship between the C_2/C_3 ratio and (**a**) the $\delta^{13}C$ of ethane, and (**b**) the $\Delta^{13}C_{C1-C2}$ difference; for samples from the KAYBOB 4-16-64-20 well, western Alberta.

Although the δ^{13} C values of ethane are less negative in the Devonian strata, a thermal maturity of 1.8%VR_{eq} in the Duvernay Formation would predict these gases to be in ethane isotope reversal or at least have $\Delta^{13}C_{C1-C2}$ approaching zero, which is not the case. Only the Gordondale–Montney interval seems to have a more unconventional character with $\Delta^{13}C_{C1-C2}$ approaching -6% and most negative δ^{13} C values of ethane. These observations will be further expanded in the discussion below.

4. Discussion

Using the distribution of stable carbon isotopes of ethane from the Barnett Shale (Figure 1a) allows us to confirm that during kerogen cracking, i.e., when the C_2/C_3 ratio is relatively constant (2.5), the δ^{13} C values of ethane tend to increase as it would be expected during normal kinetic fractionation (e.g., [13,30]). Likewise, ethane starts to deplete in ¹³C at a specific C_2/C_3 ratio (~6.6) which has been previously reported to take place circa 1.5%Ro [12,19]. From there, the C_2/C_3 ratio increases towards values of up to 40 as secondary cracking of hydrocarbons takes place, including cracking of wet gas components (C_2 - C_5). It is the time where enough radicals may be available, for example, for certain reactions to occur and regenerate ¹³C depleted ethane (e.g., [6,8]). It is particularly interesting to note in Figure 1a that with an increase in the C_2/C_3 ratio from 2.5 to 6.6, the δ^{13} C value of ethane increases, too. To the current knowledge, this interval, representing a ¹³C enrichment of ethane by 3‰ for the Barnett Shale, has not been identified before. This stage may be a transition interval from gas generation by kerogen cracking to gas generation dominated by hydrocarbon cracking (we should remember that even during hydrocarbon cracking, compounds continue to be released from kerogen [23,31,32]).

We may anticipate that the C_2/C_3 inflexions and isotope enrichment/depletion mentioned above are unique of different source rocks/reservoirs. For instance, in the Lorraine Shale from Leclercville (Figure 2a), the curve changes in C_2/C_3 ratio happen at 0.6 and ~1.6 with a ¹³C enrichment of ~4‰, whereas the same rock in the Fortierville well (Figure 2c) has C_2/C_3 ratio varying from 0.9 to ~2.4 with a ¹³C enrichment of ~4‰. This demonstrates that even for the same geological formation, chemical and isotopic composition of hydrocarbon gases can vary on relatively small scales.

Moving forward in thermal maturity, plotting the C_2/C_3 ratio versus $\Delta^{13}C_{C1-C2}$ (Figure 1b) proved helpful because it allows us to identify the C_2/C_3 value at which the ethane isotope reversal starts—~26 for the Barnett Shale. If $\Delta^{13}C_{C1-C2} > 0$ values had been reported to happen above 2%Ro [5,12], this means we are now able to identify a C_2/C_3 value for such thermal maturity boundary (i.e., dry gas zone). The same boundary for the Lorraine Shale seems to have values of 10 (in Leclercville, Figure 2b) and 5 (in Fortierville, Figure 2d). Gases in ethane isotope reversal such as those from the Fayetteville Shale (Figure 1b) and the Lorraine Shale (Leclercville, Figure 2b) have the highest C_2/C_3 ratios of their corresponding curves, as it would be expected for their maturity levels.

When interpreting the conventional gas data, both trends (Figure 3a,c) show increasing δ^{13} C values of ethane with increasing C_2/C_3 ratio, which is consistent with stable carbon isotope distributions described before unconventional gas development (e.g., [27,30,31]. However, we could also argue to be seeing the equivalent thermal maturity section approaching towards 1.5%Ro, discussed for the unconventional shales, where there is a transition from prominent kerogen cracking to prominent hydrocarbon cracking. Knowing the thermal maturity of Nemaha/Kansas (1–1.4%Ro) and Sedgwick (0.7%Ro) gases, we may infer that the mentioned transition is not necessarily the case. Another aspect to consider is migration and hydrocarbon mixing always affecting conventional gas accumulations, which overprint the original carbon isotope signature of the gas. Additionally, it is challenging to find a wide range of thermal maturity in conventional gases that come from the same source rock and develop an isotope curve such as the ones developed for the Barnett Shale and Lorraine Shale.

Although thermodynamic equilibrium or meta-stable equilibrium conditions for natural gas are more often stated in recent literature [12–15], the exact equilibrium conditions continue to be a mystery as they lack precise definitions. It seems that hydrogen exchange may play an important role in free radical activation and other transformations responsible for the equilibrium [15,33].

Some authors had considered that chemical and isotope equilibrium were perhaps limited to gases in low-permeability reservoirs that have not experienced major migration [12,17]. This was based on the significance of residence time for isotope equilibrium to be established [34]. However, other studies found that equilibrium was also possible in conventional gas [13,14] (supported by clumped isotope analysis as well). Therefore, it may simply be more difficult to study the possibility of isotope equilibrium in conventional gases due to hydrocarbon mixing and extended migration distances.

Another aspect to question is that the equilibrium is probably not reached at 1.5%Ro. This is based on the fact that the even isotopic distribution of 6‰ ("even isotopic distribution (EID)" is the situation where the difference between the δ^{13} C values of methane and ethane equals the difference between the δ^{13} C values of ethane and propane [12]) could not be explained by the isotope equilibrium calculations for a wide range of temperatures by Thiagarajan et al. (2020) [13]. It should be mentioned that the later study also included CO₂ in the equilibration process. It is possible that the even isotopic distribution of 6‰ simply represents the last stage of the quasi-equilibrium leading to a completely new type of chemical transformations, which ultimately generate ethane depleted in ¹³C.

The crossover from equilibrium to disequilibrium conditions might not occur at a specific maturity as stated before (1.5%Ro, [14]), but rather over a maturity range finishing at 1.5%Ro. For example, in the case of the Barnett Shale, the crossover might be equivalent to the interval where the C_2/C_3 ratio increases from 2.5 (initial or original value) to 6.6 (value at 1.5%Ro) as the transition from prominent kerogen cracking to prominent hydrocarbon cracking takes place. This reinterpretation has been represented in Figure 5.



Figure 5. Diagram representing the geochemical characteristics to take into account when considering an equilibrium approach. After Thiagarajan et al. (2020) [13], Cesar et al. (2020) [12], and this study. "Crossover" stands for the suggested crossover between equilibrium and non-equilibrium conditions. The exact %Ro for the equilibrium (if established) remains unknown. EID: even isotopic distribution [12].

The geochemical variability presented in Figure 5 for the generation of gas hydrocarbons may also explain why the isotopic composition of natural samples have satisfied all previous empirical models reported in the literature (usually consisting of maturity versus δ^{13} C calibrations). For instance, natural samples have satisfied equilibrium models [35], kinetic models [36–38], and adaptations of these [39]. In reality, all these processes are possible, but one dominates over the other at a particular interval of the thermal evolution of the source rock/reservoir. Understanding the order in which the isotope fractionation mechanisms take turn during thermal history will be key for fluid-fluid and fluid-source correlation studies.

4.2. Devonian Duvernay Formation—Well SCL HZ KAYBOB 4-16-64-20

In this sample set, all gases in Devonian reservoirs, including the target Duvernay Formation, have large carbon isotope differences between methane and ethane ($\Delta^{13}C_{C1-C2} < -12\%$, Figure 4b). For their level of thermal maturity (>1.5%Ro), gases formed at post-equilibrium conditions would be expected to have $\Delta^{13}C_{C1-C2}$ approaching 0 and even a methane–ethane isotope reversal (in the case of Duvernay with 1.8%Ro), which is not the case of these samples. Therefore, we can interpret that these gases are probably mixtures or gases whose molecular composition has fractionated during migration. The Duvernay Formation is a well-known source rock for conventional hydrocarbons [40], thus it is conceivable that gases from the tight sections of the same rock have migrated variable distances.

Only the gases from the Jurassic and Triassic reservoirs (Fox Creek, Alberta) seem to resemble gases from reservoirs such as the Barnett Shale. For instance, the carbon isotope difference between methane and ethane approaches -6% at a relatively constant C_2/C_3 ratio in gases from the Jurassic Fernie Formation (including its Gordondale/Nordegg Member). The $\Delta^{13}C_{C1-C2}$ also approaches values of -6% in gases from the Montney Formation associated with an increase in their C_2/C_3 ratio.

At a larger scale, the composition of gases from Montney and Fernie might be more consistent with chemical and isotope equilibration, whereas gases in Devonian strata have mixed molecular and isotope signatures. However, the amount of data density and variability in this occasion does not strongly support either conclusion. Interpreting carbon isotope data from one particular well is not a straightforward process, and comparison with additional data from nearby wells and wider ranges of thermal maturity is required. Other elements from the structural geology and basin history will also help understand the probabilities of hydrocarbon migration and mixing.

The take-home message of this study, and the real implication of "unconventional gas geochemistry" is that the possibility of chemical and isotope equilibrium needs to be taken into account particularly when analyzing gases from low-permeability reservoirs. This is especially relevant in basins producing hydrocarbons in the wet gas window, which coincides with postulated quasi-equilibrium conditions (approaching 1.5%Ro). Additionally, we know that the tendency towards quasi-equilibrium is not unique of unconventional accumulations, but gases in tight rocks are thought to have a higher probability of undergoing "equilibration" because of the longer residence time of in-situ hydrocarbons and their shorter migration/mixing distances.

The main pitfall of considering the above is that, as shown in this example, we can find all scenarios in one single well. It might also seem tedious having to take more variables into account. However, correlations (fluid-fluid or fluid-source) will be more accurate, and information about the openness of the system could also be obtained. For instance, for a reservoir section with the same maturity, we should be able to distinguish in-situ generated gas from migrated gas. The in-situ generated gas would have formed in a semi-open system over long residence times, more likely tending towards equilibrium. Instead, migrated gas would have formed in an open system (some distance away) even if its reservoir today is tight, and will more likely be non-equilibrated.

5. Conclusions

Although gas generation mechanisms are the same, low-permeability reservoirs provide the environment for particular features to be noted in unconventional gas, for instance, carbon isotope reversals and even isotopic distribution. These characteristics are probably unnoticed in conventional gas due to its lower residence time in the source rock (or where generated) and hydrocarbon mixing/migration. Geochemical parameters such as the δ^{13} C values of ethane and the C₂/C₃ ratio are helpful to characterize self-sourced reservoirs such as the Barnett and Lorraine Shales. Key changes in these parameters are associated with variations in the chemical transformations during thermal history. For instance, they increase from baseline values during kerogen cracking towards intermediate values that

might be equivalent to an equilibrium-disequilibrium crossover ending at 1.5%Ro. After this, C_2/C_3 ratio rapidly increases as the δ^{13} C values of ethane become more negative (ending in methane–ethane isotope reversal) during prominent hydrocarbon cracking. Unconventional and conventional gases cannot continue to be studied under the same isotope geochemistry principles.

6. Future Work

The ideal scenario will be to estimate a C_2/C_3 ratio versus δ^{13} C of ethane curve for every low-permeability reservoir, such as the one obtained for the Barnett Shale in Figure 1a. This curve would be used as a baseline for the interpretation of different geochemical processes taking place in that particular reservoir, considering that the parent material (either kerogen or migrated bitumen) is relatively homogeneous (not the case in most instances). A way to attempt this goal may be new isotope calculations using quantum chemistry for the estimation of the hypothetical curves. However, for these calculations, the different chemical transformations at all stages of gas generation and thermal evolution need to be pre-stablished, and some additional work is required to reach a consensus on this matter. The role played by the reversibility or carbon flows [40] as well as the influence from the structure of gas precursors and their intramolecular isotope distribution [41,42] are areas with paths ahead, too.

Having the ethane curve of a particular reservoir could also help us predict the δ^{13} C value of methane at 1.5%Ro, which would be 6‰ more negative than the δ^{13} C of ethane. This is important for identifying methane migration, not only between hydrocarbon producing intervals but also towards shallow intervals with potential environmental implications (e.g., groundwater and surface vents).

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/min12101188/s1, Table S1: molecular and stable isotope data of produced gases from the low-permeability reservoirs and conventional reservoirs included in this study; Table S2: molecular and stable isotope data of mud-gas from the Lorraine Shale; Table S3: molecular and stable isotope data of mud-gas from the Well SCL HZ KAYBOB 4-16-64-20.

Funding: This research was funded by Natural Resources Canada (NRCan) and its Geoscience for New Energy Supply (GNES) program, grant number 331403.

Data Availability Statement: The data interpreted in this study can be found as supplementary material.

Acknowledgments: The author acknowledges the editor and reviewers for their constructive feedback to improve the quality of this publication.

Conflicts of Interest: The author declares no conflict of interest.

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