Molecular and stable carbon isotope geochemistry of mud-gas-derived hydrocarbons and its application for the assessment of low-permeability reservoirs from the Montney Formation, Western Canada

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Abstract

Mud-gas isotope logging (MGIL) of hydrocarbons (methane, ethane, propane) has become a widely used approach to fingerprint gas-bearing formations during the drilling of vertical and horizontal oil and gas wells often with the goal to assess potential cross-formational gas migration. In this study, we have used mud-gas molecular and isotope data to assess the usefulness of MGIL for the geochemical assessment of a single low-permeability reservoir formation, the Montney Formation in Western Canada. An example from a well completed in British Columbia shows that hydrocarbon samples collected in IsoJars® tend towards more positive carbon isotope ratios compared to data for samples obtained using IsoTubes®, potentially attributed to ^{13}C enriched residual gas retained in the cuttings. Additionally, in publically available mud-gas data from 45 other wells, it was found that the carbon isotope ratios of mud-gas from the Montney Formation are overall consistent with the thermal maturity of this stratigraphic unit, but the data display a relatively scattered trend on a thermal maturity plot based on $\Delta^{13}C_{C1-C2}$ and $\Delta^{13}C_{C1-C3}$. Molecular parameters such as $[C_1/(C_2+C_3)]$ can be modified via processes such as desorption and diffusion after sampling gases in IsoJars®, while the i-C_4/n-C_4 ratio was found to be the most consistent molecular parameter between sampling techniques. We conclude that mud-gas molecular and isotope data derived from samples collected

in IsoTubes® are suitable for geochemical assessment (e.g. thermal maturity, fluid-fluid correlations) of low permeability hydrocarbon reservoirs such as the Montney Formation.

Key words: mud-gas, carbon isotopes, maturity, Montney Formation.

1. Introduction

Conducting mud-gas isotope logging (MGIL) has become a common practice among energy operators in the Western Canadian Sedimentary Basin (WCSB). The technique involves the isotope analysis of low concentration hydrocarbon gases, which are collected from the circulating mud stream during drilling (Ellis et al., 2003; 2007). Mud-gas samples are often collected in containers such as IsoTubes® and IsoJars®. An IsoTube® is a tube-shaped vessel that collects free formation gas that is pulled by a vacuum line to the mud-logging unit (Stratum Reservoir, 2019a). An IsoJar® is a small, sealed container used to keep cutting samples that have been scooped from the shale shakers enabling outgassing of hydrocarbons into a headspace in a partially water-filled jar (Stratum Reservoir, 2019b).

Historically, in conventional hydrocarbon reservoirs, MGIL has enabled fingerprinting of gases and helped validating hydrocarbon-charged intervals throughout the stratigraphic column, identifying source rocks for gas/condensate, assessing reservoir vertical and lateral compartmentalization and identifying low-resistivity pay zones (Ellis et al., 2003; 2007; Nair et al., 2009; Petersen et al., 2019). This information can be highly valuable in cases where gas migration into overlying units is suspected and may help to identify the source and hence depth of gas leakage (Hendry et al., 2016). In consequence, MGIL data are highly valuable to determine the origin of methane and ethane in groundwater enabling to test hypotheses whether leakage of fugitive gases from oil and gas activities is impacting aquifers or not (e.g. Hendry et al., 2016). This is possible because the isotopic compositions of mid-to-late mature hydrocarbon gases generated at great depth and shallow primary microbial gases are distinct (e.g. Schoell, 1983; Milkov and Etiope, 2018).

MGIL has however been less successful to differentiate subunits of low-permeability hydrocarbon reservoirs such as the Montney Formation in the WCSB, which has a complex history of hydrocarbon charging, generation, and hydrocarbon mixing within variable lithologies (Euzen et al., 2021; Zonneveld and Moslow, 2018). It is well known that a considerable variability of stable carbon isotope ratios of hydrocarbon gases obtained via MGIL of low-permeability reservoirs can be associated with different sampling techniques (e.g. Chatellier et al., 2013; Kirkland, 2017), vertical communication between stacked horizontal wells (Goldsmith and Abrams, 2016), as well as with lithology variations (including porosity and permeability) of the reservoir (Zumberge et al., 2009; Chatellier et al., 2013; Tilley and Muehlenbachs, 2013; Chatellier and Perez, 2016; Zhang et al., 2018). This makes it challenging to distinguish geochemical variations in sub-units of the formation from trends that are caused by operational or analytical artefacts.

Operators in the region of the Montney Formation in Western Canada continue to collect MGIL data using different sampling techniques. The obtained data for samples collected in IsoTubes® or IsoJars® are periodically reported to the regulators and are subsequently transferred to the public domain. However, the public domain records do not indicate the sampling approach, and hence it is unclear to what extent the reported measurements can be used for a reliable petroleum geochemistry characterization of the Montney Formation. For this reason, we herein present and interpret publically available mud-gas isotope data for hydrocarbons, and report comparison data from IsoJars® and IsoTubes® samples collected from a single horizontal well from the Montney Formation in Western Canada, using the latest interpretative tools for gas molecular and carbon isotope geochemistry, which are based on the thermal history of the gas. The objectives of our study are (i) to evaluate the consistency between mud-gas stable carbon isotope trends of hydrocarbons and the known thermal maturity of the Montney Formation, (ii) assess variations of geochemical parameters in samples collected using IsoJars® versus IsoTubes®, and (iii) detect chemical and isotopic fractionation during MGIL sampling using data in the public domain. The anticipated outcome is to identify the potential and the limitations of using mud-gas-derived chemical and isotope data for samples

obtained from the Montney Formation in Western Canada for geochemical interpretations (e.g. identifying the source of hydrocarbons).

2. Methods

2.1. Samples

During the drilling of the vertical and horizontal sections of a well completed in the Montney Formation in British Columbia (Canada), we collected 36 mud-gas sample pairs in IsoTubes® and IsoJars®, respectively. An IsoTube® is a tube-shaped vessel that collects free formation gas that is pulled by a vacuum line to the mud-logging unit, whereas an IsoJar® is a small, sealed container used to keep cutting samples that have been scooped from the shale shakers. Gas contained in the cutting samples is allowed to desorb with time, and the headspace gas in the partially water-filled IsoJar® is subsequently analyzed. The vertical section of the well is represented by 19 mud-gas sample pairs within a 200 m depth interval (1850 – 2050 m below ground surface) whereas 17 sample pairs were obtained from the 2.5 km horizontal section of the well (see Fig. S1 and Table S1).

In addition to the samples described above, we used compositional and carbon isotope data for additional 979 mud-gas samples from 45 wells completed in the Montney Formation (see supplementary data). These data are publicly available from the regulatory authorities, i.e., the Alberta Energy Regulator and the British Columbia Oil and Gas Commission (www.aer.ca and www.reports.bcogc.ca, last accessed on June 11, 2020). For these samples, the sampling approach has not been indicated (e.g. whether IsoTubes®or IsoJars® were used) and it is also unknown whether the samples come from vertical or horizontal sections. Therefore, depth will not be correlated among wells in this study.

2.2. The C_1-C_5 molecular composition by gas chromatography — flame-ionization detection (GC-FID)

A total of 36 gas samples collected using IsoTubes® and 36 samples collected using IsoJars® were analyzed for gas composition, using gas chromatography. A 5 mL aliquot of gas was removed from each IsoTube®/IsoJar® via a modified septum valve and locking gas-tight syringe. Gas compositional analysis (C_1 to C_5 alkanes) was performed by injecting the sample into a Scion 450/456 gas chromatograph (GC). The GC utilizes four separate analytical columns connected to three thermal conductivity detectors and a flame-ionization detector for gas separation and quantification. The lower detection limit for hydrocarbon compounds is 1 ppm. Certified gas standards were regularly analyzed to calibrate the GC immediately prior to analysis. Analytical drift was monitored by injecting the appropriate gas standards after every ten samples. The precision and accuracy for gas composition analysis is typically better than ± 2.5% of the reported concentrations. Comparable methods to determine gas composition were used by different commercial or research laboratories involved in generating the public domain data. Gas composition of methane, ethane and propane were normalized to 100% to remove the influence from nitrogen, carbon dioxide and other fixed gases, and to enable comparison of the results for different wells completed in the Montney Formation.

2.3. Compound Specific Isotope Analysis (CSIA) of natural gas by gas chromatography — isotope ratio mass spectrometry (GC-irMS)

The compound specific $\delta^{13}C$ values of methane (C_1), ethane (C_2) and propane (C_3) in the 36 sample pairs mentioned above were determined using continuous flow isotope ratio mass spectrometry using a Thermo Trace GC – GC-IsoLink system interfaced to a Thermo MAT 253 mass spectrometer via a Thermo Conflo IV. Gas sampling was conducted as indicated above for GC compositional analysis. The aliquots of gas were injected into a helium carrier stream through the inlet of the GC using a gas tight syringe. Carbon dioxide (CO_2), air, and hydrocarbon compounds were separated on a GC column before passing with a He

carrier gas through a combustion reactor maintained at 1030 ºC. The isolated hydrocarbon gas compounds were quantitatively converted to CO_2 in the combustion furnace. The separated CO_2 gas pulses were then swept sequentially, by the carrier gas, through a water trap (Nafion®) and then through an open split interface ensuring steady continuous flow of the gas into the mass spectrometer. Carbon isotope ratios of C_1, C_2 and C_3 were determined and normalized using a 2-point calibration (linear regression) against specially prepared Air Liquide Alphagaz® calibration standards analyzed at the beginning and end of each workday, which cover the $\delta^{13}C$ range of the compounds in the gas samples. The final $\delta^{13}C$ values of the unknown hydrocarbon compounds were determined using the instrument software (ISODAT 3.0) and are expressed in the usual delta notation in per mil (‰) relative to the international V-PDB standard, with an uncertainty of 0.5‰. Similar compound specific isotope analysis (CSIA) techniques were used by different commercial or research laboratories involved in generating the public domain data.

Both, the molecular and carbon isotope compositions of the 36 sample pairs, were determined in the Isotope Science Laboratory in the Deaprtment of Geoscience at the University of Calgary. Mud-gas data for samples from the other 45 wells have been generated by different commercial laboratories in Canada (e.g. Stratum Reservoir Laboratory and GeoMark).

3. Results and discussion

3.1. Thermal maturity of the Montney Formation as indicated by MGIL data

In order to assess the thermal maturity of the Montney Formation, we have plotted in Fig. 1 the public data available for samples from the 45 wells in a thermal maturity plot according to Cesar et al. (2020b). This plot establishes the thermal maturity of natural gas from low-permeability reservoirs according to the difference in $\delta^{13}C$ values between methane and ethane ($\Delta^{13}C_{C1-C2} = \delta^{13}C_{C1} - \delta^{13}C_{C2}$), and between methane and propane ($\Delta^{13}C_{C1-C3} = \delta^{13}C_{C1} - \delta^{13}C_{C3}$).

In the mud-gas samples from the 45 wells landed in the Montney Formation, the carbon isotope value difference ranges from -22.4‰ to -6.5‰ for $\Delta^{13}C_{C1-C2}$ and from -26.6‰ to -9.8‰ for $\Delta^{13}C_{C1-C3}$. This data

distribution indicates that the thermal maturity of 73% of the reported gases from the Montney Formation spans from the oil window (0.8% Ro) to wet-gas at almost 1.5% Ro, which is consistent with literature information (e.g. Rokosh et al., 2012). The rest of the samples (27%) plot in the low-maturity region (<0.8% Ro) and these samples probably do not represent the landing/target zones but shallower, less mature sections of the Montney Formation that are accessed while drilling above target intervals. It is noteworthy that more mature (dry) gas is generated within the Montney Formation (Wood and Sanei, 2016; Euzen et al., 2021, Cesar et al., 2021), but limited data are available because of the lower economic interest in producing dry gas.

The overall trend shown in Fig. 1 deviates up to 4‰ above the linear distribution expected based on produced gas samples from low-permeability hydrocarbon reservoirs worldwide analyzed by Cesar et al. (2020b). This may suggest that some mud-gas isotope logging approaches may be associated with isotopic fractionation effects that are not observed during sampling of produced gas that accesses large volumes of gas sampled at the wellhead. Unfortunately, the public database does not reveal the specific sampling techniques used for each well that typically involves the collection of free gas in IsoTubes® or the desorption of gas from cuttings collected in IsoJars®. Therefore, we investigated whether there is a systematic difference in geochemical and isotopic parameters derived from analysis of samples from the same reservoir depth in the Montney Formation collected in IsoTubes® and IsoJars® respectively.

3.2. IsoTubes® versus IsoJars®

MGIL data were obtained from a well in northeast British Columbia (Canada) and the $\delta^{13}C$ values of methane, ethane, and propane measured in IsoTube® and IsoJar® samples are summarized in Table S1, including the difference between the carbon isotope ratios obtained using the two sampling techniques and expressed as $\Delta^{13}C$ for methane (C_1), ethane (C_2) and propane (C_3), respectively. The $\delta^{13}C$ values of the gas hydrocarbon compounds collected in IsoTubes® varied little with an average carbon isotope ratio of

methane of -47.0 ± 0.9‰, ethane of -33.9 ± 2.6‰, and propane of -30.6 ± 1.9‰. The $\delta^{13}C$ values of the same compounds collected in IsoJars® were characterized by variabilities of less than 2.5‰, with average carbon isotope ratios of methane of -42.5 ± 2.3‰, ethane of -31.6 ± 1.7‰, and propane of -30.2 ± 1.7‰. These data revealed that carbon isotope ratios of headspace gases from IsoJars® are generally more positive than those of gas collected in IsoTubes®, with an average difference of 4.7‰ for methane, 3.3‰ for ethane, and 1.2‰ for propane. This finding suggests that desorbed headspace gas collected in IsoJars® is affected by isotope fractionation effects that are most pronounced for the lightest *n*-alkane, i.e., methane, and progressively decrease in ethane and propane (e.g. Wu et al., 2020).

Carbon isotope fractionation effects due to physical phenomena such as desorption and diffusion have not been conclusively observed in large gas volumes from low-permeability petroleum reservoirs (e.g. produced gases). Milkov et al. (2020) proposed that uplift and depressurization may result in isotope fractionation via desorption, causing gases from conventional and unconventional reservoirs to be in carbon isotope reversal ($\delta^{13}C_{ethane} < \delta^{13}C_{methane}$). However, they found also that the reservoirs that had experienced uplift/depressurization were associated with higher thermal maturity levels (>2 %Ro), whereas less mature reservoirs (<2 %Ro) with less uplift contained gases with normal isotope trends ($\delta^{13}C_{methane} < \delta^{13}C_{ethane}$). Therefore, we caution that in addition to desorption/diffusion effects other factors may play a role such as thermal maturity effects that had been previously suggested for the occurrence of carbon isotope reversals by other authors (e.g. Tilley and Muehlenbachs, 2013; Xia and Gao, 2018).

However, desorption istope fractionation effects are often detected in relatively small amounts of gas in laboratory experiments (Zhang and Kroos, 2001; Xia and Tang, 2012; Faiz et al., 2018). This is because the extent to which carbon isotope fractionation is expressed is inversely related to the amount of diffused gas so that isotope fractionation effects are most pronounced in progressively smaller portions of remaining gas (Zhang and Kroos, 2001; Xia and Tang, 2012). Isotope fractionation takes place because of a higher molecular mobility of the ^{12}C-containing isotopologues (Zhang and Kroos, 2001). Therefore, we infer that desorption and diffusion effects likely contribute to the carbon isotopic fractionation observed in headspace

192 gas from IsoJars® as reported in Table S1. A study by Wu et al. (2020) also reported that diffusion effects
193 were responsible for shifts in carbon isotope ratios of hydrocarbons in headspace gas in dependence on
194 nano-pore throat size and overpressure. The effects of potential carbon isotope fractionation affecting
195 headspace gas in IsoJars® (due to desorption/diffusion) have not been explicitly recognized in investigations
196 of other low-permeability hydrocarbon reservoirs (Chatellier et al., 2013; Tilley and Muehlenbachs, 2013;
197 Norville, 2014; Zhang et al., 2018).

198 Figure 2 compares the differences between $\delta^{13}C$ values of methane and ethane ($\Delta^{13}C_{C1-C2}$) and methane and
199 propane ($\Delta^{13}C_{C1-C3}$) in a thermal maturity plot for the samples collected in IsoTubes® and IsoJars®
200 respectively from one well completed in the Montney Formation. The carbon isotope difference in IsoJar®
201 samples varies from -16‰ to -7‰ for $\Delta^{13}C_{C1-C2}$ and from -19‰ to -9‰ for $\Delta^{13}C_{C1-C3}$, whereas gases
202 obtained in IsoTubes® have carbon isotope differences between -17‰ and -8‰ for $\Delta^{13}C_{C1-C2}$ and between
203 -20‰ and -13‰ for $\Delta^{13}C_{C1-C3}$. It is evident that mud-gas samples collected in IsoTubes® plot closer to the
204 trend line established using produced gases from low-permeability hydrocarbon reservoirs worldwide
205 reported in the study by Cesar et al. (2020b). In contrast, samples from IsoJars® show a significant offset
206 plotting above the trend line due to the marked differences in $\delta^{13}C$ values of methane, and to a lesser extent
207 ethane and propane (Table S1) as a result of isotope fractionation effects described above. This suggests
208 that data derived from IsoTubes® more closely resemble the isotopic composition of free gas in the here
209 investigated low-permeability hydrocarbon reservoir section of the Montney Formation.

210 Although comparisons of data from IsoTube® and IsoJar® samples have previously been reported (Kirkland,
211 2017; Wu et al., 2020), the focus has been on stable carbon isotope variations with little attention on
212 molecular indices. Therefore, we also determined and compared molecular parameters such as the
213 $[C_1/(C_2+C_3)]$ ratio and the iso-butane to n-butane ratio ($i\text{-}C_4/n\text{-}C_4$) for samples collected in IsoTubes® and
214 IsoJars® (Fig. 3). The $[C_1/(C_2+C_3)]$ ratio is expected to increase with thermal maturity due to the increasing
215 relative abundance of methane (Bernard et al., 1976; 1978), although a decrease in this parameter might be
216 initially observed at low maturity (Milkov and Etiope, 2018) depending on the organic matter type (Berner

et al., 1995). The i-C_4/n-C_4 ratio initially increases with increasing thermal maturity but decreases (or rolls over) at maturity levels above 1.5% Ro (Hao and Zou, 2013; Chatellier et al., 2013; Cesar et al., 2020b).

Except for one outlier, the (i-C_4/n-C_4) ratio in the IsoTube® samples ranges from 0.5 to 0.8, while a similar range from 0.5 to 1.0 was observed in samples from the IsoJars®. The [C_1/(C_2+C_3)] ratio varies from 4 to 14 in the IsoTube® samples but displayed a much lower range of <0.1 to 4 in the gases collected in IsoJars®. Produced gases from the Montney Formation typically have [C_1/(C_2+C_3)] ratios between 10 and 30 (Cesar et al., 2021). Chemical fractionation due to preferential retention and/or adsorption of larger molecules in smaller pore throats (Chatellier and Perez, 2016) versus a higher molecular mobility of methane (Zhang and Kroos, 2001; Xia and Tang, 2012) is likely the cause for the unrealistically low [C_1/(C_2+C_3)] ratios observed particularly in samples collected in Isojars®. For instance, relative methane concentrations were three times higher in the IsoTubes® compared to IsoJars® samples and the remaining methane retained in the cuttings appears to be slightly enriched in ^{13}C as explained earlier in this section.

More consistent i-C_4/n-C_4 ratios between the two sample sets are probably due to these isomers being less affected by differences in molecular mobility/diffusion, compared to propane, ethane and especially methane (e.g. Faiz et al., 2018). Previous statistical studies have suggested that IsoTubes® provide better molecular data with errors under 5%, whereas IsoJars® can carry uncertainties of up to 24% (Kirkland, 2017). This is consistent with our observations for data derived from IsoTubes® samples that plot closer to the thermal maturity trend line (Fig. 2) from the study by Cesar et al. (2020b), and yield more realistic [C_1/(C_2+C_3)] ratios (Fig. 3) and apparently accurate iso-butane to n-butane ratios (i-C_4/n-C_4).

A produced gas sample collected two years after drilling of the horizontal section of the well had a [C_1/(C_2+C_3)] ratio of 6.5 and an i-C_4/n-C_4 ratio of 0.6 (Cesar et al., 2020a), which is consistent with the data ranges observed for Isotube samples. Despite this good agreement, it is not unusual to observe slight discrepancies between data derived from mud-gas samples collected in Isotubes and produced gas samples, since gas molecular and isotope properties can vary with production time, particularly after more than one year of production (Norville, 2014; Wood et al., 2021). Produced gas is also a mixture of gases from the

entire horizontal borehole in various proportions, thus differences with chemical and isotopic compositions of specific mud-gas samples is not uncommon.

Given the evidence of chemical and isotopic fractionation impacting predominantly mud-gas samples collected in IsoJars®, challenges are to be expected in evaluating results from public data bases in which the sampling techniques is not clearly indicated. Therefore, it is highly recommended to indicate in the future in public data bases whether MGIL samples were collected in IsoTubes® or IsoJars®.

3.3. Additional evidence of compositional and isotopic fractionation

Figure 4 displays the $[C_1/(C_2+C_3)]$ ratio versus the iso-butane to n-butane ratio ($i\text{-}C_4/n\text{-}C_4$) only for the public mud-gas dataset, while excluding data from the horizontal well shown in Fig. 3. The $[C_1/(C_2+C_3)]$ ratio varies from 1 to 30, whereas the iso-butane ratio ranges between 0.2 and 1.4. Higher iso-butane ratios (>0.5) are more commonly observed in samples from the Montney Formation in British Columbia, which is consistent with a higher thermal maturity reported for this region compared to Alberta (e.g. BC Oil and Gas Commission, 2012). However, no clear linear correlation between the two parameters is observed in Fig. 4 in contrast to findings for produced gases from the Montney Formation in a previous study (Wood and Sanei, 2016). This indicates that chemical fractionation induced during mud-gas sample collection may compromise a conclusive interpretation MGIL data from the Montney Formation, especially if is not reported which data were derived from samples collected in IsoJars®.

We have also evaluated the C_2/C_3 ratio to investigate chemical fractionation reflected in the public gas database for the Montney Formation. The significance of the C_2/C_3 ratio has been recognised in the literature since the work by Prinzhofer and Huc (1995), and was later confirmed by Lorant et al. (1998). These studies found that the C_2/C_3 ratio remains relatively constant during kerogen craking (or bitumen cracking) and increases at higher thermal maturity during secondary cracking of the generated hydrocarbons. In fact, Cesar et al. (2020b) found that the C_2/C_3 ratio starts to increase at Ro ≈1.5%, once thermal cracking of wet-

gas components becomes increasingly prominent and a difference of 6‰ has been reached between the $\delta^{13}C$ values of C_1 and C_2, and C_2 and C_3, respectively (the even isotopic distribution or EID).

Figure 5 reveals that C isotope data reported for gases from the Montney Formation have not reached the EID ($\delta^{13}C_{C1}$- $\delta^{13}C_{C2}$<-6‰) and hence a relatively constant C_2/C_3 ratio is expected as is typical for fluids in the oil window (Prinzhofer and Huc, 1995; Lorant et al., 1998; Cesar et al., 2020b). Nonetheless, this is not observed in Fig. 5 with the C_2/C_3 ratio varying from 1 to 8 with no clear trend with respect to the carbon isotope difference between methane and ethane. The inconsistency between the C_2/C_3 ratio and the $\delta^{13}C_{C1}$-$\delta^{13}C_{C2}$ parameter may be a combination of carbon isotope fractionation affecting C_1 and to a lesser extent C_2 and chemical fractionation altering the C_2/C_3 ratio especially in samples collected in Isojars®.

A previous study reported that the C_1-C_3 molecular distribution and the C_2/C_3 ratio of produced gas samples distinguish natural gas from the British Columbia hydrocarbon play ($C_2/C_3 \approx 4$) from the Alberta hydrocarbon play ($C_2/C_3 \approx 2$) in the Montney Formation (Cesar et al. 2021). In the data reported by Cesar et al. (2021), both ratios were relatively constant for the gases in the oil window, and are marked on Fig. 5 as a variation range reference. The distinction between hydrocarbon plays (i.e. British Columbia vs. Alberta) is less clear when using mud-gas data except when calculating the i-C_4/n-C_4 ratio (see also Fig. 4), presumably in part because results from samples in IsoTubes® and IsoJars® are comingled in an indistinguishable fashion in the public database.

Another challenge when conducting MGIL for the purpose of fingerprinting producing intervals within the Montney Formation is that $\delta^{13}C$ variations were not very large within the single well investigated in this study (see also Table S1, Figs. S1 and S2). For instance, the $\delta^{13}C$ values of methane collected in IsoTubes® varied only by ± 0.9‰ around the mean value of -47.0‰ in the vertical and horizontal sections of the well. This variability is close to the uncertainty introduced by MGIL sampling approaches combined with the instrumental analytical uncertainty. Therefore, in some instances, the lack of sufficiently contrasting carbon isotope ratios makes a differentiation of gases from different units of the same formation impossible for the

Montney Formation based on data presented in this study (see also Table S1, Figs. S1 and S2). Consistent with this interpretation, evidence of strong source effects such as the organic matter type in the source rocks on the $\delta^{13}C$ values of hydrocarbons have not been identified yet for the Montney Formation (e.g. Tilley and Muehlenbachs, 2013; Cesar et al., 2020b).

Although variables such as depth and stratigraphic correlation have not been addressed in this study, our observations suggest that pursuing such a task in the future may not be promising if it is based on public data for the Montney Formation that do not contain information about the sampling approach that allows to separate data generated from IsoTube® samples from those derived from IsoJar® samples.

4. Conclusion

Mud-gas molecular and isotope data from the Montney Formation indicate the occurrence of chemical and carbon isotope fractionation of the analyzed gases especially for samples collected in IsoJars® whereas samples obtained in IsoTubes® appear to more accurately reflect free gas at reservoir conditions. The overall thermal maturity signature of the gas is relatively well preserved in isotope parameters such as $\Delta^{13}C_{C1-C2}$ and $\Delta^{13}C_{C1-C3}$ for the entire dataset, which indicate maturity consistent with the oil window to wet-gas. The $\delta^{13}C$ values of methane, ethane and propane are systematically higher in IsoJar® samples (with the extent of C isotope fractionation $C_1>C_2>C_3$) as compared to Isotube® samples that yielded results more consistent with those of produced gases.

The extension of this study to molecular geochemistry revealed that the iso-butane to n-butane ratio ($i\text{-}C_4/n\text{-}C_4$) is the most consistent molecular parameter between sampling techniques, whereas the $C_1/(C_2+C_3)$ ratio is unusually low in IsoJars® headspace gas (up to three times less methane in the IsoJars®). Furthermore, the C_2/C_3 ratio is very variable (from 1 to 8) in data from public sources that do not specify the sampling technique and cannot be used to indicate a particular stage of hydrocarbon generation (e.g. oil window versus wet-gas cracking).

The uncertainty introduced by chemical and isotope fractionation in samples obtained in IsoJars® challenges isotope fingerprinting assessments based on public data sources that do not indicate the sampling approach, especially because the intervals drilled often cover narrow maturity ranges for which carbon isotope ratio variations are only in the range of 2 ‰ or less. However, we conclude that mud-gas molecular and isotope data derived from samples collected in IsoTubes® are suitable for geochemical assessment of low permeability hydrocarbon reservoirs such as the Montney Formation.

Declaration of Competing Interest

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.

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Figure captions

Figure 1. Mud-gas stable carbon isotope data from 45 wells landed in the Montney Formation represented in a $\Delta^{13}C_{C1-C2}$ versus $\Delta^{13}C_{C1-C3}$ thermal maturity plot.

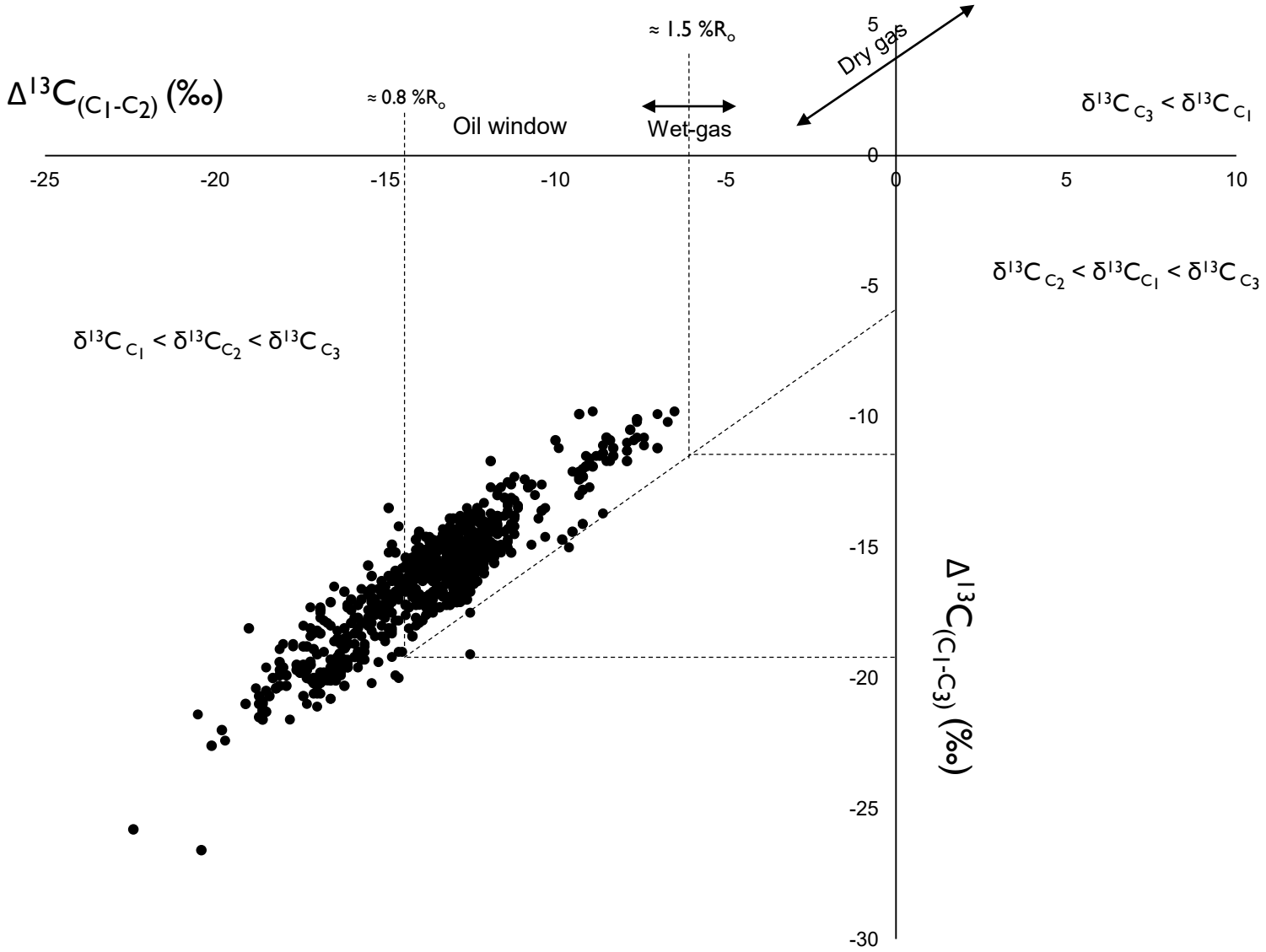
Figure 2. Comparison of IsoTube® versus IsoJar® samples from a common well and depth interval in the Montney Formation, as shown in a $\Delta^{13}C_{C1-C2}$ versus $\Delta^{13}C_{C1-C3}$ thermal maturity plot.

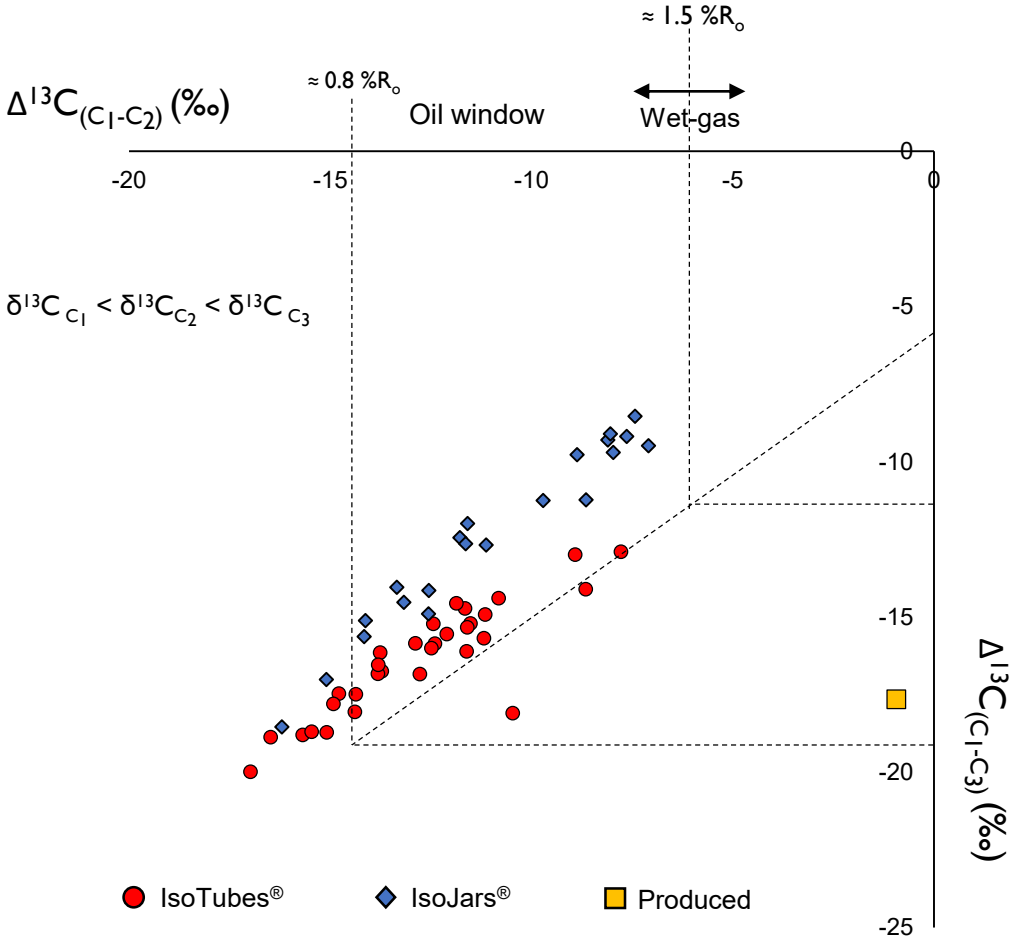
Figure 3. Comparison of the ratio of $[C_1/(C_2+C_3)]$ and the iso-butane to n-butane ratio ($i\text{-}C_4/n\text{-}C_4$) for samples obtained from IsoTube® and IsoJars® respectively from a well completed in the Montney Formation.

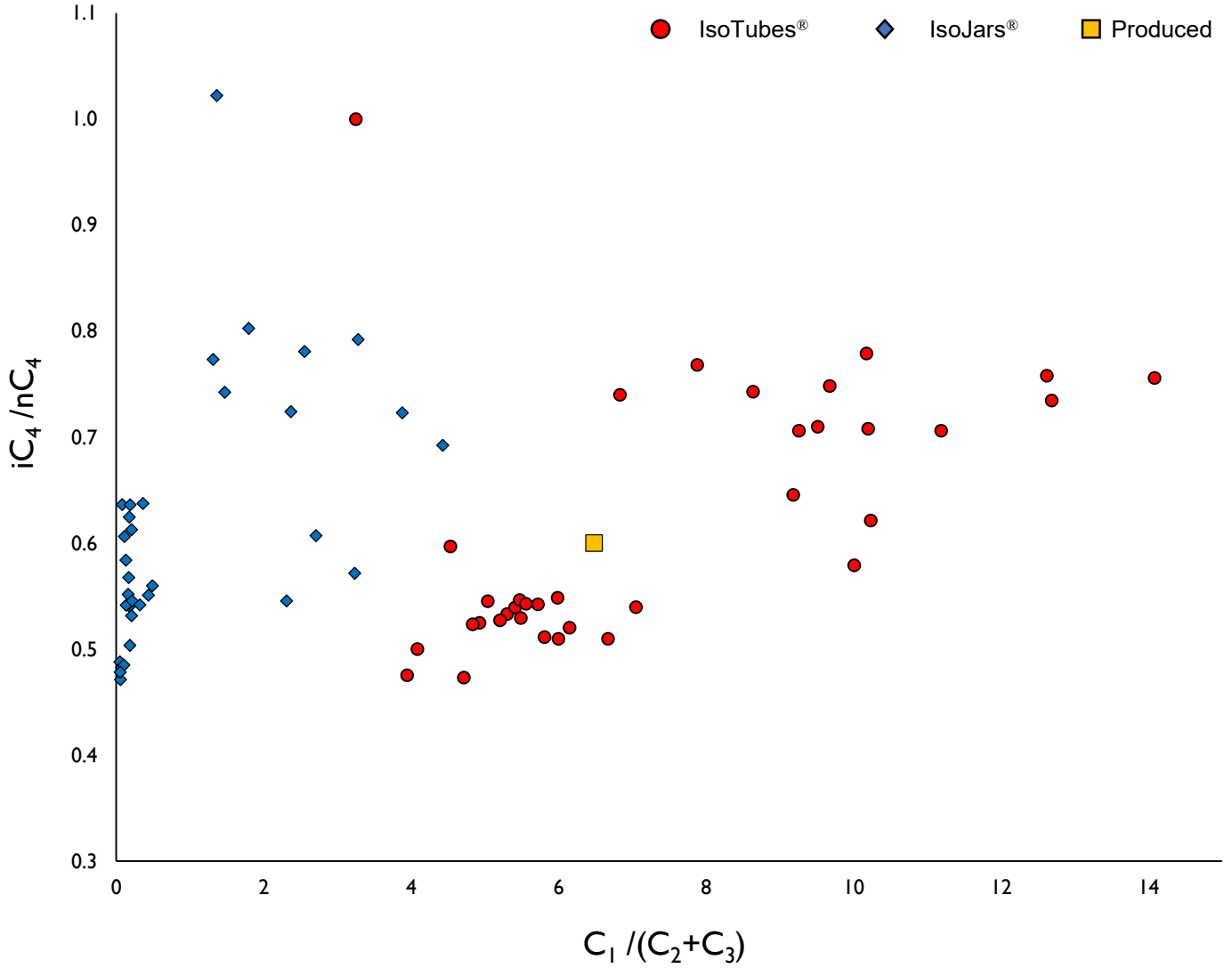
Figure 4. The $i\text{-}C_4/n\text{-}C_4$ versus $[C_1/(C_2+C_3)]$ of the mud-gas samples of 45 wells from the Montney Formation. Sampling devices (e.g. IsoTube® versus IsoJar®) are unknown.

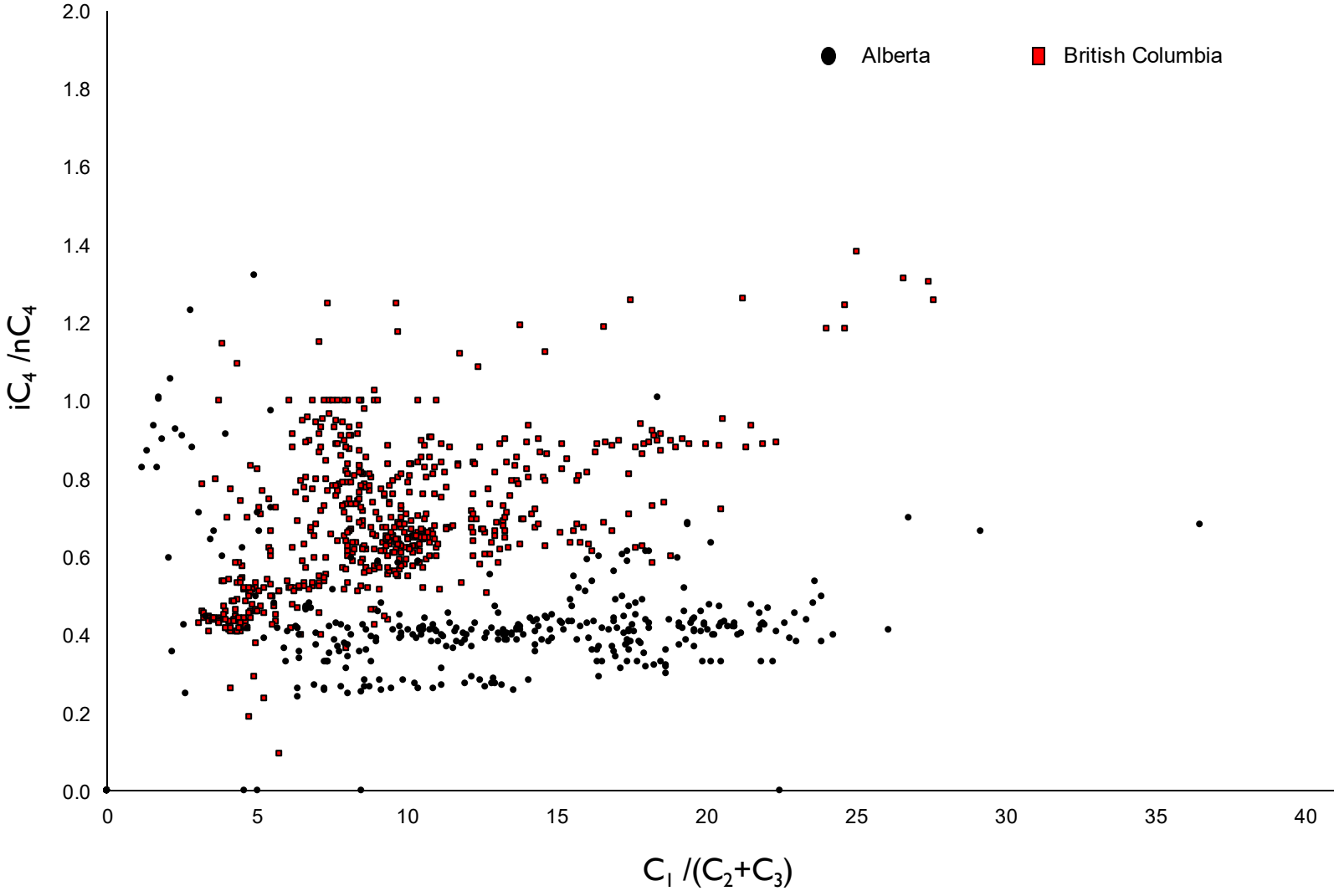
Figure 5. The C_2/C_3 ratio versus the $\Delta^{13}C_{C1-C2}$ of the mud-gas samples of 45 wells from the Montney Formation (after Cesar et al., 2020b). Sampling devices (e.g. IsoTube® versus IsoJar®) are unknown. The variation range in gray is from Cesar et al. (2021), and the increasing trend arrow is only used as an example and thus has an arbitrary slope.

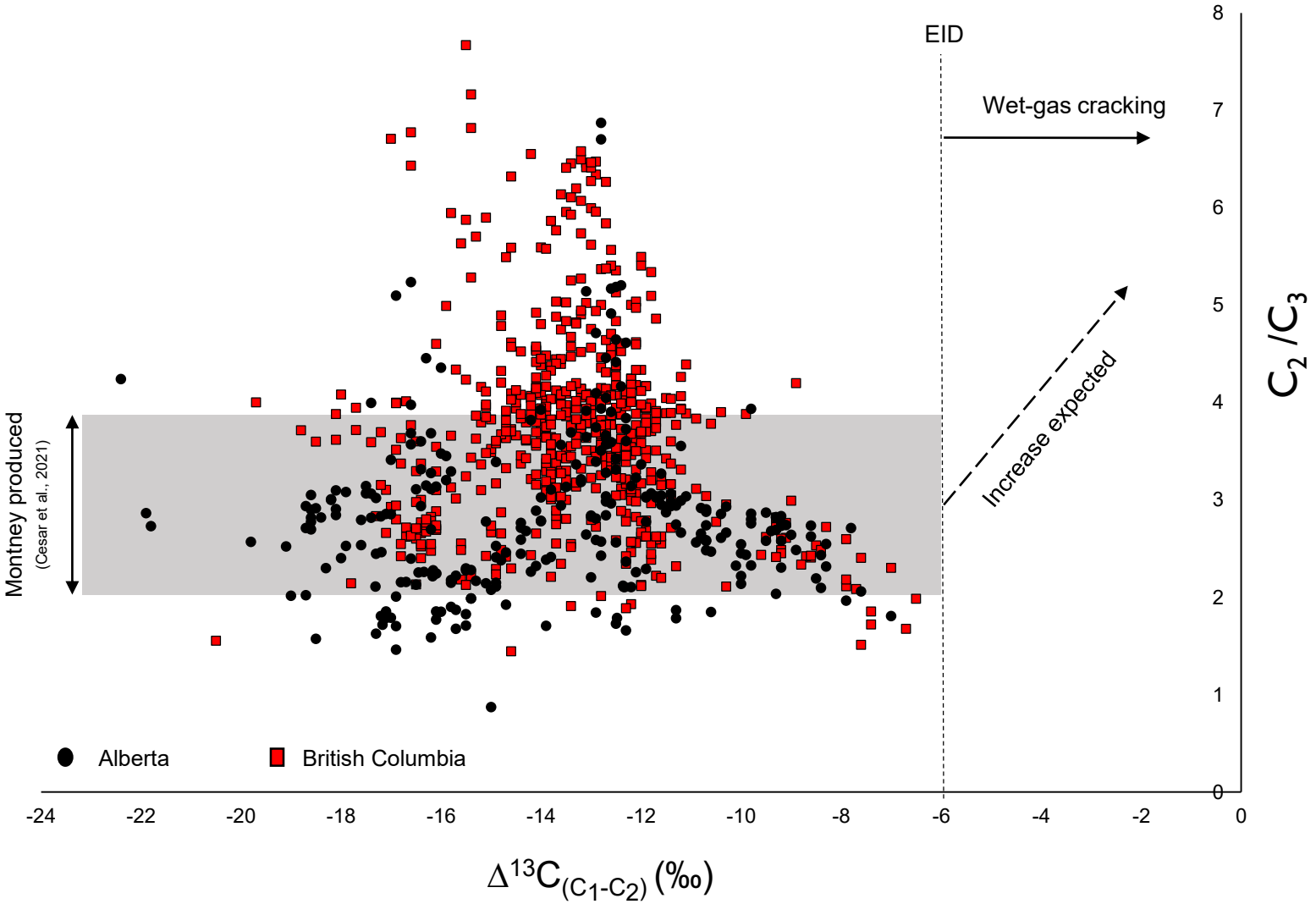
447


$\Delta^{13}C_{(C_1-C_2)}$ (‰)
≈ 0.8 %R_o
≈ 1.5 %R_o
Oil window
Wet-gas
Dry gas
$\delta^{13}C_{C_3} < \delta^{13}C_{C_1}$
$\delta^{13}C_{C_2} < \delta^{13}C_{C_1} < \delta^{13}C_{C_3}$
$\delta^{13}C_{C_1} < \delta^{13}C_{C_2} < \delta^{13}C_{C_3}$
$\Delta^{13}C_{(C_1-C_3)}$ (‰)
5
0
-5
-10
-15
-20
-25
-30
-25
-20
-15
-10
-5
0
5
10


≈ 1.5 %Ro
≈ 0.8 %Ro
Oil window
Wet-gas
Δ13C(C1-C2) (‰)
-20
-15
-10
-5
0
0
δ13CC1 < δ13CC2 < δ13CC3
-5
-10
-15
-20
-25
Δ13C(C1-C3) (‰)
IsoTubes®
IsoJars®
Produced


IsoTubes®
IsoJars®
Produced
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
iC4 /nC4
0
2
4
6
8
10
12
14
C1 /(C2+C3)


Alberta
British Columbia
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
iC4 /nC4
0
5
10
15
20
25
30
35
40
C1 /(C2+C3)


EID
Wet-gas cracking
Increase expected
Montney produced
(Cesar et al., 2021)
Alberta
British Columbia
-24
-22
-20
-18
-16
-14
-12
-10
-8
-6
-4
-2
0
1
2
3
4
5
6
7
8
$\Delta^{13}C_{(C_1-C_2)}$ (‰)
C_2/C_3