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# Fatty acids, alkanones and alcohols from a major lower Triassic low-permeability petroleum reservoir

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For the first time, polar organic compounds in extracted bitumen from the Lower Triassic Montney Formation have been analyzed. This stratigraphic unit is one of the most prolific low-permeability reservoirs in Western Canada. However, its organic geochemical characterization is a challenge due to low biomarker concentration in the liquids and frequent mixing of gas/condensate hydrocarbons. Since typical biomarkers were not available, this study focused on another group of molecules, polar oxygen-compounds, which were derivatized and subsequently resolved using chromatographic techniques. In the polar fractions, based on their contrasting molecular distributions, *n*-fatty acids and alkan-2-ones do not seem to share a common origin and do not have an apparent association with the *n*-alkanes. This study is also the first report of 1,13-, 1,14- and 1,15-diols in fossil organic matter; and in carbon number ranges of C<sub>15</sub>-C<sub>29</sub>, C<sub>16</sub>-C<sub>29</sub> and C<sub>17</sub>-C<sub>29</sub> respectively. The similar distributions of 1,14- 1,15-diols suggests a common origin for these compound classes, whereas the 1,13-diols seem to derive from a different source or mechanism. A series of alkan-3-ols has also been identified in the C<sub>12</sub>-C<sub>28</sub> range, sharing a common distribution pattern with the *n*-fatty acids. The large variability detected in the molecular distribution of oxygen-containing aliphatic compounds introduces the question whether they may record a geochemical signature that precedes thermal degradation and hydrocarbon migration events within Montney reservoirs.

## KEYWORDS

polar, diol, acid, ketone, low-permeability, Montney

## 1 Introduction

In the Western Canadian Sedimentary Basin, a significant amount of petroleum resources is currently produced from the Lower Triassic Montney Formation (unconventional estimated reserves at 12,719 billion m<sup>3</sup> of natural gas, 14,521 million barrels of natural-gas-liquids, and 1,125 million barrels of oil, [BC Oil and Gas Commission, 2012](#); [Rokosh et al., 2012](#)). Hydrocarbons in the Montney Formation are thought to originate from thermal degradation of migrated oil. This is based on the fact that the organic matter in Montney mostly consists of pore-filling solid bitumen ([Sanei et al., 2015](#); [Wood and Sanei, 2016](#); [Wood et al., 2018](#)). Maximum burial and thermal maturity reached in the Late Cretaceous/Early Paleogene caused thermal cracking of accumulated hydrocarbons which led to the petroleum accumulations we know today ([Wood and Sanei, 2016](#); [Ducros et al.,](#)

2017; Euzen et al., 2021). Primary organic matter has also been identified within Montney (Ardakani et al., 2022). However, the relative contribution from *in-situ* kerogen to the petroleum accumulations remains unknown. Source rock candidates include the Middle Triassic Doig Formation, the Lower Jurassic Gordondale Member of the Fernie Formation, and the Montney Formation (Alan and Creaney, 1991; Ejezie, 2007; Euzen et al., 2021). Nonetheless, fluid to source correlations to date (e.g., based on biomarkers) continue to be rather inconclusive.

Recent studies on gas hydrocarbons have facilitated the definition of hydrocarbon play boundaries within Montney (e.g., Cesar et al., 2020b; Cesar et al., 2021), as well as potential gas migration pathways (Wood and Sanei, 2016; Euzen et al., 2021; Wood et al., 2022) using a molecular approach. The overall geochemical signature of produced gases from these fields seems to be controlled by thermal maturity effects and fluid mixing due to migration (Cesar et al., 2020a; Cesar et al., 2021; Cesar et al., 2022; Wood et al., 2022). As a result, gas geochemical tools alone have not been successful discriminators for the identification of the source(s) of hydrocarbons.

In the liquid phase, geochemical assessment has been limited by the low abundance of biomarkers (e.g., hopanes and steranes) in the produced condensates and light oils. In the Montney Formation, little has been studied regarding the geochemistry of light hydrocarbons, which often cannot be detected in rock extracts due to volatility loss during sample handling/preparation, limiting fluid to source correlation. Research on condensate samples has suggested the possibility of mixtures of migrated hydrocarbons with hydrocarbons derived from original kerogen of the Montney Formation (Cesar et al., 2020a).

In contrast to molecules in the gas-condensate range, there is a group of compounds that have not been analyzed yet, these are polar compounds in the resin fraction of soluble bitumen. It is known that resins are scarce (or absent) in the produced condensates and light oils. However, they are preserved in the solid bitumen residue within the reservoir, and potentially record a fingerprint of the original source of migrated hydrocarbon that charged Montney productive intervals. At the same time, these polar compounds can be a source of gas/condensate, particularly when thermal alteration (cracking) takes place (e.g., Michels et al., 2000) as is the case of the Montney Formation.

In this study, and for the first time, we characterize polar compounds of extracted bitumen from the Montney Formation in order to 1) identify the main oxygen-aliphatic compound classes, 2) investigate associations between them, and 3) discuss their potential as source discriminators.

## 2 Geological setting

The Montney Formation (Figure 1A) deposited in the northwestern margin of the North American craton during the Lower Triassic (Davies, 1997; Davies et al., 2018; Zonneveld and Moslow, 2018) in a mixed siliciclastic-carbonate depositional environment that accumulated shoreface to offshore, and turbidite sediments (Davies, 1997; Davies et al., 2018; Zonneveld and Moslow, 2018). The lithology includes a complex succession of dolomitic siltstone, minor component of very fine-to fine-grained sandstone with local bioclastic carbonate rocks and minor shale

intervals (Davies, 1997; Davies et al., 2018; Zonneveld and Moslow, 2018).

The Montney Formation is divided into three main members (Davies, 1997; Davies et al., 2018; Zonneveld and Moslow, 2018). The Lower Member corresponds to multi-cyclic very fine-grained sandstone and dolomitic siltstone. It overlies the Triassic unconformity on Permian and/or older strata, and it is overlain by the base of the Middle Member in the east (where present), and by the Upper Member in the west. The Middle Member consists of a thick succession of bituminous dolomitic siltstone with interbedded very-fine grained sandstone. It overlies the Lower Member and is marked by a boundary of reworked clasts of the underlying units. The Upper Member corresponds to multicyclic, coarsening-up siltstones and very fine sandstones dominated by storm-related fabrics, with local dolomitized coquina facies; and it is overlain by the Doig Formation. The Upper Member is primarily seen in the British Columbia section (Supplementary Figure S1). In addition, the Montney stratigraphic succession deeps towards the southwest, thus the sections in British Columbia are often more mature than those from Alberta (BC Oil and Gas Commission, 2012; Rokosh et al., 2012). The general schematic stratigraphy is illustrated in Figure 1B.

## 3 Materials and methods

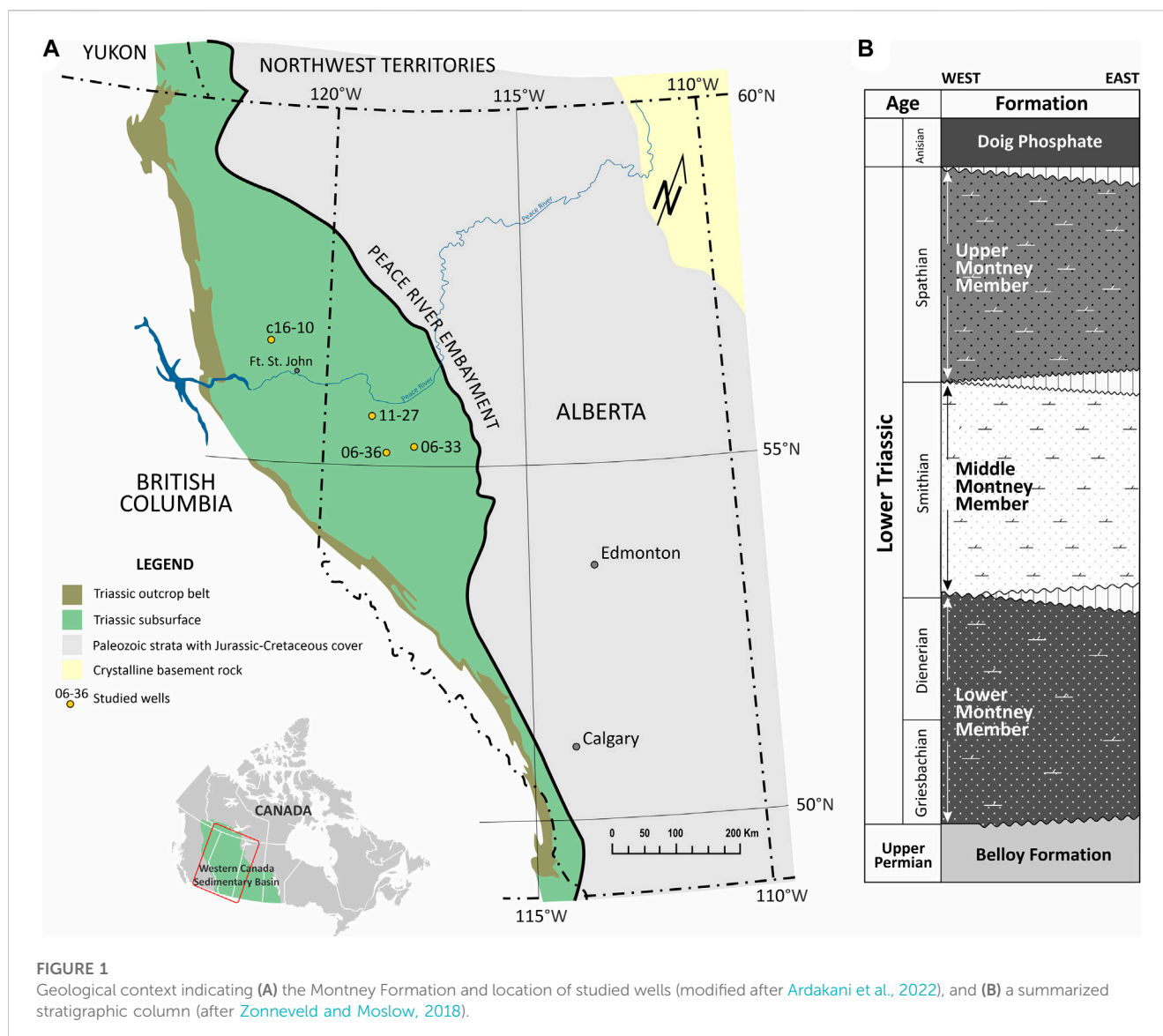
### 3.1 Sample preparation

A total of 15 powdered and homogenized rock samples were solvent-extracted using dichloromethane (DCM) in a Soxhlet apparatus for 24 h. The general characteristics of the samples are listed in Table 1. The samples selected for this study correspond to core intervals from the different stratigraphic Members (Lower, Middle, and Upper), different locations, and different thermal maturity levels as indicated by rock pyrolysis (Tmax) and aromatic ratios (Table 1).

Polar fractions were obtained from the extracted bitumen using column chromatography by elution with methanol once saturate and aromatic hydrocarbon fractions had been eluted with *n*-pentane and aromatic hydrocarbon fractions had been eluted with *n*-pentane and DCM:*n*-pentane, respectively. Aliquots of the polar fractions (0.5–1 mg) were derivatized in 200  $\mu$ L of pyridine and 300  $\mu$ L of N,O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) at 70°C for 1 h. Then, the derivatized fractions were dried under a gentle stream of nitrogen at 35°C and re-dissolved in *n*-hexane for molecular analysis as explained below. Procedural blanks were prepared and analyzed to monitor for any contamination during sample preparation, and instrument blanks and standards were run to check for instrument carry over or any other instrumental anomalies. Nonadecanol was used as internal standard.

### 3.2 Molecular analysis

Derivatized fractions were analyzed via gas chromatography time-of-flight mass spectrometry (GC-QTOF-MS) on an Agilent 7890BGC - 7200 QTOF mass spectrometer equipped with a DB5-ms column (60 m  $\times$  0.25  $\mu$ m i.d.  $\times$  0.25 mm f.t.), using splitless injection and helium as carrier gas (1.3 mL/min). The temperature program of the GC oven started at 80°C for 1 min, then ramped at 5°C/min to 325°C and held at the final temperature for 30 min. Compound identification was carried out using relative retention times and characteristic mass spectra.



The distribution of *n*-alkanes in the saturate fractions were determined using GC with flame ionization detection (FID) analysis of the saturated hydrocarbon fractions on an Agilent 7890B GC-FID. A 30 m × 0.25 mm × 0.25 μm DB-1 fused silica capillary column was used, with helium as carrier gas. The samples were injected using split injection with the injector temperature set at 300°C. The temperature program of the GC oven started at 60°C, then ramped at 6°C/min to 300°C for 30 min. The FID temperature was maintained at 300°C.

## 4 Results

### 4.1 Fatty acids

C<sub>15</sub>-C<sub>30</sub> *n*-fatty acids (carboxylic acids) are present in all samples (Figure 2A, *m/z* 117) and typically dominated by C<sub>18</sub>-C<sub>20</sub> (Figure 2A; Figure 3A). However, samples X12140 and X12143 have bimodal distributions with maximum abundance at C<sub>18</sub>-C<sub>19</sub> and C<sub>22</sub>-C<sub>24</sub> (Figures 3B, D). Samples X12141 and

X12148 display unimodal distributions that are to some extent flat tops between C<sub>19</sub> and C<sub>23</sub> (Figure 3C).

### 4.2 Alkanones

Alkanones, or more specifically alkan-2-ones, were identified using the *m/z* 58 as shown in Figure 2B, usually in the C<sub>17</sub>-C<sub>27</sub> carbon range. All the samples exhibit unimodal distributions with maximum abundance of C<sub>20</sub> as illustrated in Figure 3. Predominance of even carbon numbered homologues was found in samples X12140, X12142, X12143, X12148, X12149, X12151, and X12152 (e.g., Figure 3D).

### 4.3 Diols

Figure 4 presents the diols detected in the studied samples, which include 1,13-diols (*m/z* 257), 1,14-diols (*m/z* 271), and 1,15-

TABLE 1 Montney Formation core rock samples included in this study. Core locations shown in Figure 1A.

Sample	Core/province	Member	T <sub>max</sub> (°C)	TMNr <sup>a</sup>	Pr/ Ph <sup>b</sup>	Potential source
X12139	C16-10-88-23W6/British Columbia	Upper	446	0.90	1.42	Montney migrated? (Watt et al., 2022)
X12140	C16-10-88-23W6/British Columbia	Upper	458	0.88	1.43	
X12141	06-36-071-04W6/Alberta	Middle	434	0.60	0.84	
X12142	06-36-071-04W6/Alberta	Middle	440	0.60	1.12	Montney migrated? (Watt et al., 2022) + <i>in-situ</i> Montney (Ardakani et al., 2022)
X12143	11-27-077-06W6/Alberta	Lower	441	0.56	0.80	
X12144	C16-10-88-23W6/British Columbia	Upper	447	0.90	1.48	Montney migrated? (Watt et al., 2022)
X12145	C16-10-88-23W6/British Columbia	Upper	455	0.90	1.49	
X12146	C16-10-88-23W6/British Columbia	Upper	453	0.91	1.50	
X12147	06-33-072-25W5/Alberta	Middle	428	0.61	0.79	Montney migrated? (Watt et al., 2022) + <i>in-situ</i> Montney (Ardakani et al., 2022)
X12148	06-36-071-04W6/Alberta	Middle	440	0.64	0.78	
X12149	C16-10-88-23W6/British Columbia	Upper	456	0.91	1.53	Montney migrated? (Watt et al., 2022)
X12150	C16-10-88-23W6/British Columbia	Upper	439	0.91	1.31	
X12151	C16-10-88-23W6/British Columbia	Upper	463	0.90	1.45	
X12152	06-33-072-25W5/Alberta	Middle	430	0.61	0.51	Montney migrated? (Watt et al., 2022) + <i>in-situ</i> Montney (Ardakani et al., 2022)
X12153	11-27-077-06W6/Alberta	Lower	438	0.60	0.91	

<sup>a</sup>TMNr: trimethylnaphthalene ratio calculated as 1,3,7-trimethylnaphthalene/(1,3,7 + 1,2,5)-trimethylnaphthalene, peak areas from the m/z 170; TMNr increases with thermal maturity (van Aarssen et al., 1999).

<sup>b</sup>Pr/Ph: pristane/phytane; using peak areas from the total ion chromatogram (e.g., Peters et al., 2005).

diols (*m/z* 285). These compound classes were identified in the ranges C<sub>15</sub>-C<sub>29</sub>, C<sub>16</sub>-C<sub>29</sub>, and C<sub>17</sub>-C<sub>29</sub>, respectively.

The main carbon number distribution patterns of the diols can be observed in Figure 5. The 1,14- and 1,15- diols (Figures 5B, C) generally decrease in abundance with increasing carbon number at variable slopes, except samples X12140 and X12143 which register higher abundances in the C<sub>20+</sub> range. Another aspect to notice is the preference for odd carbon numbers in the 1,14-diols, particularly in the C<sub>20+</sub> range (Figure 5B). The odd preference is less emphasized in the 1,15-diols yet observed in samples X12145, X12151 and X12152 (e.g., Figure 5C). The 1,13-diols exhibit a more variable molecular distribution though with a preference for C<sub>18</sub> and odd carbon numbers after C<sub>20</sub> (Figure 5A).

#### 4.4 Alkan-3-ols

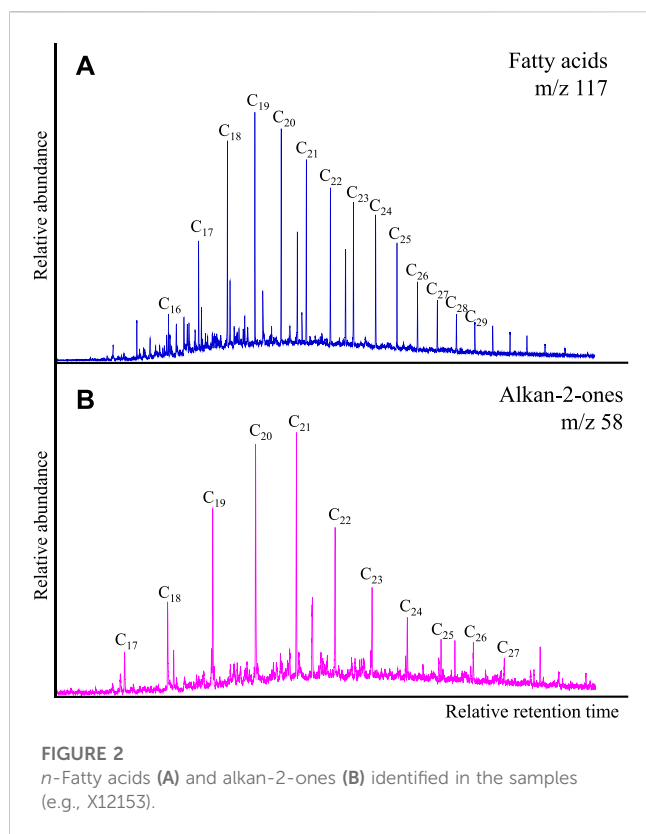
For this compound series (Figure 6A; Supplementary Figure S2), the chain length varied from C<sub>12</sub> to C<sub>28</sub> (sometimes C<sub>28+</sub> visible). The distribution patterns were found to be very similar to those of the fatty acids (Figure 3, Figure 6B): 1) mixed/bimodal distribution (e.g., X12140, X12143), 2) flatten top (e.g., X12141, X12148), and 3)

decreasing abundance with increasing carbon number after maximum peak (the rest of the samples). Certain preference for C<sub>20</sub> and C<sub>22</sub> was observed in samples X12140, X12142-X12146, and X12148-X12151.

## 5 Discussion

### 5.1 The significance of fatty acids in fossil organic matter from the Montney Formation

In recent sedimentary organic matter, fatty acids have typically been attributed to algal and bacterial (C<sub>14</sub>-C<sub>20</sub>; Perry et al., 1979; Cranwell et al., 1987; Naeher et al., 2022), aquatic macrophytes (C<sub>22</sub>-C<sub>26</sub>; Cranwell et al., 1987; Volkman et al., 1999; Naeher et al., 2022) and terrestrial plant sources (C<sub>28</sub>-C<sub>32</sub>; Rieley et al., 1991; Freeman and Pancost, 2014; Naeher et al., 2022). It is also considered that terrestrial plants synthesize longer chain fatty acids preferably (Wang and Liu, 2012; Naafs et al., 2019). However, chain length alone is not always diagnostic of the source of these compounds, particularly in environments with aquatic and terrestrial organic matter inputs (Fang et al., 2014). As well, the molecular distribution of *n*-alkanes and *n*-fatty acids are expected to be similar when the



*n*-alkanes derive from the decarboxylation of the acids during deposition/diagenesis (Barakat et al., 2000; Naafs et al., 2019).

In fossil organic matter (e.g., petroleum, bitumen), the evaluation of linear carboxylic acids is less common because of their degradation with thermal maturity and many other biomarkers being available for petroleum geochemistry studies (e.g., hopanes, steranes, aromatic markers, etc.). However, we must highlight the work by Jaffé and Gallardo (1990), Jaffé et al. (1992), Jaffé and Gallardo (1993), who suggested that most of the fatty acids identified in fossil organic matter are originally protected within more complex geo-polymer structures (later kerogen, bitumen) and released with increasing thermal maturity before the peak of oil generation. Free fatty acids, instead, would not be preserved but degrade to *n*-alkanes and/or other compounds during diagenesis. Therefore, opposite to recent environments, we may infer that in petroleum fluids and bitumen extracts from mature source rocks, the fatty acids should not be expected to have a distribution pattern similar to the *n*-alkanes as the latter would not necessarily be degradation products of the former (Jaffé and Gallardo, 1990; Jaffé et al., 1992; Jaffé and Gallardo, 1993).

This may explain why in our samples the distribution of *n*-fatty acids generally differs from the distribution of *n*-alkanes. For instance, samples X12140 and X12143, from completely different locations and stratigraphic intervals (Table 1; Figure 1), have a bimodal distribution pattern of fatty acids in common (Figures 2B, D). The same bimodality is not expressed in the *n*-alkanes distribution of these samples. It could be argued that a second group of fatty acids with highest peaks in the C<sub>22</sub>-C<sub>24</sub> range (Figures 2B, D) represents an additional terrestrial organic matter input. However, additional evidence is required to confirm terrestrial

contribution. As well, bimodal fatty acids distribution could simply result from hydrocarbon mixing before maximum burial of the Montney Formation. Post maximum burial migration events in Montney (e.g., during the Eocene uplift) consisted of gas/condensate which unlikely carried fatty acids due to insolubility of the latter.

It is important to mention that in sample X12143, primary organic matter was identified besides solid bitumen (Ardakani et al., 2022). Therefore, we cannot rule out the possibility of fatty acids bimodality resulting from the mixture of migrated hydrocarbons and *in-situ* organic matter.

Samples X12141 and X12148 are also peculiar because they showed a flatten-top distribution pattern of *n*-fatty acids, which is different to the *n*-alkanes from the same samples. These samples come from the same well (Table 1) and Middle Montney Member although 40 m apart from each other. At this stage, it is challenging to propose source variations attributed to a flatten profile, but these samples could also represent mixtures of multiple-sourced hydrocarbons.

In the rest of the samples, fatty acids abundances generally decrease with increasing carbon number after C<sub>18</sub>-C<sub>20</sub> (Figure 2A; Figure 3A), similar to the *n*-alkanes. However, there is no obvious indication that the latter are degradation products of the fatty acids. For instance, if decarboxylation was taking place (loss of a COOH group), the highest peak in the *n*-alkane distribution should be displaced one carbon number less compared to the highest peak of the fatty acids, and that is not the case in any of the samples (see also Supplementary Table S4).

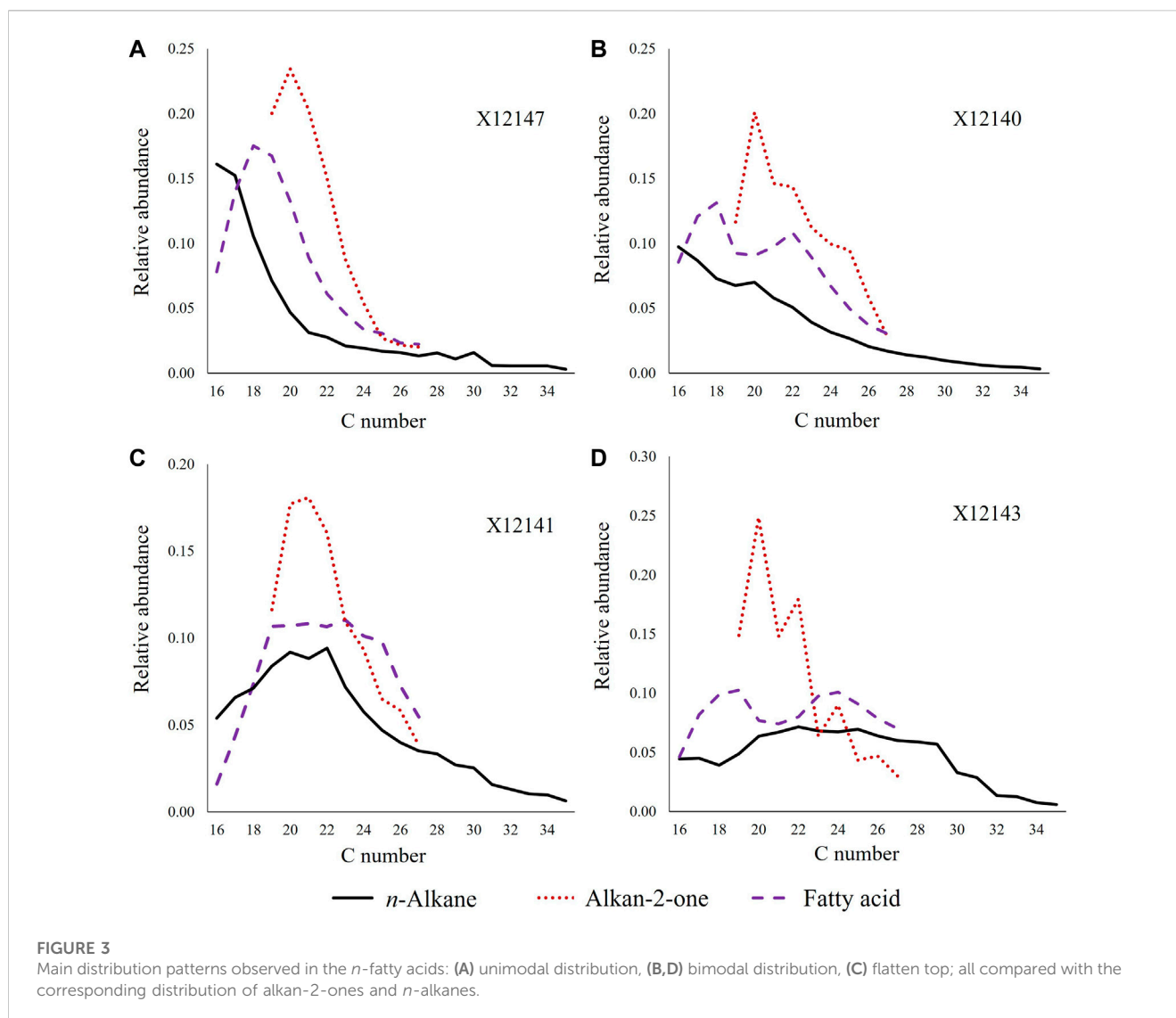
We must emphasize that comparisons between fatty acids and *n*-alkanes are also limited by the fact that the current distribution of *n*-alkanes in the Montney Formation has largely resulted from thermal cracking of migrated hydrocarbons during Montney's maximum burial, and additional fluid migration/mixing during the Eocene uplift (Wood and Sanei, 2016; Cesar et al., 2020a; Wood et al., 2022).

It is also possible that the distribution of fatty acids is responding to localized organic facies variations. A larger number of samples and geochemical constraints will provide light on this matter. Likewise, biodegradation cannot be ruled out although thermal maturity might have overprinted the molecular distribution ultimately.

## 5.2 The significance of alkan-2-ones in fossil organic matter from the Montney Formation

Alkan-2-ones are commonly present in peat and peat-forming vegetation (C<sub>17</sub>-C<sub>35</sub>; Puttmann and Bracke, 1995; Zheng et al., 2007; Naafs et al., 2019). In addition, bacterial and algal sources have been found to generate these compounds in a variety of depositional settings (C<sub>14</sub>-C<sub>31</sub>; Grimalt et al., 1990; Lopez-Dias et al., 2013; Zhang and Volkman, 2020). Although extensively studied in recent environments, alkan-2-ones have been detected in fossil organic matter of different thermal maturities with a moderate (or none) odd over even predominance of carbon chain length (Grimalt et al., 1990; George and Jardine, 1994; Leif and Simoneit, 1995; Strelnikova and Serebrennikova, 2011; Jaraula et al., 2015). Similar to the case of fatty acids, the low concentration of ketones in mature petroleum





source rocks compared to other biomarkers has probably reduced the interest in the analysis of these compounds in petroleum (Alhassan and Anderson, 2013).

Zhang and Volkman (2020) reported an even over odd predominance of alkan-2-ones in a torbanite from the Sydney Basin, Australia, similar to the C-number predominance in samples from our study. The Australian torbanite contains organic matter type I and has vitrinite reflectance of 0.4 %Ro. The same authors suggested that these compounds could have derived from cleavage of C-O bonds in the kerogen and indicated the presence of long-chain alkyl moieties in green algae (Derenne et al., 1997; Zhang and Volkman, 2017). Despite the difference in maturity, this example may explain the presence and marine origin of alkan-2-ones in Montney samples since there is no reported evidence of significant terrestrial organic matter input in the Montney Formation.

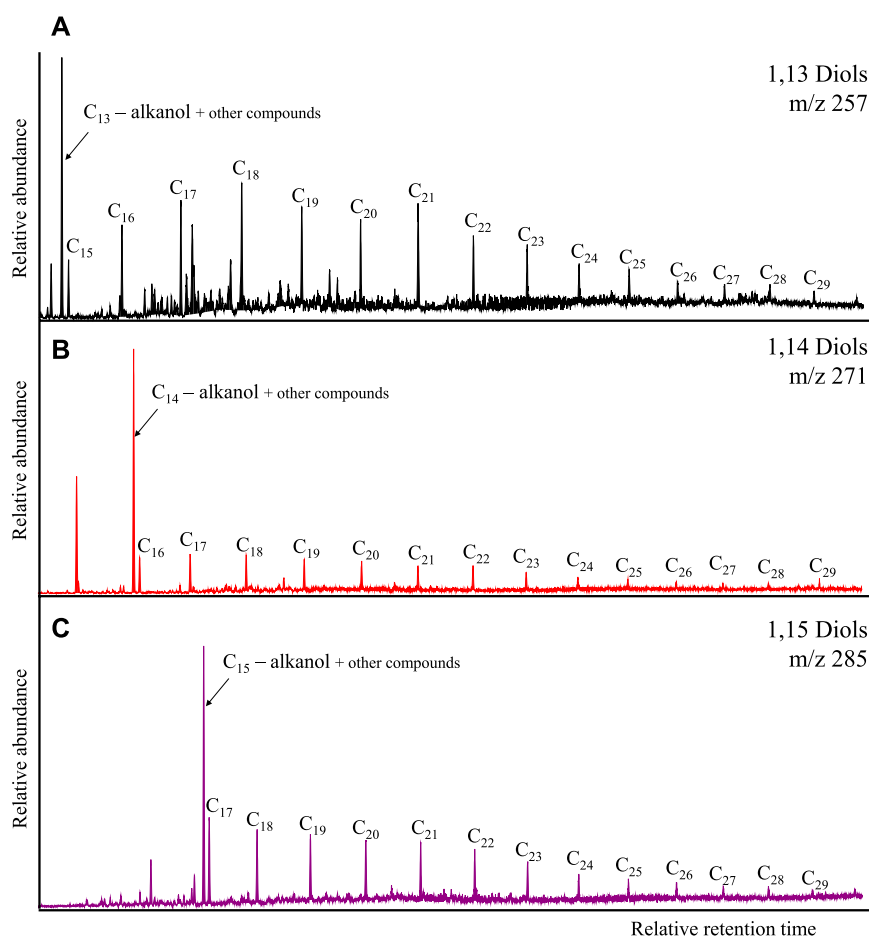
We rule out alkan-2-one generation via decarboxylation of fatty acids because of their different molecular distribution patterns. Decarboxylation would have led to alkan-2-ones with one less carbon atom, switching maximum peak heights towards lower

carbon chains (Puttmann and Bracke, 1995; Lopez-Dias et al., 2013). Instead, the highest alkanone peak found in our samples corresponds to a carbon chain (C<sub>20</sub>) longer than the highest peaks in the fatty acid distribution (C<sub>18</sub>-C<sub>19</sub>) (Figure 2; Figure 3; Supplementary Tables S1, S2). In addition, oxidation of *n*-alkanes does not seem to be a potential generation pathway either because of the contrasting molecular distribution pattern of both compound classes (Figure 3, Supplementary Tables S2, S4).

### 5.3 The significance of alcohols in fossil organic matter from the Montney Formation

Contrary to the case of fatty acids and alkan-2-ones, to our knowledge, this is the first report ever of alkyl diols in fossil organic matter.

In recent environments, these lipids typically consist of even-numbered carbon chains with hydroxyl groups at C-13, C-14, or C-15, and 28 to 32 carbon atoms (e.g., Rodrigo-Gamiz et al., 2016; Rampen et al., 2021). In the studied samples, diol distributions are



**FIGURE 4**  
Diols identified in the samples (e.g., X12153): (A) 1,13-diols, (B) 1,14-diols, (C) 1,15-diols.

characterized by an odd-numbered carbon preference after  $C_{20}$ , and shorter chain length (less than 30 carbon atoms). It is possible that the diols detected in this research are thermal breakdown products of the original long-chain diols, and the loss of a methyl group by thermal cleavage has switched the carbon length preference to odd numbers.

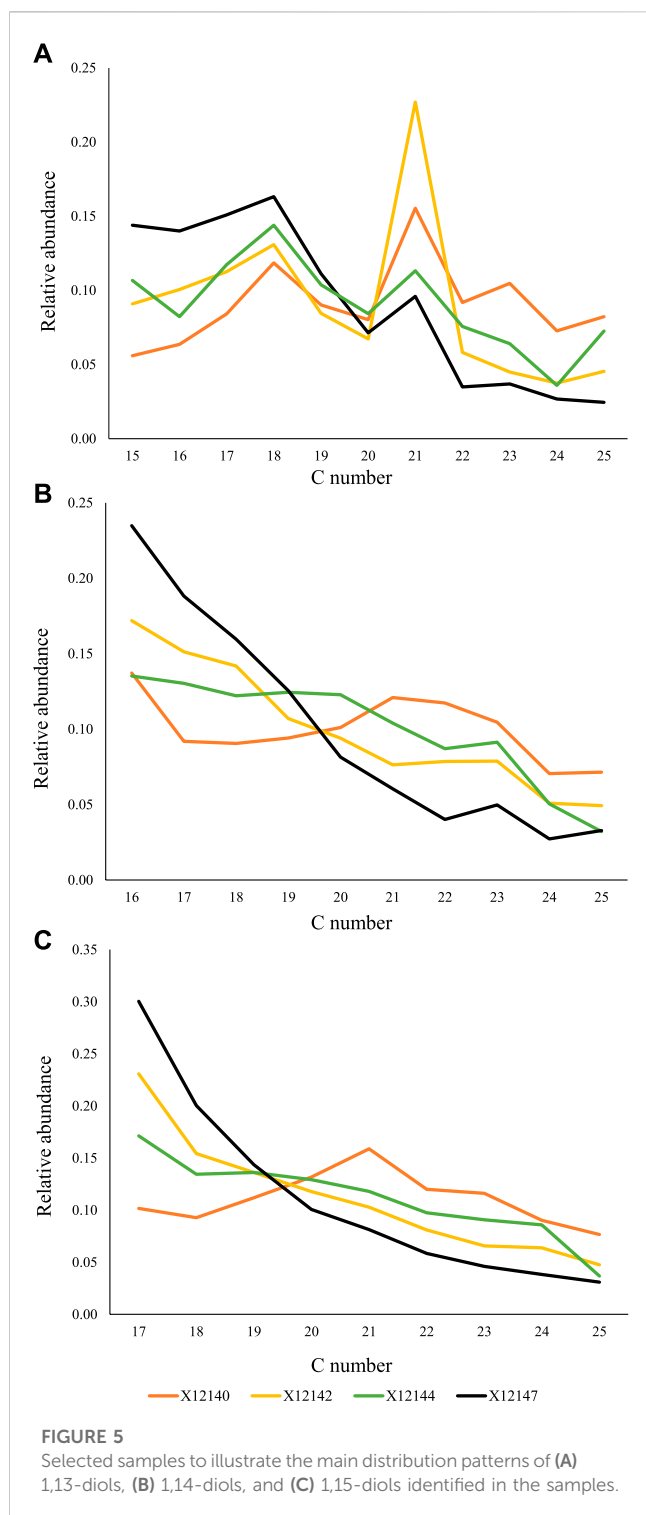
Generally, 1,14-diols are considered to be sourced by specific diatoms and are typically associated with upwelling zones (Koning et al., 2001; Wakeham et al., 2002; Damste et al., 2003), whereas 1,15-diols have been attributed to specific marine and freshwater algae (Volkman et al., 1992, 1999) in recent organic matter. However, in our sample set, 1,14- and 1,15- diols seem to share a common source (Figures 7A, B). This is interpreted based on their markedly similar distribution. In Figure 7A, we have plotted the ratios of the  $C_{16}$ - $C_{18}$  range to the  $C_{20}$ - $C_{22}$  range for both compound classes and they express an almost 1:1 correlation, with no significant thermal maturity overprint (Figure 7B). Their mutual association cannot be explained by their distribution in recent environments. It is possible that in the Mesozoic, 1,14- and 1,15- diols were synthesized by a common source/organism. The samples X12147 and X12152 stand out in Figure 7 with values  $[C_{16}-C_{18}]/[C_{20}-C_{22}]$  above three. They are the only two samples from the well 06-33-

072-25W5 (Middle Montney, Table 1), and local organic matter type variations may be responsible for their uniqueness.

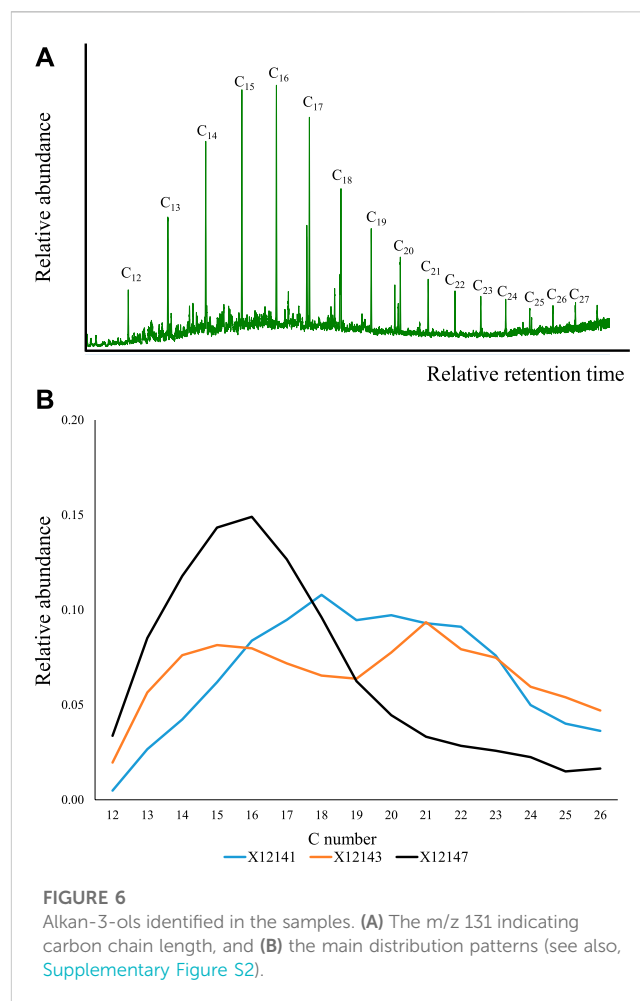
Contrary to 1,14-diols, 1,13-diols have been found to share a source with 1,15-diols in recent depositional environments (e.g., Rodrigo-Gamiz et al., 2016; Rampen et al., 2021). However, in this study, the distribution of 1,13-diols clearly differs from 1,14- and 1,15- diols (Figure 5A). Additionally, we noticed a marked preference for  $C_{21}$ 1,13-diol with respect to  $C_{20}$  and  $C_{22}$  in most of the samples, and for  $C_{18}$ 1,13-diol in sample X12152 (Figure 5A). Additional studies are necessary to investigate potential sources for the 1,13 homologues, but their origin most likely differ from the sources of 1,14- and 1,15- diols.

Another possibility is that the original distribution of alkyl-diols has simply been overprinted by other geochemical phenomena (e.g., mineral-catalyzed isomerization/cyclization, biodegradation), to which each compound class (1,13- versus 1,14- versus 1,15-) may have a different susceptibility. Under such condition, our interpretation of a common source for 1,14-diols and 1,15-diols would not necessarily be the case.

The presence of alkan-3-ols seems to be closely related to the fatty acids, probably sharing a common source since their molecular distributions are significantly similar (Figure 3; Figure 6; Figure 7C).



To our knowledge, this research is also the first time that alkan-3-ols are reported in fossil organic matter. In recent environments, alkan-3-ols have only been identified in surface-wax washings of Primulaceae (Radulovic and Zivkovic Stosic, 2021) or are perhaps usually not reported in studies of recent organic matter. At this stage, an association with plant contribution is challenged by the limited evidence of terrestrial organic matter contribution to Montney hydrocarbons (e.g., Ardakani et al., 2022). If we attempt to find

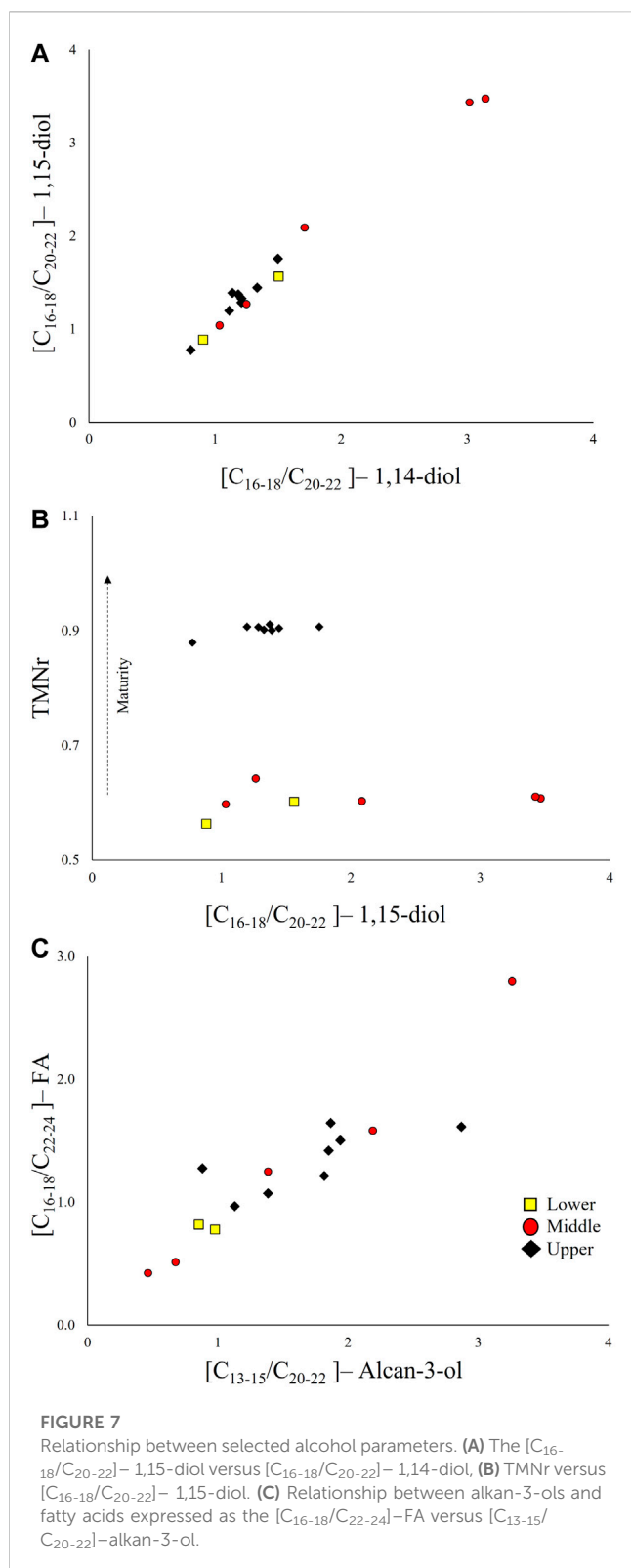


other potential precursors based on the molecular structure, a suitable candidate may be the 3-hydroxy-fatty acid compound class, which are widely distributed in aquatic environments. These acids are known to be part of cell membranes in bacterial communities (Cranwell et al., 1987; Wakeham, 1999; Wakeham et al., 2003), and have been used for temperature reconstruction due to the sensitivity of certain bacterial groups to climate change (Wang et al., 2016; Huguet et al., 2019; Yang et al., 2021). However, the potential degradation of 3-hydroxy-fatty acids to alkan-3-ols in the study samples yet lacks supporting evidence.

## 5.4 Potential associations with the general Montney Formation stratigraphy

To further investigate the applicability of oxygenated aliphatic compounds as source discriminators, we divided the data in Lower, Middle, and Upper members in Figure 7. The molecular characteristics of the samples do not seem to be specific of a particular Montney Member. The samples from the Upper Member in British Columbia are more mature (Figure 7B). The lack of differentiation among Montney Members might have resulted from hydrocarbons migrating from the same source or variable combinations of two or more sources.





Although defining source discriminators of Montney petroleum fluids remains a challenge, we have made evident that oxygenated aliphatic compounds are suitable candidates to achieve this goal, not only because they have been preserved, but also because of their

variability in the samples. The characteristics of polar compounds are also important because they have very unlikely been overprinted by hydrocarbons that migrated during the Eocene, which mostly consist of gas/condensate (very low concentration of polar compounds). Therefore, the polar compounds from the extracted bitumen are a closer approximation to the hydrocarbons that originally migrated into Montney intervals before its maximum burial.

From a broader perspective, it is intriguing that the molecular distributions observed herein do not indicate clear association with the generation mechanisms currently known for the synthesis of these compounds in recent sediments. Another pathway for investigation is to evaluate whether the polar compounds studied were as sensitive to climate variations as they are known to be in recent depositional environments.

A final aspect that is important for low-permeability reservoirs in the region is that the thermal degradation of polar compounds might also be affecting other rock properties such as organic porosity, which plays a key role in hydrocarbon production.

## 6 Conclusion

Fatty acids, alkan-2-ones, diols and alkan-3-ols have been identified in extracted bitumen from the Montney Formation. This may represent the first time that 1,13-, 1,14- and 1,15- diols as well as alkan-3-ols are reported in fossil organic matter.

Regardless of thermal maturation overprint on the original signatures of the fatty acids merely based on their distribution, we infer marine organic matter ( $<C_{20}$  range dominant) source. Exceptions include samples X12140 and 12143 where a bimodal molecular distribution was observed with additional maximum peaks in  $C_{22}$  and  $C_{24}$  respectively. Further evidence is required to suggest a terrestrial input in these samples. Both samples correspond to different stratigraphic members and thermal maturity, thus the bimodality is probably a consequence of the mixing of contrasting hydrocarbon charges within those Montney sections before maximum burial.

Based on their distinctive distribution pattern, fatty acids have not been degraded to *n*-alkanes (e.g., via decarboxylation). Likewise, the alkan-2-ones do not represent oxidation products of the *n*-alkanes. Mechanisms to explain the preference for even-numbered carbon chain of alkan-2-ones remain unknown though even-chain ketones have been identified in Australian torbanites previously.

In contrast to recent organic matter, in Montney Formation the 1,14- and 1,15- seem to share a common source or generation mechanism as expressed by their very similar molecular distribution patterns. These and the 1,13-diols could be breakdown products of their longer-chain counterparts or have otherwise precursors that have not been identified to this date. The origin of 1,13-diols is not clearly associated to the other alkyl diols as interpreted based on their different molecular patterns.

The highly similar molecular distribution of alkan-3-ols and fatty acids suggest that they are biosynthetically related and/or share a common source. Their origin from the degradation of compounds with similar structure (e.g., 3-hydroxy-fatty acids) remains unclear.

Ultimately, our research opens a new path in geochemical screening of the unconventional Lower Triassic Montney Formation and conveys renovated interest in studying oxygenated compound classes in fossil organic matter that had scarcely been considered in recent years.

## Data availability statement

The original contributions presented in the study are included in the article/[Supplementary Material](#), further inquiries can be directed to the corresponding author.

## Author contributions

JC conceptualized the study, wrote the first draft, and made [Figures 2–7](#). SN helped conceptualizing the study and identifying compounds. JC, RR, and MM generated the data. RR and OA secured funding. OA elaborated [Figure 1](#). All authors contributed to the analysis and interpretation of the data, and to writing and reviewing the manuscript.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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## Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/feart.2023.1137026/full#supplementary-material>

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