

# Basin scale distribution of organic matter in marine fine-grained sedimentary rocks: Insight from sequence stratigraphy and multi-proxies analysis in the Montney and Doig formations

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1	Basin scale distribution of organic matter in marine fine-grained
2	sedimentary rocks: insight from sequence stratigraphy and multi-
3	proxies analysis in the Montney and Doig Formations
4	
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#### 41 ABSTRACT

42 The occurrence of hydrocarbons in self-sourced reservoirs strongly depends on the concentration and maturity of organic matter in sediments. Therefore, understanding the distribution of organic 43 heterogeneity at the time of deposition is key to reduce the risk in exploration and development of 44 45 unconventional resources. This study focuses on the Lower and Middle Triassic Montney and Doig 46 Formations (Alberta and British Columbia). Samples from outcrops, cores and cuttings were analyzed 47 for organic content with a Rock-Eval VI and for major and trace element concentration using ICP-MS 48 and ICP-AES techniques. The interpretation of the analysis results in relation with the stratigraphic 49 architecture provides a mean to better understand the distribution of the organic heterogeneities and the variations of primary productivity, sedimentation rates and anoxia that control the 50 development of source rocks. 51

52 The key findings of this analysis are:

The basin-scale distribution of the organic matter suggests that the two major source-rock
 intervals of the Lower and Middle Triassic correspond to the sequence 3 (Spathian Montney
 unit) and to the transgressive systems tract of sequence 4 (Doig phosphate zone).

The dominant controls on organic matter accumulations vary through time. The Montney
 source-rock interval is interpreted to be associated with a major basin restriction triggering
 anoxia during a second-order falling stage of relative sea level. The organic accumulation of
 the Doig phosphate zone is interpreted as being controlled by a sharp decrease of the
 sedimentation rate, combined with an increase of the primary productivity.

The spatial and temporal variations of anoxia, primary productivity and dilution reflect the
 geodynamic evolution of the basin that ultimately controls the basin physiography as well as
 the sources of nutrient and sediments.

#### 64 HIGHLIGHTS

65 The Montney and Doig Formations mainly present amorphous organic matter.

66 Rock-Eval data integration in stratigraphic framework shows two organic rich layers.

67 Ni and Cu variations suggest an increased primary productivity in the Doig Phosphate.

68 Redox proxies suggest anoxic intervals in the Upper Montney and the Doig Phosphate.

69 KEYWORDS

Petroleum source rocks; Triassic; Montney and Doig Formations; Organic matter; Primary
 productivity; Redox conditions; Sedimentation rates; Canada.

#### 72 1. INTRODUCTION

With the development of self-sourced and closely associated tight reservoirs, there is a need for a 73 74 better understanding of the origin and distribution of primary organic matter (OM) in source rocks 75 (Schwarzkopf, 1993; Tommeras and Mann, 2008; Ducros et al., in press). Stratigraphic framework 76 characterization is the first and main step needed to quantify and discuss the processes controlling 77 the distribution of OM (Creaney and Passey, 1993; Myers, 1996; Huc et al., 2005; Van Buchem et al., 78 2005; Slatt and Rodriguez, 2012). Such integrated workflow gathering information on organic 79 productivity, preservation and dilution at basin scale remains a challenge especially as geodynamic 80 and climatic setting induce a large diversity of organic-rich deposits (Huc et al., 2005).

81 Our work focuses on one of the largest unconventional play of Canada: the Montney and Doig 82 Formations of the Lower and Middle Triassic interval (~ 252 - 235 Ma) of Western Canada. The amount of data available due to an extensive oil and gas exploration in the area and the presence of 83 time equivalent outcrops in the fold and thrust belt of the Canadian Cordillera, makes this interval an 84 85 attractive case study to analyze OM distribution in sedimentary basins. This study is built on a database including core, cutting and outcrop descriptions and samples as well as wireline logs. 86 Geochemical and organic petrographical analyses (palynofacies, Rock-Eval, Major and Trace Metal 87 88 Elements) were then performed on selected samples. Finally, the results were integrated in a

- sequence stratigraphic framework in order to discuss the main factors controlling the distribution of
  OM in the studied interval.
- 91 2. THE MONTNEY AND DOIG FORMATIONS

#### 92 2.1. Generalities

93 The Montney, Doig and Halfway Formations are preserved in the foreland basin of the Canadian Cordillera and in time equivalent outcrops in its fold and thrust belt (figure 1). These Lower and 94 Middle Triassic Formations have been studied since the 60's (Armitage 1962). The Montney and Doig 95 96 Formations are mostly composed of fine-grained dolomitic sandstone and siltstone with subordinate amount of shale and moderate clay content (Davies, 1997a; Zonneveld et al., 2010; Chalmers and 97 98 Bustin, 2012; Euzen et al., 2015). They were deposited on the western margin of Pangea (Davies et al., 1997). This location is considered as a passive margin during the Devonian and a foreland basin 99 during the Jurassic. Doubts remain on the precise paleogeographic settings: foreland basin (Golding 100 101 et al., 2015a) versus passive margin during the time of the deposition of the studied interval (Monger 102 and Price, 2002).

#### 103 **2.2. Stratigraphic settings and chronostratigraphy**

104 The stratigraphic framework used in this paper is based on a recent regional sequence stratigraphic 105 interpretation of the Lower and the Middle Triassic in the Western Canada Sedimentary Basin (e.g. 106 Crombez, 2016). Based on more than 400 wells, it shows that the studied interval can be subdivided 107 into two second-order sequences A and B and that sequence A can be further subdivided into three 108 third order sequences 1, 2 and 3. Within sequence A, the maximum backstepping of the sedimentary 109 system occurs during the second sequence (figure 2). Based on the biostratigraphic works of Orchard 110 and Zonneveld (2009) and Golding et al. (2015b), sequence A and B are respectively Lower Triassic 111 and Middle Triassic in age. Within sequence A, sequence 2 was deposited above the Induan-Olenekian boundary and sequence 3 lays on top of the Smithian-Spatian boundary. According to 112 113 biostratigraphic data, the top of sequence B is older than the Ladinian-Carnian boundary (Orchard

114 and Zonneveld, 2009). Integrating these recent developments (Crombez, 2016) in Davies et al., 1997 115 stratigraphic framework, the Montney Formation corresponds to sequence A. In this first second 116 order sequence, sequence 1 can be considered as the Lower Montney, the sequence 2 as the Middle 117 Montney and sequence 3 as the upper Montney whereas the Doig and Halfway Formations are part 118 of sequence B. As the Montney Formation is interpreted as a second order cycle, the sequence 1 and 119 the transgressive system tract (TST) 2 therefore represents a second order TST, the sequence 2 a 120 second order HST and the sequence 3 a second order FSST (Crombez, 2016). From this work, as 121 sequence B records the expression of a second order cycle, TST4 and HST4 can be considered as 122 second order system tracts or third order sequences.

The figure 2 illustrates the position of the studied well and outcrop (restored location) sections 123 124 within the stratigraphic framework of the basin. A recent study suggests that the Montney and Doig 125 Formations were deposited in a fore-arc basin connected with the open marine setting to the 126 Northwest (Rohais et al., 2016). The stratigraphic architecture of sequence A suggests a basin with a 127 WNW-ESE axis and sedimentary inputs coming from East and Southeast. The distribution of thickness and facies in sequence B suggests a NW-SE basin axis with an additional sedimentary source to the 128 129 West (Error! Reference source not found.). This change in sediment source areas and the clockwise 130 rotation of the basin axis are interpreted to be linked to the evolution of the proto-Canadian 131 Cordillera (Crombez, 2016; Rohais et al., 2016).

#### 132 3. DATA AND METHODS

#### 133 **3.1. Data**

For this study, data were collected from both outcrop in the Canadian Cordillera and subsurface in the foreland basin (**figure 1**). In Alberta, the cuttings from the Montney-Doig-Halfway intervals were sampled in 7 wells and in addition, 14 cores were also sampled. In British Columbia, the cuttings of the studied interval were sampled in 3 wells. Moreover, 4 cores including a 300m long core and one outcrop (Brown Hill, BH on **figure 1**) were sampled. In total, 365 samples collected from cores, 498

from cuttings and 176 from outcrops were available for this work. The results of the present study is illustrated along a SE-NW section composed of 7 wells with cuttings sampled each 5-10m and a 300m long core, sampled each 5-10m, with additional constraints from both outcrops and subsurface (figure 1).

#### 143 3.2. Methods

The workflow developed for this study unfolds as follow: (1) The characterization of the organic content in the studied interval, using Rock-Eval analyses (Espitalie *et al.*, 1986; Behar *et al.*, 2001) and palynofacies study (Tyson, 1995). (2) The study of the distribution of the organic rich layers in the stratigraphic framework. (3) The study of paleoenvironmental conditions through variations of major and trace element concentrations and mineralogy in order to highlight the dynamic of the primary productivity, the dilution by non-organic element and the O<sub>2</sub> levels along four sections (Brumsack, 2006; Tribovillard *et al.*, 2006; Algeo and Tribovillard, 2009 and references herein).

#### 151 **3.2.1.** Rock-Eval pyrolysis and hydrocarbons extraction

152 Routine source rock analyses were carried out on 900 samples with a Rock-Eval VI. The bulk-rock 153 basic cycle, used for these routine analyses, is described by Behar et al. (2001). 50 to 70 mg of 154 powdered sample is heated in an open pyrolysis system under non-isothermal condition (from 300 °C 155 to 650 °C). During this pyrolysis, the amount of hydrocarbons released is measured by a flame ionization detector (FID) and CO and CO<sub>2</sub> release are monitored with an infrared (IR) detector. The 156 157 residual sample is then put in an oxidation oven where it is heated (from 300 °C to 800 °C) under 158 artificial air ( $N_2/O_2$ : 80/20). During this combustion, the amount of CO and CO<sub>2</sub> released are 159 monitored with an IR detector.

160 In addition to the bulk-rock samples, organic solvent extraction was performed on selected samples.
161 The powdered sample was placed in a solution of dichloromethane and methanol (1/1) in an
162 ultrasonic bath for 30 min. The sample was then filtered and placed in a drying oven for 30 min.
163 Finally the sample was analyzed with the basic Rock-Eval method described above.

#### 164 3.2.2. Palynofacies

In addition to the source rock evaluation, palynofacies analyses were carried out on 26 selected samples. The preparation of the samples consists in the dissolution of 2 g of crushed rock in successive acid bath. The sample was placed in a cold solution of hydrochloric acid (70 %) for 180 min. After multiple rinsing, the residual sample was placed in a cold solution of hydrofluoric acid (70 %) for 180 min. Again, after multiple rinsing, the residual sample is place in a hot (40 °C) solution of hydrochloric acid (70 %) for 180 min. Finally, after multiple rinsing, the residual sample was sieved with a 15µm filter and the filtrate was mounted between two glass slides.

The slides were then observed with an optical microscope under different magnifications in order to classify the organic particles in three categories following the classification of Tyson (1995): the amorphous organic matter (AOM), the phytoclasts and the palynomorphs.

#### 175 3.2.3. Initial TOC computation

176 In order to better understand the distribution of organic matter at the time of deposition (before 177 thermal maturation), Rock-Eval analysis and palynofacies were used to estimate the initial total 178 organic carbon (TOC<sub>ini</sub>). The equation (**Equation** Error! Reference source not found.**1**) used for the 179 computation of the TOC<sub>ini</sub> is based on carbon mass balance and is similar to the formula proposed by 180 Jarvie (2012).

$$TOC_{ini} = \frac{TOC - (S1 + S2) \times 0.083}{1 - (HI_{ini}/_{1200})}$$
 (Equation 1)

This equation uses the total organic carbon (TOC), the free hydrocarbons (S1) and the oil potential (S2) from Rock-Eval analysis, and requires an estimation of the initial hydrogen index (HI<sub>ini</sub>). The HI<sub>ini</sub> was estimated using the palynofacies analyses that provide insight into the nature and quality of the OM. The values of HI<sub>ini</sub> used in this study are 700 mgHC/gTOC for type I organic matter, 450 mgHC/gTOC for type II and 125 mgHC/gTOC for type III (Espitalié *et al.*, 1986; Jarvie *et al.*, 2007).

# 3.2.4. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

189 Elementary analyses of samples from wells 0/14-14-76-12W6 and 0/06-33-72-25W5 and from Brown 190 Hill outcrop were performed with an ICP-MS for trace elements and an ICP-AES for major elements. 191 Samples were powdered with an agate mortar beforehand. Then, 50 mg of sample was solubilized using a solution of hydrochloric acid (70 %) and a solution of boric acid (45 %). In order to dissolve 192 193 entirely the OM, 2 ml of a hydrogen peroxide solution were added to the samples with a high TOC. 194 The residual samples were then diluted 10,000 times for the ICP-MS analyses and 1,000 for the ICP-195 AES analyses. International (ATHO-G from Borisova et al., 2010; AGV-1, BCR-2, BH-VO2 and BIR-1 196 from the USGS) and in house standards were used and several duplicates were analyzed in order to 197 control the accuracy of the measurements. A total of 244 samples were analyzed with this method. 198 Elementary analyses from well 0/16-17-83-25W6 were performed by ACT Labs following their 4A-4B 199 protocols. A total of 138 samples were analyzed with this method. In the present work element 200 concentration (ppm or %) refers to weigh ratios.

201 In order to investigate the vertical and the lateral variations of metal trace elements (MTE), the 202 concentration of MTE was divided by the Aluminum content of the sample and normalized to the 203 upper continental crusts (UCC) by computing an enrichment factors (EF) (Taylor and McLennan, 204 1985; McLennan, 2001):

$$EF_E = \frac{[E]}{[Al]} sample / \frac{[E]}{[Al]} UCC$$
 (Equation 2)

206 With  $EF_E$  the enrichment factor of E; [E] the atomic concentration of E (ppm) and [AI] the 207 concentration of aluminum (ppm).

#### 208 3.2.5. Mineralogical analyses

In addition to core and outcrop descriptions, cuttings from one well were sampled in order to quantify the mineralogy of the Triassic strata. QEMSCAN analyses (Gottlieb *et al.,* 2000) were performed by SGS Canada Inc. on 72 samples. QEMSCAN automated mineralogical analysis is based on backscattered-electron imaging and energy dispersive X-ray spectroscopy techniques.

213 **3.2.6.** Weathering index of Parker (WIP) and chemical index of alteration (CIA)

Based on elemental major element concentrations, the weathering index of parker (WIP, Parker, 1970) and the chemical index of alteration (CIA, Nesbitt and Young, 1982) provide information on the maturity of siliciclastic sediments:

217 
$$WIP = \left(\frac{[Na]^*}{0.35} + \frac{[Mg]^*}{0.9} + \frac{[K]^*}{0.25} + \frac{[Ca]^*}{0.7}\right) \times 100 \quad \text{(Equation 3)}$$

218 
$$CIA = \left(\frac{[Al_2O_3]}{[Al_2O_3] + [Na_2O] + [K_2O] + [CaO]}\right) \quad (Equation 4)$$

219 Where [E] is the atomic concentration of E (ppm) and [E]\* represent the atomic concentration of an 220 element divided by its atomic weight. In order to reflect chemical variations associated with climatic 221 changes and the weathering of siliciclastic minerals, the [Ca] and [CaO] values used in the equation 3 and 4 were corrected for each samples to remove the effect of carbonate minerals using QEMSCAN 222 223 analysis. WIP and CIA indexes were only calculated on one well where both elemental analysis and 224 QEMSCAN data were available on the same samples (0/14-14-76-12W6). Furthermore, the sodium 225 (Na) concentration was not measured on this well, but the impact of Na on these indexes is likely 226 negligible based on its low concentration in other wells of this study (average of 0.8% in well 0/16-227 17-83-25W6).

228 4. RESULTS

#### 4.1. Characterization of the organic content

#### 230 4.1.1. Rock-Eval analyses

231 Most of the studied samples have Rock Eval TOC values ranging between 0.25 and 1.75 wt%, with a 232 mean TOC of 1.28 wt% (see figure 7). However locally, organic-rich intervals present TOC higher than 233 4 wt% in the Montney Fm. and can reach up to 13 wt% in the Doig phosphate zone (TST4). The wide 234 range of Tmax (from 397 to 479 °C) of our dataset is globally consistent with published vitrinite 235 reflectance data (Rokosh et al. 2012; Romero et al., 2016) and suggests NE-SW increasing maturity 236 trend from immature to overmature. The wide range of maturity may induce an under or over 237 estimation of the in-situ TOC. Indeed, the dysmigration of the generated HC will lead to the 238 underestimation of the TOC whereas the contamination by migrated HC will lead to the 239 overestimation of the TOC. Rock-Eval pyrolysis results of the low maturity samples show that most of 240 the HI values fall between 150 and 450 mgHC/gC. This observation suggests that the OM found in the 241 Montney and Doig Formations is mainly of Type II and Type III (figure 3).

242 Detailed analysis of Rock-Eval pyrograms shows that the S2 peak often presents a shoulder during the beginning of the temperature increasing (between 300 °C and 450 °C, figure 4). This shoulder can 243 244 be interpreted in two different ways: there are two types of kerogen in the sample, or there is a presence of heavy hydrocarbons (Grundman et al., 2012). Figure 4 presents the pyrogram of both 245 246 bulk-rock (BR) and extracted bulk-rock (eBR) samples. The analysis of both bulk-rock and extracted 247 sample shows that the S2 is composed of both soluble and non-soluble OM, likely representing 248 respectively heavy hydrocarbons and primary kerogen (figure 4). According to the work of Behar et 249 al. (2008) and considering the low maturity of this sample (Tmax = 439 °C), those heavy hydrocarbons may come from the early cracking of the kerogen. 250

#### 251 4.1.2. Palynofacies studies

The investigated samples contain mainly AOM (**figure 5**). In the analyzed samples, only a small proportion of the OM derives from woody and terrestrial debris, regardless of the sedimentary facies (SP and PM on **figure 5 B, C and I**). The absence of damaged terrestrial OM showing a transformation

255 from undamaged particles to AOM suggests that the AOM was more likely derived from marine 256 rather than terrestrial sources (Tyson, 1995).

#### 4.2. Distribution of the organic content in the stratigraphic framework

#### 258 **4.2.1. TOC and TOC**<sub>ini</sub> in the stratigraphic framework

259 The Rock-Eval results show that the two samples with the lowest maturity present high to moderate 260 HI (respectively 549 and 373 mgHc/gTOC). This is consistent with of a good Type II marine kerogen 261 and a fair Type II/III kerogen. The palynofacies analyses paired with the Rock-Eval measurements suggest that regardless of the sedimentary facies, the AOM mainly derives from marine sources, 262 typically having an initial HI (HI<sub>ini</sub>) between 350 and 600 mgHC/gTOC. These two values were used to 263 264 compute a maximum and a minimum value of TOC<sub>ini</sub>. In low maturity areas (Tmax < 450°C), the computed TOC<sub>ini</sub> values likely reflect the initial organic content of the sediment. On the other hand, 265 266 in more mature areas (Tmax > 450°C), TOC<sub>ini</sub> computation can be affected by the secondary cracking of migrated oil. Figure 6 and 7 illustrate that sequence 3 and TST4 are the two main organic-rich 267 intervals of this succession based on TOC<sub>ini</sub> computation. In low maturity areas TOC<sub>ini</sub> is close to 268 269 present day TOC, whereas in more mature areas, TOC<sub>ini</sub> can be up to twice as high as present day 270 TOC (with  $HI_{ini} = 600$ ).

271 The vertical distribution of TOC values within the stratigraphic framework highlight major differences 272 between sequences (figure 6 and 7). Sequences 1 and 2 have low background present day TOC 273 (respectively 1.3 and 0.9 wt% on average), with localized organic-rich intervals up to about 3 wt% 274 (figure 7). Sequence 3 has higher background TOC (average of 2.2 wt%) and fewer low TOC values (<1 275 wt%) than sequence 1 and 2. TOC<sub>ini</sub> values can reach up to 9 wt% in LST3. The base of Sequence 4 is 276 the richest interval in OM, with TOC<sub>ini</sub> up to 14% (TST4=phosphate zone), but the rest of sequence 4 is organic-lean (average of 1.1wt%). The two main organic-rich intervals LST3 and TST4 show 277 278 contrasting spatial distributions of the OM:

In LST3, the organic content increase in the deeper central part of the basin at that time(offshore environment).

- In TST4, TOC increase towards both margins of the basin (well 0/16-17-83-25W6 and 07-1474-06W6 on figure 6) while lower values are observed toward the axis of the basin (well
  0/14-14-76-12W6 on figure 6).

#### 284 **4.2.2.** Sedimentology of organic rich intervals

285 In this section, we illustrate the sedimentological features of the organic-rich intervals of sequence 3 286 and 4. Figure 8 presents a synthetic sedimentary section from the sequence boundary 3 (SB3) up the 287 maximum flooding surface 4 (MFS4). This interval dominantly consists of wave-dominated deposits, 288 from offshore (bathymetry  $\approx$  200 m) to shoreface depositional environments (figure 8, Crombez, 289 2016). In both sequences, organic-rich intervals correspond to offshore depositional environments. 290 Sequence 3 presents a thick continuous interval of prograding deposits from offshore to lower 291 shoreface (e.g. from 2380 to 2260 m on figure 8) whereas TST4 consists of thinly interbedded 292 offshore and offshore transition deposits (e.g. from 2255 to 2240 m on figure 8). In sequence 3, the 293 high TOC intervals are associated with pyrite and phosphate grains, but with only rare bioturbations 294 (from 2380 to 2320 m on figure 8). In contrast, organic-rich layers in TST4 are associated with erosive 295 lags, shell debris as well as pyrite and phosphate grains whereas bioturbations are present in the 296 coarse-grained interbedded shallower deposits (from 2255 to 2240 m on figure 8). These differences 297 suggest that the organic rich offshore deposits of TST4 are shallower than the offshore deposits of 298 sequence 3

#### 299 4.2.3. Vertical and lateral variation of the sediment rates

300 Sequence stratigraphic surfaces provide time lines across the basin (Crombez, 2016) and allowed for 301 the computation of average sedimentation rates (SR) in the studied intervals. The sequence A was 302 deposited during the lower Triassic (approximately 5 My) and the sequence B during the Middle 303 Triassic (approximately 8 My).

The figure 9 presents a cross-plot of the distribution of  $TOC_{ini}$  versus the SR in the third order 304 sequences along 8 sections. It shows that sequence B presents lower sedimentation rates (SR < 6 305 306 cm/ka) than sequence A (SR < 16 cm/ka). More precisely it shows that sequences 1 to 3 present 307 increasing average sedimentation rates (average SR from 4 cm/ka to 12 cm/ka) whereas HST4 308 present lower sedimentation rates than TST4 (respectively average SR: 2 cm/ka and 3 cm/ka). On figure 9, the sequences 1 and 2 present decreasing TOC<sub>ini</sub> concentration (from 3 to 0.2 wt%) with 309 310 increasing SR (from 16 to 4 cm/ka). The sequence 3 presents a similar evolution but with a steepest trend (TOC<sub>ini</sub> from 7 to 3 wt% and SR from 12 to 16 cm/ka). The TST4 does not present a clear 311 312 relation between TOC<sub>ini</sub> accumulation and SR. On one side, the **figure 9** presents high TOC<sub>ini</sub> (up to 15 313 wt%) associated with the highest SR of the TST4 (4 cm/ka) and on the other side it shows decreasing 314 TOC<sub>ini</sub> (from 2.5 to 0 wt%) with increasing SR (from 1 to 2 cm/ka). Lastly HST4 presents an increasing then decreasing TOC<sub>ini</sub> (from 1 to 2.5 wt% then from 2.5 to 0 wt%) with increasing SR (from 0.3 to 4 315 316 cm/ka).

Tyson (2001) highlighted the impact of SR on OM accumulation. On one side, this study showed that, 317 318 in oxic environments, a range of SR (from 2 to 20 cm/ka) is increasing OM preservation. In oxic 319 intervals, the impact of the SR results in an increasing then decreasing TOC concentration with a 320 maximum accumulation above 5 cm/ka. The cross-plots of sequences 1, 2 and of the HST4 highlight 321 the direct impact of organic particles dilution: sequences 1 and 2 only present the decreasing TOC<sub>ini</sub> 322 whereas the HST4 presents both the increasing and decreasing trends linked to the ideal sedimentation rates interval. On the other side, in anoxic environments the preservation of the 323 organic matter is assured and an increasing SR will only decrease the TOC (Tyson, 2001). The rapid 324 325 increase of the TOC<sub>ini</sub> in the Seq 3 and the complex relation between TOC<sub>ini</sub> and SR in TST4 suggest 326 that organic matter accumulation in TST4 and sequence 3 is not solely controlled by the dilution but 327 by a complex combination of primary productivity, preservation and dilution.

328 4.3. Trace metal element variations

#### 329 4.3.1. Copper (Cu) and Nickel (Ni) variations

Organic productivity can be studied through several proxies, including Cu and Ni which are micronutrients assimilated by the micro and macro-organisms (Calvert and Price, 1983; Calvert and Pedersen, 1993; Whitfield, 2001; Brumsack, 2006; Tribovillard *et al.*, 2006; Schoepfer *et al.*, 2014). In the present study, the vertical evolution of Ni/Al and Cu/Al are chosen to reflect the variations of nutrients input in the basin which may be associated with primary organic productivity variations (Whitfield, 2001; Brumsack, 2006; Tribovillard *et al.*, 2006)

The **figure 10** presents a cross-plot of the EF of Cu vs Ni at four different locations in the basin. In this figure, most of EF of Cu and Ni are higher than 1. In comparison to black shale (Cretaceous and present day, Brumsack, 2006) the EF of Cu and Ni remain low in the Montney and Doig Formations. TST4 shows the highest EF in sections 0/16-17-83-25W6 section (3 < EF(Ni) < 10; 2 < EF(Cu) < 30) and 0/14-14-76-12W6 ( $EF(Ni) \approx 10$ ;  $EF(Cu) \approx 2.5$ ). In these wells, samples with High TOC always have high EF, however high EF does not automatically imply high TOC. No simple linear relation exists between EF(Ni) or EF(Cu) and TOC.

The **figure 11** presents the vertical evolution of Cu/Al and Ni/Al along the four sections. In these sections, Cu/Al ranges from  $3.10^{-4}$  to more than  $30.10^{-4}$  whereas Ni/Al ranges from  $5.10^{-4}$  to  $55.10^{-4}$ .

345 0/16-17-83-25W6:

In sequences 1 and 2, both ratios show little variations and stay low (Cu/Al  $\approx$  5.10-4 and Ni/Al  $\approx$ 7.5.10-4), slightly higher than the Upper crust average (Cu/Al = 3.1.10-4 and Ni/Al = 5.5.10-4). Sequence 3 records a small increase in Cu/Al (from 5.10-4 to 6.10-4) and in Ni/Al (from 7.5.10-4 to 11.10-4). In contrast, sequence 4 shows high Ni/Al and Cu/Al ratios (Cu/Al > 20.10-4 and Ni/Al > 25.10-4). These higher concentrations of Cu and Ni in TST4 are associated with high TOC value.

351 *0/14-14-76-12W6:* 

In this section, TST4 shows a strong increase of Ni/Al ratio from  $7.5.10^{-4}$  to  $50.10^{-4}$  and a slight increase of Cu/Al ration from  $5.10^{-4}$  to  $9.10^{-4}$ . No other significant variations are present along this section (Cu/Al  $\approx 5.10^{-4}$  and Ni/Al  $\approx 7.5.10^{-4}$ ).

355 *0/06-33-72-25W5:* 

This section shows low values for both ratios (Cu/Al  $\approx 5.10^{-4}$  and Ni/Al  $\approx 7.5.10^{-4}$ ), consistent with a more proximal depositional setting dominated by detrital inputs.

358 Brown Hill:

In sequences 1 and 2, the low Cu/Al and Ni/Al (respectively 6.10<sup>-4</sup> and 8.10<sup>-4</sup>) are punctuated by peaks of higher Cu/Al (up to 22.10<sup>-4</sup>). Along this section, the highest peaks of both ratios are not linked to an important concentration of Ni and Cu but to a very low concentration of Al, it is therefore an artifact of normalization.

363 Interpretation:

On the four sections, the only significant increase in Cu/Al and Ni/Al ratios occurs during TST4, 364 suggesting a strong increase in organic paleoproductivity during this interval. High amplitude 365 366 variations of both ratios in this interval also highlight cyclic fluctuations of paleoproductivity during 367 TST4. It is important to note that the increase of the authigenic Ni and Cu occurred after a sharp drop 368 of the sedimentation rates across the boundary between sequence A and B. Even though HST4 present low Ni/Al and Cu/Al ratios, the influence of low sedimentation rates on TST4 enrichment 369 370 cannot be ruled out. However, it is also worth noting that both Cu and Ni concentrations are 371 positively correlated to Al during sequence A, whereas no such relations were observed in TST4. This 372 evidence supports the hypothesis of a change of nutrient source between sequence A and B, with an 373 increase of primary productivity during TST4. In sequence 3, the small increase of Ni and Cu 374 concentration can be either linked to a small increase of the primary productivity or to a better preservation of the OM (confirmed by U/Th and Mo/Al proxies) at the water sediment interface that 375 376 will induce a lower recycling of the nutrients included in the OM (Riquier *et al.*, 2005).

#### 377 4.3.2. Uranium (U), Molybdenum (Mo) and Vanadium (V) variations

Some trace elements present in the water are sensitive to redox condition (e.g. U, Mo, V and Ce) and provide information on the oxygen and sulfur content in the water at the time of the deposition (Emerson and Huested, 1991; Calvert and Pedersen, 1993; Crusius *et al.*, 1996; Brumsack, 2006; Algeo and Lyons, 2006; Tribovillard *et al.*, 2006; Algeo and Tribovillard, 2009).

- 382 The figure 12 presents a cross-plot of the U/Th and V/Cr ratios from four different sections across the 383 basin. In these ratios, the redox-sensitive elements (U and V) are normalized to Th and Cr which are 384 both assumed to be linked to detrital inputs. These ratios therefore present the authigenic variation of U and V that are linked to anoxic episodes. These cross-plots show a link between the ratios and 385 386 the TOC content along wells 0/16-17-83-25W6 and 0/14-14-76-12W6: samples with high ratios 387 present the highest TOC. These cross-plot also show that sequence 1 and 2 present higher oxygen content (U/Th < 0.75 and V/Cr < 2) than sequence 3 and part of sequence 4 (most of U/Th > 0.75 and 388 389 V/Cr > 2).
- The **figure 13**Error! Reference source not found. presents the vertical evolution of U/Th and Mo/Al along four sections. In the four sections, U/Th ranges from 0.3 to 4.5 whereas the Mo/Al ranges from  $1.10^{-4}$  to 24.10<sup>-4</sup>.

393 0/16-17-83-25W6:

From SB1 up to MFS2, both ratios stay low (U/Th  $\approx$  0.3and Mo/Al  $\approx$  1.10<sup>-4</sup>). The interval between MFS2 and SB3 shows an increase, then a decrease of U/Th and Mo/Al ratios (U/Th: from 0.3 up to 1.25 down to 0.3 and Mo/Al: from 1.10<sup>-4</sup> up to 7.5.10<sup>-4</sup> down to 1.10<sup>-4</sup>). In sequence 3 the interval presents moderate U/Th (> 0.75) and high Mo/Al (> 5.10<sup>-4</sup>) that seems to oscillate with no correlation with the transgressive and regressive trends of the sedimentary system. Lastly in the TST4, U/Th and Mo/Al both show significant increases (U/Th: from 0.3 up to 4.5; Mo/Al: from 2.10<sup>-4</sup> up to 25.10<sup>-4</sup>).

400 *0/14-14-76-12W6*:

401 Along this section, U/Th and Mo/Al mainly present low values (U/Th < 0.75 and Mo/Al <  $5.10^{-4}$ )

402 except in the TST4 where both ratios increase significantly (up to U/Th  $\approx$  2.25 and Mo/Al < 15.10<sup>-4</sup>).

403 *0/06-33-72-25W5:* 

404 On this section no significant increase of both ratios are present (U/Th < 0.75 and Mo/Al <  $5.10^{-4}$ )

405 Brown Hill:

As for the 0/06-33-72-25W5, both proxies along Brown Hill section show very low values. The only
high values of both ratios are linked to very low concentration of Al or Th.

408 Interpretation:

409 Figures 12 and 13 present sedimentary records of redox sensitive elements. These figures suggest 410 that the water column was oxic to dysoxic during sequence 1 and 2. In sequence 2, the small increase 411 then decrease of the U/Th and Mo/Al ratios is interpreted as the development of small anoxic puddle 412 in the deepest part of the basin. Above SB3, redox sensitive trace elements suggest variations of O<sub>2</sub> 413 concentrations in the water column and the occurrence of dysoxic to anoxic layers in the deepest 414 part of the basin (located near the well 0/16-17-83-25W6 at that time). In this sequence, the high 415 concentration of Mo suggests that water/sediment interface may contain H<sub>2</sub>S (Jones and Manning, 416 1994). In sequence 4, due to the geodynamic evolution and the changes in the basin physiography, 417 the well 0/16-17-83-25W6 present more proximal deposits. In the TST4, the high U/Th and Mo/Al ratios show the occurrence of anoxic to euxinic conditions. In this interval,  $O_2$ -depleted and possible 418 419 H<sub>2</sub>S enriched conditions took place along the more proximal areas. As already mentioned for Ni/Al 420 and Cu/Al ratios, the drop of sedimentary fluxes across the boundary between sequence A and B may 421 influence the dilution of authigenic molybdenum and uranium. However, when corrected from 422 dilution effect based on computed sedimentation rates (dilution 4 times lower in sequence B 423 compared to sequence A), U/Th and Mo/Al ratios are still characteristic of anoxia (respectively 1 and 5.10<sup>-4</sup>). 424

#### 425 4.3.3. Molybdenum (Mo) and TOC variations

426 Changes in basin restriction can be investigated thanks to molybdenum and TOC covariations. Figure 14 presents molybdenum versus TOC cross-plot along four sections. On these cross plots, TOC values 427 428 range from 0 to 15.2 wt%, with the maximums located in the sequence 4 and, the molybdenum 429 concentration ranges from 0 to 101.6 ppm with the maximums located in the sequence 3. The TOC 430 and Mo concentrations from wells 0/14-14-76-12W6 and 0/06-33-72-25W5 and from Brown Hill 431 outcrop stay very low (TOC < 3wt% and Mo < 25) except for two cutting samples located near SB3 432 and SB4. Mo and TOC covariations in different restricted basins (the Saanich inlet, the Cariaco basin, 433 the Framvaren fjord and the Black sea, respectively SI, CB, FF and BS on figure 14) are presented by 434 Algeo and Lyons (2006). All the low TOC and Mo samples of the present cannot be related to one of 435 these case studies. The samples of well 16-17-83-25W6 present more significant results with 436 moderate to high TOC and molybdenum concentration (1.5 < TOC < 15.2 wt% and 0 < Mo < 101.6 437 ppm). Along this well, values for sequences 1 to 3 fall between the Cariaco basin trend and the Black sea trend, whereas sequence 4 values clearly fall along the Black sea trend. 438

439 In restricted basin, due to low water and molybdenum reservoir renewal, the Mo/TOC ratio generally stays low (< 15) whereas in open marine settings, due to the water circulation, the Mo/TOC ratio is 440 441 relatively high (> 60). The cross-plots of figure 14 show that regardless of the well and the sequence, 442 samples always presents relatively low Mo/TOC ratios (< 35) which tend to highlight a moderately to 443 highly restricted basin (Algeo and Lyons, 2006). The cross-plots of 0/14-14-76-12W6, 0/06-33-72-444 25W5 and Brown Hill sections are consistent with figure 13: anoxia proxies (U/Th, V/Cr and Mo/Al) 445 do not highlight major anoxic event along those three sections excepted in the early sequence 4 of 446 the 0/14-14-76-12W6 well which induced a low concentration of Mo. Along the well 0/16-17-83-447 25W6, the interpretation of the basin restriction evolution between sequence A and sequence B 448 must be done with caution: firstly only some intervals of sequence 3 and the TST 4 present anoxia. 449 Secondly, the significant drop of the sedimentary supply across the boundary between sequence 3 450 and 4 (see figure 9) may also impact the concentration of Mo and the TOC. In order to remove this 451 impact, Mo and TOC values from sequence 4 were divided by 4. (which represents the average

sedimentary supply decrease between sequence A and B, Crombez, 2016). This correction puts the sequence 4 samples in the lower left side (with sequences 1 and 2) of the cross plot in an area where a restriction is uncertain. All these observation tends to show that both sequence A and B were deposited in a restricted basin, that may be more restricted in sequence 3 that in the other sequences.

457 4.3.4. Weathering index of Parker (WIP) and chemical alteration index (CIA) variations

Figure 15 presents a cross-plot of the WIP and CIA along the 0/14-14-76-12W6. On this figure, the WIP ranges from, 20 to 80 but most of the samples are comprised between 35 and 50 whereas the CIA ranges from 45 to 85. This figure does not show any maturity trend along the four sequences. Sediment maturity trend are likely to reveal climatic evolution of an area (Parker, 1970; Nesbitt and Young, 1982; Bahlburg and Dobrzinski, 2011), the cross plot presented in figure 15 suggests that no major climatic changes took place over the western Canada sedimentary basin during the Lower and Middle Triassic.

#### 465 **5. DISCUSSIONS**

In the following section, we discuss the source of OM in the Montney and Doig Formations, the spatial and temporal variations of controlling factors on the accumulation and preservation of this OM and finally, their relationship with relative sea level variations and the basin physiography.

469 **5.1. Organic matter in the Montney and Doig Formations** 

470 Rock-Eval analyses show that the OM in the Montney and Doig Formation represents Type II/III 471 source rocks (**figure 3**), which is consistent with the studies of Riediger *et al.* (1990) and Riediger 472 (1997). In the Montney and Doig Formations, two intervals present significant enrichment in OM: the 473 sequence 3 (Upper Montney) and the TST4 (Doig phosphate) which is also consistent with previous 474 studies (Ibrahimbas and Riediger, 2004).

475 Our Rock-Eval analyses data on extracted, low maturity samples, confirm the presence of kerogen in 476 the studied samples (figure 4) whereas palynomorphs analyses (figure 5), show that this primary OM 477 derives from planktonic sources. Lastly, the analysis of trace elements shows the occurrence of Cu, 478 Ni, U and Mo enrichments in the Montney and Doig Formations. In the present work, these 479 enrichments are interpreted to be linked to redox conditions and/or primary productivity variations 480 (Tribovillard et al., 2006). As crude oil contains important concentration of trace metal elements 481 (Lord, 1991; Duyck et al., 2002), the enrichments that are highlighted in sequence 3 could also be 482 linked to bitumen associated with secondary cracking of migrated oil. In the present study, we were 483 unable to establish a clear relation between TOC concentration and the trace metal element 484 concentrations, or the Al-normalized concentration of those elements and the TOC. It is therefore unlikely that all the organic content in the Montney Formation comes from migrated hydrocarbons. 485

486 In the present work, the study of Rock-Eval S1 values does not allow for the recognition of good 487 conventional reservoir intervals. In the Montney and Doig Formations, average S1 value is low (< 0.4 488 mgHC/gRock) and high S1 values within low maturity areas, which correspond to good conventional reservoir, are absent. Recent works of Sanei et al. (2015) and Wood et al. (2015) concluded that most 489 490 of the organic content in the Montney Formation derives from migrated hydrocarbons. In their 491 studies, the most part of the organic content in the Montney Formation is considered to be 492 pyrobitumen, resulting from the secondary cracking of migrated oil. Regarding the low maturity 493 (Tmax < 450) of the primary organic matter in some part of the basin and the very low permeability 494 of the Montney and Doig Formation (< 0.01 mD, Chalmers and Bustin, 2012), it is unlikely that the 495 organic matter is coming from the secondary cracking of a migrated bitumen (due to the le 496 permeability) or from the secondary cracking of a light oil (due to the low thermic maturity). Our 497 study does not question the presence of pyrobitumen in the Montney-Doig Formations, but it also 498 emphasizes the occurrence of primary kerogen in this interval. Analysis of the elementary proxies 499 shows that the sequence 3 and part of sequence 4 present propitious redox conditions and primary 500 productivity for source rocks development, whereas sequences 1 and 2 present less conductive

501 conditions to organic rich sediment accumulation (**figure 10 to 13**). Estimating the relative proportion 502 of migrated versus in place hydrocarbons in the Montney Formation is beyond the scope of the 503 present study and would necessitate a quantitative basin analysis.

#### 504 **5.2.** Spatial variations and temporal evolution of primary productivity, anoxia and dilution

#### 505 and their impacts on organic matter distribution

506 Recent works (Sageman et al., 2003; Bohacs et al., 2005; Katz, 2005) showed that the organic 507 richness of sedimentary rocks is controlled by a combination of three mains factors: (1) the primary 508 organic production by flora and fauna, (2) its dilution by non-hydrogenated particles and (3) its 509 preservation. Bohacs et al. (2005) showed that a high productivity combined with a low dilution rates is not the most efficient way to produce and preserve an organic rich rock. Indeed, an extremely high 510 511 planktonic productivity will dilute the organic content in the tests of the micro-organisms and a low 512 SR will minimize the burial efficiency and will allow a higher bacterial degradation and oxidation at 513 the water sediment interface and therefore lead to weak preservation.

514 In the present study, the palynofacies analyses mostly revealed AOM coming from marine planktonic 515 faunas. In a sedimentary basin, the OM can be degraded or destructed by various processes 516 occurring in the water column and in the first centimeters below the water-sediment interface 517 (Demaison and Moore, 1980; Southam et al., 1982; Einsele, 1992; Calvert et al., 1996): (1) In the 518 production areas, the OM produced by micro-organisms can be consumed and recycled by macro-519 organisms (Eppley and Peterson, 1979). However assuming that the macro organisms also produce 520 OM, this phenomenon only has a small impact on the total OM production. (2) While settling through the water column, the OM can be oxidized and therefore degraded by the oxygen present in the 521 522 water (Karl et al., 1988; Wakeham and Lee, 1993). Therefore, at a constant production rate, the OM is better preserved in anoxic or dysoxic water (Cowie and Hedges, 1992; Canfield, 1993). However, if 523 524 production is high enough, sinking OM consume all the oxygen leading to the creation of Oxygen 525 Minimum Zone (OMZ) and the preservation of the remaining OM (Southam et al., 1982; Einsele,

1992; Paulmier and Ruiz-Pino, 2009). (3) In the first centimeter below the water/sediments interface, rapid degradation of the OM takes place as long as oxygen is present. The occurrence of macroorganism in oxic sediments results in bio-degradation of the OM present in the sediments (Ingall *et al.*, 1993). Most of OM degradation will stop a few centimeters below the water/sediments interface due the depletion in oxygen in the buried layers (Wenzhofer and Glud, 2002). Globally, the preservation of OM is highly linked to the oxygen content in the water and sediments.

#### 532 **5.2.1.** Basin scale variations of primary productivity, anoxia and dilution

533 The relative contribution of the three main factors (production-dilution-preservation) controlling 534 initial TOC of sediment can be estimated by integrating sequence stratigraphy interpretation with 535 trace element analysis. Based on trace elements analyses from wells 0/16-17-83-25W6; 0/14-14-76-536 12W6 and 0/06-33-72-25W5 and based on the Rock-Eval analyses of five additional wells, the figure 16 presents an interpretation of the vertical and the lateral variations of the factors that drive 537 538 organic richness in sedimentary rocks. It confirms that there is no simple relation between SR 539 (dilution) and the organic content in the studied interval. Tyson (2001) concluded that SR close to 5 540 cm/ka may enhance the concentration of the OM which is observable in sequence 1, 2 and the HST4 541 (figure 9).

On the figure 16, it is apparent that local OM enrichment occurs near MFS or parasequence flooding 542 543 surfaces, similar to trends observed by Creaney and Passey (1993). However, a low SR alone cannot 544 explain the organic enrichment of condensed layer, indeed low burial efficiency resulting from a low 545 SR will promote the degradation of OM (Tyson, 2001; Bohacs, 2005; Katz, 2005). In the studied 546 interval, small increases of anoxia proxies are commonly associated with organic rich intervals, 547 suggesting occurrence of small anoxic puddles, most likely linked to basin floor physiography. Local 548 and punctual enrichment would therefore be linked to a combination of starved intervals and local 549 anoxic layers (Algeo and Rowe, 2012).

550 Figure 16 illustrates that low to moderate organic productivity, mainly oxic water (85% of the U/Th 551 ratio < 0.75, Jones and Manning, 1994) and high sedimentation rates prevailed during sequence 1 552 and 2, regardless of the position along the depositional profile. In this interval, rare TOC peaks are 553 present and are interpreted to be associated with either local dysoxic to anoxic episodes (U/Th ratio 554 increase) or punctual decrease SR (e.g. near MFS). Above sequence 1 and 2, figure 16 shows a major 555 change in the paleo-redox conditions. At that time the oxic to dysoxic water of sequence 2 turns into 556 dysoxic to anoxic water marked by an increase of U/Th and Mo/Al ratios (Emerson and Huested, 557 1991; Tribovillard et al., 2004; Brumsack, 2006). These anoxic conditions are clearly present in the 558 deepest part of the basin, in offshore facies and are weaker in the shoreface facies on the edges on 559 the basin (figure 16). This major change of the water's oxygen content is not interpreted to be 560 associated with an important variation of primary productivity. Indeed, the small increases in Cu/Al 561 ratio observed on the 0/16-17-83-25W6 are interpreted to be linked to the better preservation of the 562 OM (Riquier et al., 2005). In sequence 3, the organic-rich deposits are located in the central part of 563 the basin where oxygen content is minimum (figure 16). In this interval, the fluctuation of anoxic conditions are associated with the progradation and backstep of the depositional system. 564

565 Above this anoxic episode, the figure 16 shows for the first time an important increase of primary 566 productivity associated with anoxic water marked by important increase of Cu/Al, Ni/Al, U/Th and 567 Mo/Al ratios (Tribovillard et al., 2004; Algeo and Lyons, 2006; Tribovillard et al., 2006). In this 568 interval, organic rich deposits are located in periphery of the basin. Unlike in sequence 3, anoxia is 569 strongest at the edges of the basin and alternate with dysoxic periods, suggesting the onset of an 570 OMZ, triggered by the high primary productivity at sea surface. Above the MFS4, the basin returns to 571 similar conditions as in sequence 1 and 2: low to moderate productivity and high oxygen content in 572 the water, leading to low production and poor preservation of OM (figure 16).

#### 573 5.2.2. Models for organic-rich rocks deposition

- 574 In this study, we highlight four main stages characterized by contrasted depositional dynamics that
- result in different temporal and spatial distributions of OM in the basin:
- 576 Sequence 1 and 2: oxic water and low paleoproductivity.
- 577 Sequence 3: dysoxia/anoxia takes place in the deepest part of the basin.
- 578 TST4: the anoxia is associated with an increase of paleoproductivity on the basin margins.
- 579 Above MSF4, the basin returned to its initial condition: oxic water associated with a low
  580 productivity.

Based on these observations we propose a model for the deposition of the organic-rich layer in the Montney and Doig Formations (**figure 17**). These models split the investigated interval in 3 conceptual basin types: Type 1: an oxic basin, that prevailed during sequence 1 and 2 and HST4. Type 2: a restricted basin that is representative of the sequence 3. Type 3: a high primary productivity basin that is diagnostic of the TST4.

586 During sequence 1, 2 as well as HST4, the low primary productivity along the coast, the high oxygen 587 content in the water lead to limited organic accumulation in the basin (**figure 16 and 17 A**).

588 In sequence 3, a restriction of the connection between the open marine settings and the basin due to 589 low relative sea level induced a decrease of water circulation and therefore a stratification of the 590 water column that to the development of anoxia in the deepest part of the basin (figure 16 and 17 B, 591 Demaison and Moore, 1980; Huc, 1988; Arthur and Sageman, 1994; Brumsack, 2006; Algeo et al., 592 2008; Algeo and Rowe, 2012). The stratification is supposed to take place below the storm weather 593 wave base (SWWB) where water mixing is limited. This stratification associated with a primary 594 productivity similar to sequence 1 and 2 allows for the preservation of produced OM transported in 595 the deepest part of the basin. On the edges of the basin, where the bathymetry does not go below the SWWB, OM is poorly preserved (figure 16). 596

597 This study highlighted an increase in primary productivity and the occurrence of anoxic water along 598 the margin of the basin In the TST4 (**figure 16 and 17 C**, Demaison and Moore, 1980; Calvert and 599 Price, 1983; Emeis *et al.*, 1991; Wignall and Newtown, 2001; Brumsack, 2006; Algeo *et al.*, 2008). This

productivity, associated with the anoxia controlled the preservation of very rich organic layers on the
edges of the basin. In this systems tract, anoxic condition and increased productivity were also
highlighted in the central part of the basin, but with a lower intensity than on the edges of the basin.

The integration of geochemical analyses in the stratigraphic framework highlighted three different types of basin in the studied interval. Those three types of basin present drastically different distribution of OM due to differences in dynamic of anoxia and primary productivity.

606 Sequence stratigraphy study shows that the deposition of the Montney and Doig Formations most 607 likely took place in an oval shaped basin between the proto-cordillera and the western margin of 608 Pangea (Crombez, 2016; Rohais et al., 2016). In these settings, OM is poorly preserved in type 1 basin 609 (figure 17 A). In a type 2 basin (figure 17 B), organic rich deposits are located in the central part of 610 the basin where the oxygen content is minimum. This type of basin is very similar to the present-day Black Sea where the production of the OM takes place along the margin of the basin and OM is 611 612 accumulated in the central part of the basin (Huc, 1988; Wilkin et al., 1997; Arthur and Dean, 1998; 613 Algeo and Lyons, 2006; Algeo et al., 2008). In this type of basin, the organic rich area will likely be 614 round-shaped in the deep basin. Lastly, in a type 3 basin (figure 17 C), the organic-rich layers are 615 located below the production areas, where the oxygen content is minimum due to the development 616 of OMZ. As the production areas can be considered a function of the distance to the shore (Calvert, 617 1987; Baudin et al., 2007), the organic rich areas resulting from this type of basin are likely to be 618 halo-shaped parallel to the shoreline.

#### 619 **5.3. Controls on primary productivity and anoxia**

Our analysis suggest that during the Lower and Middle Triassic in Western Canada, the evolution of primary productivity and anoxia through time was associated with major stratigraphic surfaces (**figure 16**). In particular, physiographic changes of the basin across the boundary between thirdorder sequence 2 and 3 as well as between second-order sequence A and B (Crombez, 2016) appear

to have a major impact on the distribution of organic matter. These changes likely reflect the earlygeodynamic evolution of the Canadian Cordillera.

#### 626 5.3.1. Primary productivity

A strong increase of primary productivity occurred during TST4, above a major erosional unconformity that modified the physiography of the basin. Several models explain the increase of organic productivity by an augmentation of nutrients inputs from the continent due to climate enhanced continental weathering (Algeo et al., 2008) or associated with a marine transgression (Wignall and Newton, 2001). Other studies explain the increase of primary productivity by the input of deep marine nutrients associated with upwelling cells (Heckel, 1977; Demaison and Moore, 1980; Calvert and Price, 1983; Emeis et al., 1991).

During sequence A, the positive correlation of detrital supply proxies (AI) with organic productivity 634 635 proxies (Ni, Cu) suggests that nutrients were supplied by the continent and their low concentration 636 resulted in low to moderate organic productivity in the Montney Formation. During TST4, such a 637 relation between detrital input and organic productivity was not observed, suggesting another 638 source of nutrients. A recent study (Krajewski, 2013) on Triassic strata from Svalbard archipelago, 639 shows that the increase of primary productivity in the basin is mainly controlled by the stratigraphic 640 evolution that establish the connection between upwelling cells and a moderately restricted basin 641 (figure 14). A major change of basin physiography across the boundary between sequence A and B, 642 associated with the early geodynamic evolution of the foreland basin might have resulted in the 643 connection with upwelling cells present during the Triassic along the NW margin of Pangea (Parrish 644 and Curtis, 1982). Accordingly, the increase of nutrients delivery during TST4 is probably linked to a 645 combination of the transgressive trend and the regional geodynamic evolution that connect the 646 basin with upwelling cells.

647 **5.3.2.** Anoxia

Anoxia in sedimentary basin is mainly driven by two processes: the basin restriction (e.g. the Black Sea, Demaison and Moore, 1980; Huc, 1988; Arthur and Sageman, 1994; Brumsack, 2006; Algeo and Rowe, 2012) and the primary productivity (e.g. the Peruvian Margin, Demaison and Moore, 1980; Arthur and Sageman, 1994; Emeis *et al.*, 1991; Calvert and Price 1983; Arthur and Dean, 1998; Brumsack, 2006; Paulmier and Ruiz-Pino, 2009).

The Montney and Doig Formations present two intervals of anoxia during sequence 3 and TST4. The anoxia in sequence 3 is associated with a moderate to low productivity and a major falling stage of relative sea level whereas TST4 is a second order transgressive period associated with increased primary productivity.

During sequence 3, the lowstand relative sea level lead to restricted connections between the basin and the open marine settings and resulted in reduced water exchange between the two domains and a stratification of the water column. In this setting, the anoxia in the basin is controlled by both the physiography of the basin and the stratigraphic settings that allow for the occurrence of a threshold area.

In the TST4, the high primary productivity triggered the development of an oxygen minimum zone directly below the production area. Unlike in sequence 3, the anoxia in TST4 was controlled by the primary productivity, although the additional impact of basin restriction on anoxia is difficult to estimate.

In the Montney and Doig Formations, the two anoxic episodes present different extension and dynamic. (1) The anoxic episode at the upper part of the Montney Formation was mainly linked to the physiography of the basin and to its stratigraphic evolution. (2) The anoxic areas in TST4 were likely controlled by organic productivity and therefore were not located in the center of the basin but instead in halo-shaped belts associated with up-welling cells. Further work involving forward stratigraphic modeling would help addressing the relative impact of primary productivity versus basin restriction on the resulting anoxia.

#### 673 6. CONCLUSIONS

The work presented in this paper is based on well and outcrop data. It integrates geochemical analyses in a stratigraphic framework in order to understand the distribution of organic-rich layers in a sedimentary basin and the dynamic of the key controlling factors: primary productivity, dilution and preservation of OM at basin scale. This multidisciplinary study shows:

- 678 The occurrence of primary OM in the Montney and Doig Formations. The palynofacies
  679 analyses reveal the occurrence of planktonic OM (figure 5).
- The need for a large scale sequence stratigraphic framework to understand local
   variation of OM accumulation. In the studied interval, the time lines provided the
   opportunity to understand the major spatial and temporal changes of organic primary
   productivity and redox conditions.
- The impact of these variations of redox conditions and productivity on the vertical distribution of OM in the Montney and Doig Formations. Sequences 1 and 2 present low TOC content, whereas sequence 3 and TST4 present some organic-rich accumulations.
   This complex distribution is linked to the development of a "Restricted basin" in sequence 3 and a "High primary productivity basin" in the TST4.
- The lateral variation of OM content due to different rates of productivity and different
  types of anoxia. In a "High primary productivity basin", the organic rich layers are located
  along the coast below the production areas whereas, in a "Restricted basin", the organic
  rich layers is deposited in the center basin.
- The occurrence of two different types of anoxia. In the Montney Formation, sequence 1
  and 2 may show small episodic "Restricted basins" (ponds) in the basin center and the
  sequence 3 can be considered as a large "Restricted basin" (figure 17 B). In the TST4, the
  anoxia is located along the basin margin ("High primary productivity basin", figure 17 C).
  In the Montney Formation, the anoxia is induced by the physiography of the basin and by

- the sea level falling stage whereas in the Doig phosphate unit, the anoxia is linked to
  organic primary productivity associated with a second order transgressive trend induced
  by major geodynamical changes.
- The primary controls of the basin physiography and stratigraphic settings on anoxia. In
   the studied interval, the "Restricted basin" is the result of a major sea level falling stage
   in a threshold basin whereas the "High primary productivity basin" is linked to a major
   transgressive interval. In the present study, the threshold is linked to the proto-Canadian
   Cordillera accretion and induces strong restriction.
- 706 The second order transgressive periods do not always present high organic accumulation.
- In our case study anoxia and primary productivity are the two main controls on organic
   richness, while dilution as only a marginal impact.

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#### 980 FIGURES CAPTIONS

Figure 1: Location map of the data available for this study. The names 0/06-33, 0/14-14 and 0/16-17,
respectively stand for wells: 0/06-33-72-25W5, 0/14-14-76-12W6 and 0/16-17-83-25W6. The map on
the upper right side indicates the location of the study area within the Western Canada sedimentary
basin and the Montney Formation subcrop area. BC – British Columbia; AB – Alberta; CC – Canadian
Cordillera; WCSB – Western Canada Sedimentary Basin; CS – Canadian Shield; UC – Ursula Creek
outcrop; BH – Brown Hill outcrop.

Figure 2: Simplified sedimentary architecture of the Lower and Middle Triassic strata of the Western
Canada sedimentary basin (modified from Crombez, 2016). On this sketch, the Brown Hill outcrop
(BH) located near to Williston Lake in the fold and thrust belt of the Canadian Cordillera, was moved
to its estimated original position at the time of deposition. TST – Transgressive systems tract; HST –
Highstand systems tract; FSST – Falling stage systems tract; LST – Lowstand systems tract.

Figure 3: A. HI vs Tmax cross-plots for core samples with TOC values. B. HI vs Tmax cross-plots for cuttings samples with TOC values. These figures show that most of the OM in the Montney and Doig Fm is Type II and Type III. Here, the increase of the TOC with the maturity is biased by the data sampling: in the basin the most mature areas contain the richest samples. HI – Hydrogen index.

996 Figure 4: FID curves from the Basic Rock–Eval pyrolysis of an early mature cutting sample before and

Figure 5: Palynofacies view of the Montney and Doig Fm. showing that most of the primary OM of
 the studied interval is amorphous. On these pictures only few terrestrial particles (spores, pollen
 grains or woody debris) are present and no damaged terrestrial particles can be observed. PM –
 Palynomaceral = Terrestrial organic matter; SP – Spore/Pollen; AOM – Amorphous organic matter; Py
 – Pyrite.

Figure 6: Well section across the Montney and Doig Fm with TOC measurements and estimations of
 the TOC<sub>ini</sub> for two initial Hydrogen index (IH<sub>ini</sub> = 350 and IH<sub>ini</sub> = 600) in a stratigraphic framework. This
 figure shows that the organic content of sequence 3 and 4 is higher than in sequence 1 and 2.

**Figure 7:** Distribution of the TOC and computed TOC<sub>ini</sub> in the studied interval and in the four sequences. Solid bars represent actual TOC and hatched bars represent TOC<sub>in</sub>. It shows that the mean TOC in the studied interval is 1.28 wt% and present heterogeneities: the TOC content of sequence 3 and TST4 is higher than the content of sequence 1 and 2.

Figure 8: Sedimentary section of sequences 3 and 4 from the core description of the 0/16-17-8325W6. This figure shows that low energy facies were dominant in the LST3 whereas during the TST4
high energy facies are dominant.

**Figure 9:** Cross-plots of the TOC<sub>ini</sub> and the SR. Here, SR are based on undecompacted sediments. White symbols show intervals where SR may be underestimated due to an erosional top. These cross-plots, present two types of relation between TOC<sub>ini</sub> and SR. In sequence 1, 2 and HST4 a linear relation exists between TOC<sub>ini</sub> and SR that reflect organic dilution by non-organic sediments. In sequence 3 and TST4, this relation is not evident which suggests others controls on organic accumulation and preservation.

Figure 10: Cross-plots of the enrichment factors (EF) of Ni and Cu. The EF are computed based on the
 UCC (McLennan, 2001). Red lines in the cross-plots represent the Upper Continental Crust. This figure

shows that paleoproductivity increased significantly in the TST4 whereas it remains stable in the restof the studied interval.

Figure 11: Vertical evolution of paleoproductivity proxies (Cu/Al and Ni/Al) in relation to TOC and TOC<sub>ini</sub>. This figure shows that paleoproductivity increased significantly in the TST4 and that along Brown Hill, small increases of Ni/Al often occur is sequence 2, but no increases in TOC can be related to these peaks.

1028 **Figure 12:** Cross-plots of paleoredox proxies (U/Th and V/Cr). Limit values between 1029 oxic/dysoxic/anoxic domains are from Jones and Manning (1994). This figure shows the occurrence 1030 of anoxic layers in sequence 3 and 4.

Figure 13: Vertical evolution of paleoredox proxies (U/Th and Mo/Al) in relation to TOC and TOC<sub>ini</sub> in
the stratigraphic framework. This figure shows a major change above the SB3 and above the
TS4/SB4. During sequence 3, the basin seems to be anoxic in its deepest parts whereas in the TST4,
the basin presents anoxia to euxinia along its margin.

**Figure 14**: Cross-plot of the molybdenum versus the TOC in the stratigraphic framework. This figure shows that in the Lower and Middle Triassic strata of the western Canada sedimentary basin, the Mo/TOC ratio is low (< 30.10<sup>-4</sup>) which suggests a basin restriction. SA: Saanich inlet; CB: Cariaco basin; FF: Framvaren fjord; BS: Black sea. Grey arrows highlight the potential effect of maturity on TOC values.

Figure 15: Cross-plot of the weathering index of Parker (WIP) and the chemical index of alteration (CIA) in the stratigraphic framework. This cross-plot suggests that no major change of sediment maturity occurred during the Lower and Middle Triassic strata of the western Canada sedimentary basin.

Figure 16: TOC distribution and its controlling factors. This figure shows that high TOC values may
 result from different combinations of controlling factors

1046	Figure 17: Conceptual models of basin types proposed for the controls of organic matter
1047	accumulations in the Lower and Middle Triassic of Western Canada. A. Type1: Oxic basin, with low
1048	OM accumulation. B. Type 2: Restricted basin, with the occurrence of organic rich layer in the central
1049	part of the basin due to stratified water. C. Type 3: High primary productivity basin, with the
1050	occurrence of organic rich intervals along the proximal parts of the basin due to high productivity.

<text><text><text>



Chillip Mark



CHR MAR









CHR HIM













	(mgHC/gTOC)		(°C)	(%)
	S1	S2	Tmax	тос
BR	0.46	1.96	443	1.05
eBR	0.07	1.40	439	0.92







Ser



