Organic matter geochemistry and petrography of Late Cretaceous (Cenomanian-Turonian) organic-rich shales from the Belle Fourche and Second White Specks Formations, west-central Alberta, Canada

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Abbreviations are explained in the text, Table and Figure captions ¹

¹ SWS - Second White Specks Formation, BF - Belle Fourche Formation, WIS – Western Interior Seaway, UWI - Unique Well Identifier, T - township, W - range, R_o - vitrinite reflectance, AOM - amorphous organic matter, SB – solid bitumen.

ABSTRACT

Organic-rich mudstones with up to 10 wt% TOC from the upper portion of the Belle Fourche Formation and the lower part of the Second White Specks Formation in the Western Canada Sedimentary Basin were evaluated as source rocks. Both geochemistry and organic petrography indicate an open marine paleoenvironment with deposition of Type II kerogen based on the predominance of marine alginite and amorphous organic matter (OM), limited amounts of terrigenous vitrinite and inertinite macerals, the presence of marine fossils, and the low ratio of TOC to total sulfur (~1.26). The prevalence of short-chain *n*-alkanes (*n*-C₁₃ to *n*-C₁₉), a predominance of C₂₈- $\alpha\beta\beta$ (H)-20S steranes, and small concentrations of oleanane confirm the dominantly algal and planktonic origin of OM. Alternating oxic to anoxic paleoenvironmental sedimentary conditions are proposed based on common bioturbation, abundant inoceramid prisms, and good organic richness. Biomarker distributions are consistent with intermittent anoxia, without unequivocal evidence for water column stratification or hypersalinity. The thermal maturity measured in seven sediment cores by different methods consistently indicates a westward increase in maturity according to vitrinite reflectance, T_{max}, and hopane and sterane biomarkers. Two cores are thermally immature (~0.42 %Ro), one is early mature (~0.65 %Ro), and four cores are within the oil window (~0.78 to 0.89 %Ro). All thermally mature cores retain good to very good hydrocarbon potential (248 mg HC/g rock) and are dominantly oil-prone and minor gas-prone based on their maceral compositions. The upper Belle Fourche and lower Second White Specks Formations represent potential targets for unconventional light shale oil production.

Keywords: Second White Specks Formation, Belle Fourche Formation, Western Canada Sedimentary Basin, unconventional reservoir, organic petrography, thermal maturity, source rock, biomarker.

1. Introduction

Interest in Cenomanian-Turonian (Late Cretaceous) sediments of Canada relates to the most significant transgression event of the Mesozoic Era that resulted in an expansion and widening of the Western Interior Seaway, dissection of North America, and the deposition of thick and often organic-rich sediments along the western margin (Kauffman, 1977; Hancock and Kauffman, 1979; Kauffman, 1984; Prokoph et al., 2013 and publications therein). Concurrently, increased submarine volcanism and hydrothermal activity resulted in: (i) atmospheric CO₂ emissions contributing to a warming climate (Vermeij, 1995), and (ii) the release of large quantities of nutrients into the ocean that triggered intensified marine primary productivity within the photic zone (Larson and Erba, 1999). The resulting enhanced organic carbon burial is indicated by a positive $\delta^{13}\text{C}$ excursion in carbonates and organic carbon (Schlanger et al., 1987; Arthur et al., 1988; Leckie et al., 2002). Additionally, during Oceanic Anoxic Event 2 (Arthur and Schlanger, 1979; Jenkyns, 1980; Prokoph et al., 2001; Erba, 2004; Gale et al., 2008; Dale et al., 2012), formation of a stratified water column (Erbacher et al., 2001) and expansion of the oxygen minimum zone (Schlanger and Jenkyns, 1976) with alternating oxic/dysoxic to anoxic bottom-water conditions (Simons and Kenig, 2001) resulted in formation of favorable conditions for organic matter (OM) preservation (Arthur et al., 1987).

The Belle Fourche Formation is a largely laminated silty (non- to slightly calcareous) mudstone with moderate bioturbation and presence of *Inoceramus* prisms and agglutinated foraminifera. The Second White Specks Formation is primarily laminated calcareous mudstone with abundant fecal pellets composed of calcareous coccolithic debris representing the white specks (Goodman, 1951), foraminifera (dominantly planktonic), fish scales and bones, abundant *Inoceramus* prisms, and no or sparse bioturbation (Bloch et al., 1993; Schröder-Adams et al., 1996; Tyagi et al., 2007). Organic-rich deposits from the early Turonian Second White Specks

Fm. are known to have an attractive hydrocarbon potential, but as low permeability rocks they were precluded from hydrocarbon production until technological advances in horizontal drilling and multi-stage hydraulic fracking led to heightened realization of their viability as potential shale to hybrid light oil plays within the Western Canada Sedimentary Basin (Kwan and Mooney, 2010; Clarkson and Pedersen, 2011). Strata of the Second White Specks Fm. have generated and expelled significant amounts of crude oil and gas in the geologic past and supplied hydrocarbons to the enveloping Late Cretaceous sandstone reservoirs of the Viking, Cardium, and Belly River Formations (Creaney and Allan, 1990). In contrast, strata from the late Cenomanian Belle Fourche Fm. have not been clearly identified as potential source rocks in the literature, although Creaney and Allan (1990) implied the presence of oil-prone marine intervals between the Second White Specks and Fish Scales Formations in the southern part of the Western Canada Basin. As a result, we suggest that in west-central Alberta the organic-rich Belle Fourche Fm. might serve as an effective source rock because it is sandwiched between the Second White Specks and Fish Scales Formations.

This paper discusses the types and origins of OM, depositional paleoenvironments, maturity levels, hydrocarbon potential, and oil/gas proneness of sediments from drill cores in seven wells from west-central Alberta deposited during late Cenomanian to early Turonian within the Western Interior Seaway (WIS). Data obtained from a combination of laboratory techniques, including biomarkers, bulk geochemistry, and organic petrography, contribute to a better understanding of the distribution of hydrocarbons generated and stored within these emerging shale plays. In contrast to previous studies of the geochemistry, sedimentology, stratigraphy, and organic petrography of sediments from the WIS (Stasiuk and Goodarzi, 1988; Kovac and Last, 1991; Bloch and Leckie, 1993; Bloch et al., 1993, 2002; Möslé et al., 1993;

Bloch, 1995; Schröder-Adams et al., 1996, 2001; Leckie et al., 2000; Tu et al., 2007; Tyagi et al., 2007 Prokoph et al., 2013) this study provides a comprehensive regional characterization of OM from the Belle Fourche and Second White Specks Formations (part of the Colorado Group deposits) and contributes interpretations based on biomarkers that are previously underrepresented in the Alberta geological literature (Creaney and Allan, 1990; Möslé et al., 1993; Simons et al., 2003; Furmann et al., 2014).

Conventional petroleum accumulations remain a major energy source, but unconventional oil and gas resources play an increasingly important role as unconventional reservoirs have become more intensively explored worldwide. Advances in exploration and production technologies in the United States and Canada are contributing significantly to the global increase in unconventional energy reserves. In a report prepared for the Energy Information Administration (EIA, 2013) the Colorado Group shales in southwestern Alberta are not considered as viable shale oil resources. However, data provided by this study show that organic-rich sediments from west-central Alberta do represent a potential target for shale oil exploration.

2. Materials and methods

2.1. Sample material

A total of 131 rock samples from west-central Alberta, Canada (Fig. 1) were collected from seven drill cores stored at the Alberta Energy Regulator (AER), Core Research Centre in Calgary, Canada. The basic characteristics of the cores, including geographic coordinates, times of drilling and sample collection, recovered core intervals, thickness of formations, and number of samples collected are listed in Table 1. Our selection of 33 samples from core in well No. 7

(100/60-36-63-04W6; Fig. 1) was guided by results from 33 samples described in a previous unpublished report (TR09-10501041 from December 2009) prepared by TerraTek, Schlumberger (Utah, USA) for EOG Resources Canada Inc. (Alberta, Canada). The earlier report had provided data on geochemistry, petrophysical reservoir properties, petrology, gamma ray log analysis, and vitrinite/solid bitumen reflectance, but OM petrographic characterization was limited to six samples. Here we expand and complement the organic petrographic data set based on 33 samples that were collected from the same core directly below the previous sample intervals. The depth differences of a few centimeters between earlier and our new adjacent sampling are insignificant and should not jeopardize the compatibility of our new data with those in the original EOG report.

The selection of the seven well locations was guided by a need for regional characterization of sediments from the Belle Fourche and Second White Specks Formations within west-central Alberta (Fig. 1). The chosen cores from a north to south transect within the foredeep (Fig. 2A), a west to east transect from the foredeep to the eastern platform (Fig. 2B), and their different burial depths represent a range of thermal maturity. The stratigraphy of the chosen cores was adapted from Tu et al. (2007), Tyagi et al. (2007), and Schröder-Adams et al. (2012). Since there is a slight discrepancy in the literature over the age of the base of the Second White Specks Fm., we have here, for simplicity, placed the base of the Second White Specks Fm. in our study area at the Cenomanian-Turonian boundary.

The sediments are typically gray to black pyritic mudstones and shales with abundant sandy/silty and/or calcareous laminations, calcareous bivalves, and pyrite nodules. A detailed description of mudstone facies, petrography, and geochemical data based on 19 samples from core in well No. 3 (Fig. 1) is available in Furmann et al. (2014). Here we provide complementary

new information related to characterization of OM in seven sediment cores from wells, including well No. 3. All 131 samples were initially analyzed for total organic carbon (TOC) content to aid in the selection of 72 samples for more detailed analyses with the goal of describing the organic petrography and geochemical properties of the Belle Fourche and Second White Specks Formations. These analyses were performed on gray to black mudstone and shale. We avoided any macroscopically visible concentrations of carbonates, pyrite, sandy/silty ripples, and macrofossils. Invert (oil-based) drilling mud was used to recover the cores from wells No. 4 and 7 (102/12-31-39-09W5 and 100/60-36-63-04W6, respectively; Fig. 1), so Rock-Eval S1 data (and possibly S2 values) may be affected according to the type of drilling mud used (Peters, 1986). Nonetheless, as it is difficult to assess the extent of this influence on the Rock-Eval parameters at this point, hence they should be used with caution.

2.2. Organic petrography

Macerals (i.e., particulate OM constituents in rocks) were analyzed in polished blocks under reflected white and fluorescent light with an optical microscope using oil immersion. A Zeiss Photoscope was used to measure vitrinite reflectance %Ro values as indicators for thermal maturity and to characterize the composition of macerals according to American Society for Testing and Materials (ASTM) standard test method D7708 (ASTM, 2014). Relative abundances of primary maceral groups (i.e. liptinite, vitrinite, and inertinite) and solid bitumen (secondary maceral) were assessed visually for all samples. Leitz Orthoplan and Leica DM2500P microscopes were used to take photomicrographs under both white and fluorescent light. The recycled nature of many vitrinite particles in some samples made it difficult to find sufficient

indigenous particles and therefore limited the number of reliable vitrinite reflectance measurements.

2.3. Organic geochemistry

TOC and total sulfur (TS) concentrations were quantified on powdered samples with an Eltra CS-2000 elemental analyzer at Indiana University. A Rock-Eval 2 analyzer was used to characterize the geochemistry and hydrocarbon potential (i.e. $T_{\max}$, HI, OI, etc.) at Weatherford Laboratories, Texas. The same instrumentation was used for samples from all cores, except for core samples in well No. 7, where a LECO RC632 carbon analyzer was utilized for TOC values and Rock-Eval 6 for geochemical data at TerraTek, Schlumberger, Utah. The original hydrogen index (HI_o) and the original TOC (TOC_o) concentrations, as well as the transformation ratio (i.e. the degree of kerogen conversion to hydrocarbons) were calculated for 64 samples from thermally mature cores from wells No. 3 to 7 according to Jarvie et al. (2007). The calculated original values of HI_o and TOC_o for mature rocks are expected to be comparable with those measured on immature to low-thermal-maturity equivalent rocks. Cores from wells No. 1 and 2 were excluded from calculations because the algorithm does not apply to immature rocks.

Gas chromatography-mass spectrometry (GC-MS) was used to determine the abundance of selected families of molecular biomarkers (i.e. *n*-alkanes and acyclic isoprenoids, terpanes and steranes) in saturate fractions of whole rock extracts for 15 selected samples analyzed by Weatherford Laboratories, Texas. Volumetric aliquots of 0.1 μ L of medium pressure liquid chromatographic (MPLC) saturate fractions were injected in cool, on-column mode with a Hewlett Packard 6890 series injector. A Hewlett Packard 6890 Series Plus GC system was coupled to a Hewlett Packard 5973 Series Mass Selective Detector operated in Selective Ion

Monitoring (SIM) mode. A 5 m guard column and a Phenomenex Zebron GC column (60 m length; 0.25 mm i.d.; 0.25 μ m film thickness) were operated with a GC program starting at 100 °C with no initial hold time, ramping from 100 °C to 140 °C at 20 °C/min, keeping an isothermal temperature of 140 °C for 6 min, ramping from 140 °C to 320 °C at 2 °C/min, and finally holding isothermally for 20 min at 320 °C. The total analysis time was 118.5 min. The flow rate of zero grade helium as carrier gas varied for each ramp of the GC program to optimize the separation of peaks. Compound-specific components were quantified relative to an internal standard of 100 ppm 5 β -cholane that was added to each fraction after the MPLC separation of the total organic extract. Data were acquired and processed using ChemStation software. Mass spectrometry of diagnostic ions (Brassell et al., 1980) assisted in the identification of homologous series of *n*-alkanes (m/z 99; Robinson et al., 1991), acyclic isoprenoids (m/z 183; Petrov et al., 1990), terpanes (m/z 191; Seifert and Moldowan, 1978; Hoffmann et al., 1984), and steranes and diasteranes (m/z 217 and 218; Seifert and Moldowan, 1978; Mackenzie et al., 1985; Grantham and Wakefield, 1988). Concentrations of identified compounds and their ratios were calculated from integrated peak areas on mass chromatograms.

3. Results

3.1. Maceral composition and vitrinite reflectance

The average maceral composition (vol%) and vitrinite reflectance (%Ro) values for selected samples in each core for the Belle Fourche and Second White Specks Formations are shown in Fig. 3 with the number of samples indicated in Table 2. About 67-94 vol% of total OM in samples from the seven cores from both formations is represented by the liptinite maceral group, which includes (i) alginite (A in Fig. 4E, F), (ii) amorphous organic matter (AOM, Fig.

4D), and (iii) ‘other liptinite’ (liptodetrinite, i.e., small fragments indicating fluorescence; not indicated on a figure). Sporinite (Sp, Fig. 4D) was included into the ‘other liptinite’ category on Fig. 3. Vitrinite (V, Fig. 4G) and inertinite (I, Fig. 4H) jointly represent a minor component and account for about 1-3 vol% of total OM in most samples with a maximum of 9 vol% in sample #20 in core No. 3 (Furmann et al., 2014). Vitrinite is often reworked (RwV, Fig. 4G) and oxidized (OxV, Fig. 4E, F), and granular forms of vitrinite are present (gV, Fig. 4A). Solid bitumen (SB) is present in four forms (listed in order of decreasing abundance) as (1) bitumen fillings in small, 1-2 μm size pores within elongated, most likely clay-rich zones (EZ, Fig. 4C, G); (2) granular bitumen that is sometimes found along the contacts with carbonate grains (gSB, Fig. 4B, H); (3) elongated micronized bitumen (mSB, Fig. 4H); and (4) bitumen filling foraminifera tests (not shown on figure; calcareous ‘foram’ is visible in Fig. 4C). Solid bitumen is typically present in amounts from 5 to 15 vol%, with the exception of sample #11 from core No. 5 with 55 vol% bitumen, sample #24 from core No. 4 with 60 vol% bitumen, and sample #5 from core No. 3 containing 90 vol% bitumen. Maceral composition and contents of maceral groups are similar for the Belle Fourche and Second White Specks Formations in all cores (Fig. 3). The presence of solid bitumen in low maturity samples from cores No. 1 and 2 is related to the low-temperature solid bitumen formation during early diagenesis from fossilized algal material (Jacob, 1989; Landis and Castaño, 1995), which is ubiquitous in studied samples.

The average vitrinite reflectance %Ro for samples from each well increases from 0.42 to 0.89 across west-central Alberta (Fig. 3 and Table 2). Complete data sets for the analyzed samples are provided in Table S3 as part of the supplementary materials.

3.2. TOC, Rock-Eval, and transformation ratio

The contents of TOC and TS, data from Rock-Eval pyrolysis, calculated values of the transformation ratio, TOC_o , and HI_o are provided in Table 2 and Fig. 5 based on averaged values in samples from each core. The numbers of samples (n) used in each type of analysis, i.e. (i) vitrinite reflectance %Ro and oil/gas proneness, (ii) present-day TOC and TS data (TOC_{pd} and TS_{pd} , respectively), (iii) Rock-Eval data, and (iv) calculated values are provided in parentheses in Table 2. Complete data sets for analyzed samples are provided in Tables S1-S5 as part of the supplementary materials.

The TOC_{pd} values generally decrease with increasing maturity (Fig. 5A); however, the concentrations of TOC_o and TOC_{pd} (4.15 and 3.14 wt% on average, respectively) are largest in samples from core No. 7 located in west-central Alberta (Fig. 1) within the early oil window as indicated by ~0.65 %Ro and 434 °C T_{max} (Table 2). The concentrations of TS_{pd} for samples in seven cores express limited variance across west-central Alberta and oscillate around an average value of 2.57 wt%. The resulting $\text{TOC}_{pd}/\text{TS}_{pd}$ ratio represents a narrow range from 0.58 (minimum value in core No. 4) to 2.39 (maximum value in core No. 5; Table 2). The average T_{max} values increase with maturity from 421 °C in cores No. 1 and 2 to 447 °C in cores No. 4 and 5 (Table 2). Values of the S1 parameter generally increase with maturity, while S3 fluctuates among cores (Table 2). With increasing maturity, S2 values first increase from cores No. 1 and 2, reach a maximum of 48.2 mg HC/g rock in core No. 7, and later decrease in cores 6, 3, 5 and 4. The present-day oxygen index (OI_{pd}) generally oscillates around 30 mg CO_2 /g TOC among cores with the exception of much lower average value for core No. 7 (4 mg CO_2 /g TOC, Table 2). The present-day hydrogen index (HI_{pd}) generally decreases with increasing maturity and expresses its greatest decline from the original to present-day HI values in the higher-maturity core samples from wells No. 3, 4, and 5 (Fig. 5B). The decreasing trends in TOC_{pd} , HI_{pd} , and S2 values with

increasing thermal maturity correspond well to the increase in transformation ratio (Fig. 5B). The contents of organic carbon (TOC_{pd}) and hydrogen (HI_{pd}) in source rocks are lowered due to enhanced thermal cracking of organic matter and expulsion of generated hydrocarbons (S2). Variations in discussed values between the Belle Fourche and Second White Specks Formations are provided in Table S5 as part of the supplementary materials.

3.3. Molecular analysis

Gas chromatograms of the saturated hydrocarbon fractions show the acyclic isoprenoid hydrocarbons, pristane (Pr; C₁₉) and phytane (Ph; C₂₀) to be present in extracts of all samples selected for biomarker assay (m/z 99; Fig. 6). The Pr/Ph ratios for all samples fall in a relatively narrow range from 0.8 to 1.9, as well as for isoprenoid/*n*-alkane ratios, i.e. Pr/*n*-C₁₇ and Ph/*n*-C₁₈ in the ranges of 0.5-1.8 and 0.3-1.8, respectively (Table 3A). The extracts generally contain a wide range of *n*-C₁₂ to *n*-C₃₉ alkanes (Fig. 6) with few samples reaching only to *n*-C₃₂ or extending to *n*-C₄₁. The *n*-alkane patterns are dominated by short (*n*-C₁₃ to *n*-C₁₉) to middle-chain (*n*-C₂₀ to *n*-C₂₇) *n*-alkanes. The carbon preference indices (CPI within a *n*-C₂₃ to *n*-C₃₃ range) are equal to 1.0 in all but one sample, i.e., #5 from core No. 2 with a CPI = 1.1 (Table 3A). The distribution of *n*-alkanes in extracts of samples from cores No. 1 and 2 is bimodal (e.g., in Fig. 6A) with a maximum at *n*-C₁₄ to *n*-C₁₇ alkanes and a second maximum at *n*-C₂₁ to *n*-C₂₂. In contrast, a unimodal distribution of *n*-alkanes is observed in extracts of samples from the five other cores in wells No. 3 to 7 (e.g., in Fig. 6B, C).

The compounds detected in the m/z 191 chromatograms in extracts of all samples are tricyclic terpanes (TR; C₁₉ – C₃₀) and pentacyclic hopanes (H; Fig. 7). Extracts of samples from seven cores contain hopanes in a range from C₂₇ to C₃₅. Also, extracts of samples from cores No.

1 and 2 are dominated by H29 (C_{29} 17 α ,21 β (H)-norhopane) and H30 (C_{30} 17 α ,21 β (H)-hopane) compounds (Fig. 7A), whereas sample extracts from cores No. 6 and 7 show a dominance of H30 only (Fig. 7B). Extracts of samples from cores No. 3, 4, 5 show a dominance of TS (Ts 18 α (H)-trisnorneohopane), H29, C29Ts (C_{29} Ts 18 α (H)-norneohopane), DH30 (C_{30} 17 α (H)-diahopane), and H30 compounds (Fig. 7C). Among hopanes C_{31} - C_{35} the clear predominance of C_{31} hopanes is observed for all samples (Fig. 8) with slightly elevated concentrations of C_{35} hopanes only for immature samples from wells No. 1 and 2 (Fig. 8B). Ratios calculated for this biomarker group, such as gammacerane (GAM) to H30, oleanane (OL) to H30, and H32 22S/(22S+22R), generally increase with maturity, whereas the opposite trend is observed for the Tm/Ts ratio (Table 3B). No clear trend is observed for the moretane to hopane ratio (M30/H30) with values generally ranging from 0.11 to 0.25 with a few samples showing lack of moretane.

Extracts of samples represent similar ranges of regular steranes (C_{27} - C_{30}) and diasteranes (C_{27} - C_{29}) in mass chromatograms (m/z 217; Fig. 9). The sterane distribution is predominated by C_{28} steranes in all extracts, although samples from the Belle Fourche Fm. in core No. 4 also have significant contributions from C_{27} steranes (Table 3C). The calculated ratios related to this group of biomarkers generally increase with maturity (Table 3C). Sample extracts from cores No. 1 and 2 are dominated by the $\alpha\alpha\alpha$ (H)-20R steranes, whereas samples from cores No. 3, 4, 5, 6 are dominated by $\alpha\beta\beta$ (H)-20S steranes. The concentrations of steranes and diasteranes decrease with increasing maturity relative to the peak height of the added internal standard 5 β -cholane (Fig. 9). The absolute concentrations (in ppm), based on this internal standard, are listed for gammacerane and for the sum of compounds identified in each biomarker group (i.e., total *n*-alkanes, hopanes, and steranes) in Table 3.

4. Discussion

4.1. Depositional paleoenvironment and origin of organic matter

4.1.1. Petrographic observations and the TOC/TS ratio

The maceral compositions of samples from the Belle Fourche and Second White Specks Formations (Fig. 2) are dominated by macerals from the liptinite group (i.e. hydrogen-rich alginites, AOM and liptodetrinites) with limited input of terrestrial hydrogen-poor vitrinite and inertinite (Fig. 3). The predominantly marine origin of macerals classifies the insoluble part of OM as marine kerogen Type II. A marine paleoenvironment for samples from both formations is also indicated by foraminifera with tests either filled with carbonates or solid bitumen. Caldwell et al.'s (1978) evidence for the presence of pelagic foraminifera of the *Hedbergella loetterlei* Zone in the early Turonian deposits in Alberta confirms an open marine depositional paleoenvironment for the Second White Specks Fm. Bloch et al. (1993) and Schröder-Adams et al. (1996) mentioned the presence of agglutinated foraminifera within the Belle Fourche Fm. transitioning to the lower Second White Specks Fm.

The Albian benthic foraminiferal assemblage had experienced an extinction at the Albian-Cenomanian boundary associated with fluctuating paleoecological conditions within the Canadian WIS, followed by a poor recovery during the Cenomanian and later mid-Santonian turnover (Schröder-Adams et al., 2012), with the result that benthic foraminifera were sparse during the late Cenomanian and early Turonian (Prokoph et al., 2013). Hence, the presence of foraminifera and fish fossils (scales, bones) and the preponderance of marine macerals in samples from both formations support the interpretation of an open marine paleoenvironment in west-central Alberta. Furthermore, this interpretation is consistent with the presence of Type II

kerogen in the upper portion of the Belle Fourche Fm. in facies that transition into the overlying Second White Specks Fm. in central and southern Alberta (Bloch et al., 1993; Simons et al., 2003), even though kerogen in the Belle Fourche Fm. is generally classified as dominantly Type III (Bloch et al., 1993; Schröder-Adams et al., 1996).

The elemental ratio of $\text{TOC}_{\text{pd}}/\text{TS}_{\text{pd}}$ has been used as a broad proxy for distinguishing marine from freshwater sedimentary rocks (Berner and Raiswell, 1984). The average $\text{TOC}_{\text{pd}}/\text{TS}_{\text{pd}}$ ratios for samples in each core from a given well cover a narrow range from 0.92 to 1.65 (Table 2) and confirm an open marine depositional paleoenvironment for the Belle Fourche and Second White Specks Formations (Fig. 10).

4.1.2. Rock-Eval pyrolysis

The relatively low values of HI_{pd} and the wide range of the OI_{pd} values (2 to 48 mg CO_2/g TOC) influences the positioning of kerogens in the modified van Krevelen diagrams relative to typical ranges of kerogen Type II and Type III (Fig. 11). The kerogen typing based on these present-day (measured) geochemical data is inconsistent with our petrographic and $\text{TOC}_{\text{pd}}/\text{TS}_{\text{pd}}$ observations. The observed decrease in HI_{pd} values with increasing maturity mainly results from organic hydrogen depletion in residual OM along with kerogen cracking and expulsion of hydrocarbons, which also increases the transformation ratio (Fig. 5B). The low hydrogen content in higher maturity rocks from cores No. 3, 4, 5, and 6 therefore does not result from a presence of hydrogen-depleted terrestrial OM (e.g., vitrinite group macerals), but instead follows from the loss of hydrogen from originally hydrogen-rich liptinite macerals (e.g., alginites) with increasing thermal maturity. Earlier reported OI_{pd} values of 4-9 mg CO_2/g TOC for 16 samples from core No. 3 (Beaton et al., 2009) are much lower than our values of 19-48 mg CO_2/g TOC measured

on 19 samples from the same core (Table 1; Furmann et al., 2014 and this study). Beaton et al.'s (2009) earlier data plotted along the maturation path of kerogen Type II (i.e. cross-hatched area in Fig. 11A) instead of plotting close to kerogen Type III like our data. We speculate that oxidative diagenesis of OM during years of core storage may have contributed to our higher OI_{pd} values (Table 2) relative to the earlier data of Beaton et al. (2009). Furthermore, early microbial degradation of OM within the water column or OM oxidation associated with temporarily oxygenated bottom water conditions (Kenig et al., 2004 and publications therein) can deplete the hydrogen content of the original kerogen and increase its oxygen content. Simons et al. (2003) associated oxidative degradation of OM with a similar spread of OI_{pd} data (0-50 mg CO_2 /g TOC) for the late Cenomanian and early Turonian sediments from southern Alberta (Mill Creek and Highwood River area) and easternmost central Saskatchewan. An even wider range of OI_{pd} data (up to 200 mg CO_2 /g TOC) was documented by Simons and Kenig (2001) in time-equivalent sediments with dominantly marine OM from the U.S. portion of the Western Interior Basin, but their explanation implies variations in redox conditions between oxic and anoxic within the uppermost sediment during early diagenesis. In effect, it is not possible to distinguish between microbial oxic degradation of OM occurring in the water column *versus* the topmost sediment. Regardless of the variations in OI_{pd} values, if we plot the calculated HI_o data for samples from wells No. 3-6 (i.e., between 400 and 500 mg HC/g TOC; Fig. 5B) on the modified van Krevelen diagram instead we would observe a much closer proximity to the Type II kerogen path. We also agree with Katz's (1983) advice that type characterization of OM based solely on Rock-Eval has limited reliability as both hydrogen and oxygen indices are strongly affected by matrix mineralogy and organic richness. A critical synopsis of petrography and Rock-Eval data is better suited to avoid misinterpretation. Therefore, we place higher diagnostic value on organic

petrography and characterize the original OM in the Belle Fourche and Second White Specks samples from all cores as marine kerogen Type II with a limited input of terrestrial material.

4.1.3. Biomarkers

The predominance of *n*-alkanes in the range *n*-C₁₃ to *n*-C₁₉ reflects a dominantly marine algal and cyanobacterial source of extractable OM for all samples (Gelpi et al., 1970; Brassell et al., 1978; Tissot and Welte, 1984). The carbon-number preference index (CPI) is generally close to unity with the exception of sample #5 from core No. 2, which possesses a slight odd-over-even preference (CPI=1.1; Table 3A) attributable to a minor terrestrial contribution to its OM. The slight odd-over-even preference in samples #5 and #12 from core No. 1 only applies to a narrow range of *n*-alkanes from *n*-C₂₈ to *n*-C₃₃ (Fig. 6A) in agreement with organic petrographic findings of minor amounts of vitrinite. Pristane (Pr) to phytane (Ph) ratios in this study are predominantly greater than unity (0.8-1.9 range; Table 3A) and are therefore typical of the range generally considered to describe a normal marine environment (Didyk et al., 1978). Although such relatively high Pr/Ph ratios may perhaps represent a genetic characteristic of extractable OM in Late Cretaceous marine deposits of the Western Interior Seaway, as suggested by Pratt's (1984) study of the time-equivalent deposits from Pueblo in Colorado, USA. Minor concentrations of oleanane, reflected by low OL/H30 ratios (Table 3B), is concordant with petrographic observations of minor amounts of terrigenous material that dilute the marine-derived component. The sterane inventory (C₂₇-C₂₉; Table 3C) is typical for planktonic and algal sources of OM (Fig. 12) and is in agreement with the prominence of marine-derived C₃₀ steranes (Fig. 9) in all extracts denoting marine OM sources (Moldowan, 1984; Moldowan et al., 1985; Peters et al., 1986). The greater proportion of C₂₈ steranes over C₂₉ steranes previously reported

for the Second White Specks Fm. in Alberta (Creaney and Allan, 1990) and Saskatchewan (Mösle et al., 1993) is confirmed in this study for both the Second White Specks and Belle Fourche Formations (Table 3C) and underscore the limited presence of terrestrial C₂₉ steranes and related terrestrial OM in our samples. A similar preponderance of C₂₈ steranes occurs in other Cenomanian-Turonian sequences from epicontinental seas (Farrimond et al., 1990). The predominance of steranes over hopanes in samples from the Second White Specks Fm. in Saskatchewan (Mösle et al., 1993) can therefore be deemed a general characteristic of the Second White Specks and Belle Fourche Formations (Table 3C). Overall, biomarkers confirm petrographic observations of a predominantly marine algal and planktonic character of OM with minor contributions from terrestrial sources.

Water column stratification with intermittent anoxic (euxinic) conditions during sediment deposition within the Late Cretaceous Western Interior Seaway were previously demonstrated by studies of the time-equivalent deposits from the Pasquia Hills in eastern Saskatchewan (Schröder-Adams et al., 2001), southern Alberta and eastern Saskatchewan (Simons et al., 2003) and from the Colorado, Kansas, and New Mexico in the U.S. (Simons and Kenig, 2001). Such conditions were proposed based on the presence of isorenieratene derivatives, including isorenieratane, in the aromatic fraction of the rock extracts. We would expect to have encountered similar characteristics if analysis of aromatic fractions were within the scope of our study, thereby reiterating previous conclusions. In the absence of such aromatic data, we consider, nonetheless, that the suite of biomarker indicators examined in our study (Table 3) cannot provide unequivocal evidence of water column stratification or density stratification related to hypersalinity (Brassell et al., 1978; ten Haven et al., 1988; de Leeuw and Sinninghe Damsté, 1990; Peters and Moldowan, 1991; Sinninghe Damsté et al., 1995). The Pr/Ph ratios are

generally greater than unity (i.e., not < 1.0) and there is no pronounced dominance of C_{35} hopanes (other than its enhancement in immature samples, as C_{31} hopanes are predominant, Fig. 8). Moreover, CPI values are mainly equal to unity (and not < 1.0), and the concentrations of gammacerane are very low (2-100 ppm and $GAM/H_{30} < 0.28$; Table 3B), while only large GAM contents are indicative. The $Pr/n-C_{17}$ and $Ph/n-C_{18}$ ratios represent intermediate values (thereby differing from values associated with a strictly reducing environment; Shanmugam, 1985). Hence, alternating oxic to anoxic bottom-water conditions are proposed, based on the overall characteristics of the biomarker signals and the sedimentary features observed in cores, including common bioturbation with mainly horizontal to sub-vertical burrows and abundant inoceramid prisms, as well as good preservation of OM (TOC up to 10 wt%; Table 2).

4.2. Maturity

4.2.1. Petrography and Rock-Eval pyrolysis

The observed westward increase in thermal maturity within the Western Canada Sedimentary Basin results from the deeper sediments burial along the Cordillera (Kauffman, 1977) as a consequence of tectonic down flexure of foreland basin (Catuneanu et al., 1997). The earlier proposed boundaries of thermal maturity zones for the Second White Specks Fm. within Alberta (Creaney and Allan, 1990; Kwan and Mooney, 2010) are here adjusted (Fig. 1) in response to our petrographic and geochemical data. The lowest vitrinite reflectance values of $\sim 0.43\% R_o$ derive from thermally immature rocks from the easternmost wells No. 1 and 2 (Fig. 1 and Table 2) commensurate with the shallowest burials. Samples from the five other wells express increasing maturity (Fig. 1) starting from (i) the north-western core No. 7 representing early mature rocks with $\sim 0.65\% R_o$, (ii) mid-mature cores No. 6 ($\sim 0.78\% R_o$), No. 3 ($\sim 0.79\%$

R_o), and No. 4 (~0.85 % R_o), and arriving at (iii) the late mid-mature core No. 5 with ~0.89 % R_o. The range of Rock-Eval-based maturity parameters T_{max} from ~425 to 470 °C is indicative of thermally mature rocks (Peters, 1986 Baskin, 1997). Therefore, samples from cores No. 1 and 2 with ~421 °C T_{max} value are immature, whereas samples from core No. 7 with ~434 °C T_{max} represent early maturity. Samples from the remaining cores No. 3, 4, 5, and 6 are thermally mature as indicated by T_{max} ~441-447 °C (Fig. 11B). These T_{max}-based thermal maturities agree with respective vitrinite reflectance (%R_o) data in our study (Table 2 and Table S5 for comparison of values between formations).

4.2.2. Biomarkers

The bimodal distribution of *n*-alkanes in extracts of samples from immature wells No. 1 and 2 show elevated concentrations of relatively longer-chain *n*-alkanes *n*-C₂₁ and *n*-C₂₂ (Fig. 6A) in comparison to sample extracts from more mature wells with unimodal *n*-alkane distributions (Fig. 6B, C). Bimodal *n*-alkane distributions with maxima at *n*-C₁₇ and *n*-C₂₁ were also found in immature samples from the Pasquia Hills area in Saskatchewan (Simons et al., 2003). Similar to our samples from core No. 7, a unimodal *n*-alkane distribution with maxima at *n*-C₁₃ to *n*-C₁₅ was reported in early mature samples from the Mill Creek area in southern Alberta (Simons et al., 2003). The increasing abundance of total *n*-alkanes with rising maturity (Table 3A) is consistent with increasing S1 Rock-Eval parameters (Table 2) as a result of free hydrocarbon generation and accumulation in more mature rocks (Tissot et al., 1971). On the other hand, concentrations of total steranes and total hopanes decrease drastically from lower-maturity samples from wells No. 1 and 2 to higher-maturity samples from wells No. 4 and 5

(Table 3B, C), even if steranes/hopanes ratios relating to lower- and higher-maturity wells (wells No. 1 and 2 vs. well No. 5) remain similar (~3.6; Table 3C).

Hopane-based thermal maturity indicators $H_{32} 22S/(22S+22R)$ correlate with vitrinite reflectance %Ro values ($R^2 = 0.88$; Fig. 13A). The narrow $H_{32} 22S/(22S+22R)$ range of 0.58 to 0.62 (Table 3B) for samples from cores No. 3, 4, 5, 6, and 7 corresponds to the oil generation window, where the 0.60 value marks the transition from early to peak oil generation (Seifert and Moldowan, 1986; Matchette-Downes, 2009). Values ranging from 0.37 to 0.43 for samples from cores No. 1 and 2 indicate thermally immature rocks.

The generally decreasing trend in T_m/T_s ratios with increasing maturity (Table 3B) is related to the reduced stability of T_m relative to T_s during catagenesis (Seifert and Moldowan, 1978; Moldowan et al., 1986). Intermediate T_m/T_s ratios of 0.66 and 1.04 for samples from core No. 7 (Table 3B) correspond to early mature oil generation and are in approximate agreement with respective %Ro values averaging 0.65 ($R^2 = 0.89$; Fig. 13B). With increasing maturity, the conversion of C_{30} moretane (M_{30}) to C_{30} hopane (H_{30}) is expected to be expressed by a decreasing M_{30}/H_{30} ratio (Seifert and Moldowan, 1986), yet no significant difference was observed among our samples (Table 3B).

A strong linear correlation with $R^2 = 0.94$ was observed between %Ro values and the $C_{29} 20S/(20S+R)$ sterane maturity indicator (Fig. 13A). The narrow $C_{29} 20S/(20S+R)$ range of 0.46 to 0.58 for samples from cores No. 3, 4, 5, 6, and 7 (Table 3C) corresponds to the oil generation window (Mackenzie et al., 1980; Waples and Machihara, 1991; Matchette-Downes, 2009). Lower $C_{29} 20S/(20S+R)$ values around 0.18 for samples from cores No. 1 and 2 indicate thermal immaturity (Table 5). The ratio of diasteranes to regular steranes (i.e. 'Dia/Reg Sterane' in Table 3C) increases with maturity and expresses a moderately strong linear correlation with %Ro

values ($R^2 = 0.83$; Fig. 13B). We observed no consistent pattern in the ratios of short- (C_{21} and C_{22}) to long-chain homologs (C_{27} - C_{29} 20S+R) of steranes in samples with increasing maturity, except for low values of 0.02 to 0.03 in samples from immature cores No. 1 and 2 and much larger values of up to 1.89 in samples from mature wells (Table 3C). The longer-chain homologs are more susceptible to thermal cracking and are preferentially incorporated into hydrocarbons (Mackenzie et al., 1981), while the shorter-chain homologs are retained within the rock (Fig. 9).

4.3. Organic richness, hydrocarbon potential and proneness

Samples from the Belle Fourche and Second White Specks Formations across west-central Alberta express good to very good organic richness with > 2 wt% TOC_{pd} in all cores (Table 2 and Tables S1 and S5 from supplementary materials). The largest TOC_{pd} values were determined in samples from the Second White Specks Fm. in the early mature core No. 7 (Fig. 14), but samples from the Belle Fourche Fm. in thermally-mature cores No. 3, 4, and 5 show even slightly higher TOC_{pd} than the Second White Specks Fm. (Table S5 from supplementary materials). The remaining hydrocarbon potential is expressed by the Rock-Eval S2 peak area that is related to the cracking of kerogen to generate hydrocarbons (Peters, 1986; Dembicki, 2009) and the greatest values (up to 48.2 mg HC/g rock) were found in samples from core No. 7 (Table 2). Overall, samples from the early-mature section in core No. 7 are characterized by greater TOC_{pd} contents (~ 5.03 wt%; Table 2) and express larger hydrocarbon potentials than samples from the mid-maturity zone in core No. 4 with lower TOC_{pd} contents (~ 2.01 wt%; Table 2). The calculated transformation ratios of kerogen to hydrocarbons (i.e. representing the loss of organic carbon and hydrogen from original kerogen with increasing maturity; Table 2) reflect the latter comparison by indicating only 12% transformation in samples from the early mature core No. 7.

This means that the remaining 88% of organic carbon and hydrogen from the original kerogen can potentially still be transformed to hydrocarbons upon maturation. In contrast, up to 79% transformation was found for samples from the most mature cores No. 4 and 5 (Table 2).

The proneness towards oil and gas generation is usually determined based on modified van Krevelen diagrams (Fig. 11), but here we also consider the maceral composition from petrographic observations (Fig. 3). The cumulative evidence suggests that mixed oil and gas generation can be expected in the Belle Fourche and Second White Specks Formations. Additional quantitative indications of oil/gas proneness are provided by maceral compositions, where the fluorescent macerals of the liptinite group (i.e. alginite, liptodetrinite and fluorescent AOM, by vol%) are here considered as the oil-prone fraction, whereas the sum of non-fluorescent AOM and vitrinite (vol%) is the gas-prone fraction. The largest fraction of the generated hydrocarbons is expected to be in the form of oil with smaller amounts being gas (i.e. on average 54-70% oil vs. 12-29% gas for samples from mature cores; Table 2 and Table S3 from supplementary materials with data for each formation).

5. Conclusions

Our characterization of OM type, depositional environment, and thermal maturity of organic-rich mudstones and shales from the upper Belle Fourche and lower Second White Specks Formations deposited during late Cenomanian to early Turonian (early Late Cretaceous) is based on 131 samples from seven wells in west-central Alberta, Canada. Our multi-disciplinary analytical approach employs a combination of organic petrography, geochemistry (TOC and Rock-Eval), and biomarkers to constrain present-day organic richness, remaining hydrocarbon potential, transformation ratio of kerogen to hydrocarbons, and oil/gas proneness in

order to assess the quality and prospect of these geological formations for unconventional hydrocarbon production. We have identified a dominantly marine algal and planktonic origin of extractable OM with minor contributions from terrestrial sources is indicated by: (i) the prevalence of short-chain n -C₁₃ to n -C₁₉ n -alkanes, (ii) the general predominance of C₂₈ steranes with a slightly pronounced contribution from C₂₇ steranes, and (iii) small concentrations of oleanane. The presence of Type II marine kerogen is indicated by petrographic observations of macerals in samples from both formations. Macerals of the marine-derived liptinite group (i.e. alginites, AOM, and liptodetrinites) predominate and comprise up to 94 vol% of all macerals, whereas terrigenous macerals of the vitrinite and inertinite groups average only 1-3 vol%. An open marine depositional paleoenvironment is also indicated by the TOC/TS ratio. The suite of biomarker indicators suggests a normal marine environment and does not provide unequivocal evidence for either water column stratification or hypersalinity. An investigation of isorenieratene derivatives might help to resolve the likelihood of intermittent anoxia during the sediment paleodeposition, but investigation of aromatic fractions from extracts was not included in our study. Alternating oxic to anoxic conditions of bottom and interstitial waters above and immediately below the seafloor can be inferred from bioturbation features with mostly horizontal to sub-vertical burrows and abundant inoceramid prisms as well as good preservation of OM. Vitrinite reflectance %Ro as a proxy for thermal maturity correlates well with: (i) Rock-Eval T_{max} values and (ii) thermal maturity indicators based on biomarkers, such as H₃₂ 22S/(22S+R) hopanes and C₂₉ 20S/(20S+R) steranes. Thermal maturity increases westward starting from %Ro ~0.42 and T_{max} of ~421 °C in immature cores No. 1 and 2, then progressing to the west into central Alberta entering the oil window at %Ro from 0.78 to 0.89 and T_{max} from 441 to 447 °C in cores No. 3, 4, 5, and 6. Towards the north-west from these wells, the early mature core No. 7

reaches %R_o ~0.65% and 434 °C average T_{max}. Core samples from both formations across west-central Alberta express good to very good organic richness (>2 wt% TOC) with present-day TOC reaching up to 10 wt% in core No. 7. Samples from thermally mature cores exhibit good to very good remaining hydrocarbon potentials with Rock-Eval S2 values from 2 to 48 mg HC/g TOC. Reduced present-day hydrogen indices (HI_{pd} < 300 mg HC/g TOC) relative to the original values (HI_o ~ 450 mg HC/g TOC) in samples from higher-maturity cores No. 3 to 6 are interpreted in terms of hydrogen loss during hydrocarbon expulsion rather than representing a significant presence of terrigenous kerogen Type III. Calculated transformation ratios of kerogen to hydrocarbons increase with maturity from 12% in early mature core No. 7 to 79% in the most mature cores No. 4 and 5 as a result of organic carbon and hydrogen loss from the original kerogen in the form of expelled hydrocarbons. Results from Rock-Eval and organic petrography indicate that mixed oil and gas generation can be expected from the upper Belle Fourche and lower Second White Specks Formations with greater amounts of oil than gas production (54-70% oil vs. 12-29% gas).

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References

- Adegoke, A.K., Abdullah, W.H., Hakimi, M.H., Yandoka, B.M.S., 2014. Geochemical characterisation of Fika Formation in the Chad (Bornu) Basin, northeastern Nigeria: Implications for depositional environment and tectonic setting. *Applied Geochemistry* 43, 1-12.
- Arthur, M.A., Schlanger, S.O., 1979. Cretaceous "Oceanic Anoxic Events" as causal factors in development of reef-reservoired giant oil fields. *American Association of Petroleum Geologists Bulletin* 63, 870-885.
- Arthur, M.A., Schlanger, S.O., Jenkyns, H.C., 1987. The Cenomanian-Turonian Oceanic Anoxic Event, II. Palaeoceanographic controls on organic-matter production and preservation. *Geological Society, London, Special Publications* 26, 401-420.
- Arthur, M.A., Dean, W.E., Pratt, L.M., 1988. Geochemical and climatic effects of increased marine organic carbon burial at the Cenomanian/Turonian boundary. *Nature* 335, 714-717.
- American Society for Testing and Materials (ASTM), 2014. D7708e11 Standard Test Method for Microscopical Determination of the Reflectance of Vitrinite Dispersed in Sedimentary Rocks. sec. 5, v. 05.06. In: *Annual Book of ASTM Standards: Petroleum Products, Lubricants, and Fossil Fuels; Gaseous Fuels; Coal and Coke*. ASTM International, West Conshohocken, PA, 10 pp.

596 Baskin, D.K., 1997. Atomic H/C ratio of kerogen as an estimate of thermal maturity and organic
 597 matter conversion. American Association of Petroleum Geologists Bulletin 81, 1437-
 598 1450.

599 Beaton, A.P., Pawlowicz, J.G., Anderson, S.D.A., Rokosh, C.D., 2009. Rock Eval™, total
 600 organic carbon, adsorption isotherms and organic petrography of the Colorado Group:
 601 shale gas data release. Energy Resources Conservation Board/Alberta Geological Survey
 602 Open File Report 2008-11, 88 pp.

603 Berner, R.A., Raiswell, R., 1984. C/S method for distinguishing freshwater from marine
 604 sedimentary rocks. *Geology* 12, 365-368.

605 Bloch, J., 1995. Source-rock potential and reservoir characteristics of the Lower (Albian-
 606 Turonian) Colorado Group, Western Canada Sedimentary Basin. Geological Survey of
 607 Canada Open File 3036, 72 pp.

608 Bloch, J., Leckie, D.A., 1993. Rock-Eval data of the Cretaceous Colorado Group, Western
 609 Canada Sedimentary Basin. Geological Survey of Canada Open File 2676, 21 pp.

610 Bloch, J., Schröder-Adams, C., Leckie, A.D., McIntyre, D.J., Craig, J., Staniland, M., 1993.
 611 Revised stratigraphy of the lower Colorado Group (Albian to Turonian), western Canada.
 612 Bulletin of Canadian Petroleum Geology 41, 325-348.

613 Bloch, J., Schröder-Adams, C.J., Leckie, A.D., 2002. The petrology of Late Cretaceous Colorado
 614 Group shales from the Pasquia Hills, east-central Saskatchewan: preliminary results. In:
 615 Summary of Investigations 2002, Volume 1, Saskatchewan Geological Survey; Misc.
 616 Rep. 2002-4.1, pp. 126-133.

617 Brassell, S.C., Eglinton, G., Maxwell, J.R., Philp, R.P., 1978. Natural background of alkanes in
 618 the aquatic environment. In: Hutzinger, O., van Lelyveld, L.H., Zoeteman, B.C.J. (Eds.),
 619 Aquatic Pollutants: Transformation and Biological Effects, Pergamon, Oxford, pp. 69-86.

620 Brassell, S.C., Goward, A.P., Eglinton, G., 1980. Computerized gas chromatography-mass
 621 spectrometry in analyses of sediments from the Deep Sea Drilling Project. *Physics and*
 622 *Chemistry of the Earth* 12, 421-426.

623 Caldwell, W.G.E., North, B.R., Stelck, C.R., Wall, J.H., 1978. A foraminiferal zonal scheme for
624 the Cretaceous System in the Interior plains of Canada. In: Stelck, C.R., Chatterton,
625 B.D.E. (Eds.), *Western and Arctic Canadian Biostratigraphy*. Geological Association of
626 Canada Special Paper 18, pp. 495-575.

627 Catuneanu, O., Beaumont, C., Waschbusch, P., 1997. Interplay of static loads and subduction
628 dynamics in foreland basins: Reciprocal stratigraphies and the “missing” peripheral
629 bulge. *Geology* 25, 1087-1090.

630 Clarkson, C.R., Pedersen, P.K., 2011. Production analysis of Western Canadian unconventional
631 light oil plays. In: Society of Petroleum Engineers. *Canadian Unconventional Resources*
632 Conference, 15-17 November 2011, Calgary, Alberta, Canada, 22 p.

633 Creaney, S., Allan, J., 1990. Hydrocarbon generation and migration in the Western Canada
634 sedimentary basin. In: Brooks, J. (Ed.), *Classic Petroleum Provinces*. Geological Society
635 Special Publication 50, pp. 189-202.

636 Dale, A.W., Meyers, S.R., Aguilera, D.R., Arndt, S., Wallmann, K., 2012. Controls on organic
637 carbon and molybdenum accumulation in Cretaceous marine sediments from the
638 Cenomanian-Turonian interval including Oceanic Anoxic Event 2. *Chemical Geology*
639 324-325, 28-45.

640 Dembicki Jr., H., 2009. Three common source rock evaluation errors made by geologists during
641 prospect or play appraisals. *American Association of Petroleum Geologists Bulletin* 93,
642 341-356.

643 de Leeuw, J.W., Sinninghe Damsté, J.S., 1990. Organic sulfur compounds and other biomarkers
644 as indicators of palaeosalinity. In: Orr, W.L., White, C.M. (Eds.), *Geochemistry of Sulfur*
645 in Fossil Fuels, ACS Symposium Series 429, 417-443.

646 Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., Eglinton, G., 1978. Organic geochemical
647 indicators of palaeoenvironmental conditions of sedimentation. *Nature* 272, 216-222.

648 Energy Information Administration (EIA), 2013. *EIA/ARI world shale gas and shale oil resource*
649 *assessment*. U.S. Energy Information Administration, June 2013, 707 pp.

650 Erba, E., 2004. Calcareous nannofossils and Mesozoic oceanic anoxic events. *Marine*
651 *Micropaleontology* 52, 85-106.

652 Erbacher, J., Huber, B.T., Norris, R.D., Markey, M., 2001. Increased thermohaline stratification
653 as a possible cause for an ocean anoxic event in the Cretaceous period. *Nature* 409, 325-
654 327.

655 Ericksen, D.E., 1994. NAD 83: what is it and why you should care. SBE National Convention
656 and World Media Expo, Los Angeles, California.

657 Farrimond, P., Eglinton, G., Brassell, S.C., Jenkyns, H.C., 1990. The Cenomanian/Turonian
658 anoxic event in Europe: an organic geochemical study. *Marine and Petroleum Geology* 7,
659 75-89. [http://dx.doi.org/10.1016/0264-8172\(90\)90058-O](http://dx.doi.org/10.1016/0264-8172(90)90058-O)

660 Furmann, A., Mastalerz, M., Schimmelmann, A., Pedersen, P.K., Bish, D., 2014. Relationships
661 between porosity, organic matter, and mineral matter in mature organic-rich marine
662 mudstones of the Belle Fourche and Second White Specks formations in Alberta, Canada.
663 *Marine and Petroleum Geology* 54, 65-81.

664 Gale, A.S., Voigt, S., Sageman, B.B., Kennedy, W.J., 2008. Eustatic sea-level record for the
665 Cenomanian (Late Cretaceous) - extension to the Western Interior Basin, USA. *Geology*
666 36, 859-862.

667 Gelpi, E., Schneider, H., Mann, J., Oró, J., 1970. Hydrocarbons of geochemical significance in
668 microscopic algae. *Phytochemistry* 9, 603-612.

669 Goodman, A.J., 1951. White specks in Colorado Shale. *American Association of Petroleum*
670 *Geologists Bulletin* 35, 2427-2433.

671 Grantham, P.J., Wakefield, L.L., 1988. Variations in the sterane carbon number distributions of
672 marine source rock derived crude oils through geological time. *Organic Geochemistry* 12,
673 61-73.

674 Greff, K., Cheadle, B., 2012. Conventional oil petroleum system of the Cenomanian-Turonian
675 Blackstone Formation, Ferrier-Willesden Green-Gilby area, west-central Alberta.
676 GeoConvention 2012, 14-18 May 2012, Calgary, Canada.

677 Hakimi, M.H., Abdullah, W.H., Sia, S-G., Makeen, Y.M., 2013. Organic geochemical and
678 petrographic characteristics of Tertiary coals in the northwest Sarawak, Malaysia:
679 Implications for palaeoenvironmental conditions and hydrocarbon generation potential.
680 *Marine and Petroleum Geology* 48, 31-46.

681 Hakimi, M.H., Abdullah, W.H., 2014. Source rock characteristics and hydrocarbon generation
682 modelling of Upper Cretaceous Mukalla Formation in the Jiza-Qamar Basin, Eastern
683 Yemen. *Marine and Petroleum Geology* 51, 100-116.

684 Hancock, J.M., Kauffman, E.G., 1979. The great transgressions of the Late Cretaceous. *Journal*
685 *of the Geological Society* 136, 175-186.

686 Hoffmann, C.F., Mackenzie, A.S., Lewis, C.A., Maxwell, J.R., Oudin, J.L., Durand, B.,
687 Vandenbroucke, M., 1984. A biological marker study of coals, shales and oils from the
688 Mahakam Delta, Kalimantan, Indonesia. *Chemical Geology* 42, 1-23.

689 Hoppie, B.W., Blum, P., Shipboard Scientific Party, 1994. Natural gamma-ray measurements on
690 ODP cores: Introduction to procedures with examples from Leg 150. In: Mountain, G.S.,
691 Miller, K.G., Blum, P., et al. (Eds.), *Proceedings of the Ocean Drilling Program, Initial*
692 *Reports, Vol. 150. College Station, TX (Ocean Drilling Program), pp. 51-59.*

693 Huang, W.Y., Meinschein, W.G., 1979. Sterols as ecological indicators. *Geochimica et*
694 *Cosmochimica Acta* 43, 739-745.

695 Hunt, J.M., 1979. *Petroleum Geochemistry and Geology*. Freeman, San Francisco.

696 Jacob, H., 1989. Classification, structure, genesis and practical importance of natural solid oil
697 bitumen ("migrabitumen"). *International Journal of Coal Geology* 11 65-79.

698 Jarvie, D.M., Hill, R.J., Ruble, T.E., Pollastro, R.M., 2007. Unconventional shale-gas systems:
699 The Mississippian Barnett Shale of north-central Texas as one model for thermogenic
700 shale-gas assessment. *American Association of Petroleum Geologists Bulletin* 91, 475-
701 499.

702 Jenkyns, H.C., 1980. Cretaceous anoxic events: from continents to oceans. *Journal of the*
703 *Geological Society* 137, 171-188.

704 Katz, B.J., 1983. Limitations of 'Rock-Eval' pyrolysis for typing organic matter. *Organic*
705 *Geochemistry* 4, 195-199.

706 Kauffman, E.G., 1977. Geological and biological overview: Western Interior Cretaceous basin.
707 *The Mountain Geologist* 14, 75-99.

708 Kauffman, E.G., 1984. Paleobiogeography and evolutionary response dynamic in the Cretaceous
709 Western Interior Seaway of North America. In: Westermann, G.E.G. (Ed.), *Jurassic-*
710 *Cretaceous Biochronology and Paleogeography of North America*, Geological
711 Association of Canada Special Paper 27, 273-306.

712 Kenig, F., Hudson, J.D., Sinninghe Damsté, J.S., Popp, B.N., 2004. Intermittent euxinia:
713 Reconciliation of a Jurassic black shale with its biofacies. *Geology* 32, 412-424,
714 <http://dx.doi.org/10.1130/G20356.1>.

715 Kovac, L.J., Last, W.M., 1991. Mineralogy and geochemistry of Cretaceous oil shales in
716 Manitoba. In: Christopher, J.E., Haidl, F.M. (Eds.), *Sixth International Williston Basin*
717 *Symposium*, Saskatchewan Geological Society, Special Publication Number 11, 275-282.

718 Kwan, R., Mooney, R., 2010. Going straight to the 'Source': A spotlight on the emerging
719 Canadian shale oil plays. *Macquarie Equities Research*, Canada, 25 p.

720 Landis, C.R., Castaño, J.R., 1995. Maturation and bulk chemical properties of a suite of solid
721 hydrocarbons. *Organic Geochemistry* 22, 137-149.

722 Larson, R.L., Erba, E., 1999. Onset of the mid-Cretaceous greenhouse in the Barremian-Aptian:
723 Igneous events and the biological, sedimentary, and geochemical responses.
724 *Paleoceanography* 14, 663-678.

725 Leckie, R.M., Bralower, T.J., Cashman, R., 2002. Oceanic anoxic events and plankton evolution:
726 Biotic response to tectonic forcing during the mid-Cretaceous. *Paleoceanography* 17, 1-
727 29.

728 Leckie, D.A., Schröder-Adams, C.J., Bloch, J., 2000. The effect of paleotopography on the late
729 Albian and Cenomanian sea-level record of the Canadian Cretaceous interior seaway.
730 *Geological Society of America Bulletin* 112, 1179-1198.

731 Matchette-Downes, 2009. Guide to Optical Microscopy in Petroleum Geochemistry. Report
 732 prepared for the MDOIL LIMITED on 01/02/95, updated 14/01/2009, 21 pp.

733 Mackenzie, A. S., Hoffmann, C. F., Maxwell, J. R., 1981. Molecular parameters of maturation in
 734 the Toarcian shales, Paris Basin, France. III. Changes in aromatic steroid hydrocarbons.
 735 *Geochimica et Cosmochimica Acta* 45, 1345-1355.

736 Mackenzie, A.S., Patience, R.L., Maxwell, J.R., Vandenbroucke, M., Durand, B., 1980.
 737 Molecular parameters of maturation in the Toarcian shales, Paris Basin, France. I.
 738 Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes.
 739 *Geochimica et Cosmochimica Acta* 44, 1709-1721.

740 Mackenzie, A.S., Rullkötter, J., Welte, D.H., Mankiewicz, P., 1985. Reconstruction of oil
 741 formation and accumulation in North Slope, Alaska, using quantitative gas
 742 chromatography-mass spectrometry: source rock evaluation including isotopes and
 743 biomarkers. In: Magoon, L.B., Claypool, G.E. (Eds.), *Alaska North Slope Oil/Rock*
 744 *Correlation Study*, American Association of Petroleum Geologists Studies in Geology 20,
 745 319-377.

746 Marzi, R., Torkelson, B.E., Olson, R.K., 1993. A revised carbon preference index. *Organic*
 747 *Geochemistry*, 20, 1303-1306.

748 Moldowan, J.M., 1984. C₃₀-steranes, novel markers for marine petroleum and sedimentary
 749 rocks. *Geochimica et Cosmochimica Acta* 48, 2767-2768.

750 Moldowan, J.M., Seifert, W.K., Gallegos, E.J., 1985. Relationship between petroleum
 751 composition and depositional environment of petroleum source rocks. *American*
 752 *Association of Petroleum Geologists Bulletin* 69, 1255-1268.

753 Moldowan, J. M., Sundararaman, P., Schoell, M., 1986. Sensitivity of biomarker properties to
 754 depositional environment and/or source input in the Lower Toarcian of SW-Germany.
 755 *Organic Geochemistry* 10, 915-926.

756 Mossop, G., Shetsen, I. (compilers), 1994. *Geological Atlas of the Western Canada Sedimentary*
 757 *Basin*. Alberta Geological Survey.

758 Möslé, B., Fowler, M.G., Kalkreuth, W.D., 1993. Organic Petrology and Geochemistry of
759 Cretaceous (Albian-Turonian) black shales from the Western Canada Sedimentary Basin.
760 The Society of Organic Petrology, 10th Annual Meeting Abstracts and Program, pp. 94-
761 96.

762 Peters, K.E., 1986. Guidelines for evaluating petroleum source rock using programmed
763 pyrolysis. American Association of Petroleum Geologists Bulletin 70, 318-329.

764 Peters, K.E., Moldowan, J.M., 1991. Effects of source, thermal maturity, and biodegradation on
765 the distribution and isomerization of homohopanes in petroleum. Organic Geochemistry
766 17, 47-61.

767 Peters, K.E., Moldowan, J.M., Schoell, M., Hemphins, W.B., 1986. Petroleum isotopic and
768 biomarker composition related to source rock organic matter and depositional
769 environment. Organic Geochemistry 10, 17-27.

770 Petrov, A.A., Vorobyova, N.S., Zemskova, Z.K., 1990. Isoprenoid alkanes with irregular “head-
771 to-head” linkages. Organic Geochemistry 16, 1001-1005.

772 Pratt, L.M., 1984. Influence of paleoenvironmental factors on preservation of organic matter in
773 Middle Cretaceous Greenhorn Formation, Pueblo, Colorado. American Association of
774 Petroleum Geologists Bulletin 68, 1146-1159.

775 Prokoph, A., Villeneuve, M., Agterberg, F.P., Rachold, V., 2001. Geochronology and calibration
776 of global Milankovitch cyclicity at the Cenomanian-Turonian boundary. Geology 29,
777 523-526.

778 Prokoph, A., Babalola, L.O., El Bilali, H., Olagoke, S., Rachold, V., 2013. Cenomanian-
779 Turonian carbon isotope stratigraphy of the Western Canadian Sedimentary Basin.
780 Cretaceous Research 44, 39-53.

781 Robinson, N., Eglinton, G., Lafferty, C.J., Snape, C.E., 1991. Comparison of alkanes released
782 from a bituminous coal via hydropyrolysis and low temperature hydrogenation. Fuel 70,
783 249-253.

784 Schlanger, S.O., Arthur, M.A., Jenkyns, H.C., Scholle, P.A., 1987. The Cenomanian-Turonian
785 oceanic anoxic event, I. Stratigraphy and distribution of organic carbon-rich beds and the

786 marine C excursion. In: Brooks, J., Fleet, A.J. (Eds.), *Marine Petroleum Source Rocks*.
787 Geological Society Special Publication 26, 371-399.

788 Schlanger, S.O., Jenkyns, H.C., 1976. Cretaceous oceanic anoxic events: causes and
789 consequences. *Geologie en Mijnbouw* 55, 179-184.

790 Schröder-Adams, C.J., Cumbaa, S.L., Bloch, J., Leckie, D.A., Craig, J., Seif El-Dein, S.A.,
791 Simons, D.-J. H.A.E., Kenig, F., 2001. Late Cretaceous (Cenomanian to Campanian)
792 paleoenvironmental history of the eastern Canadian margin of the Western Interior
793 Seaway: Bonebeds and anoxic events. *Palaeogeography, Palaeoclimatology,*
794 *Palaeoecology* 170, 261-289.

795 Schröder-Adams, C.J., Herrle, J.O., Tu, Q., 2012. Albian to Santonian carbon isotope excursions
796 and faunal extinctions in the Canadian Western Interior Sea: Recognition of eustatic sea-
797 level controls on a forebulge setting. *Sedimentary Geology* 281, 50-58.

798 Schröder-Adams, C.J., Leckie, D.A., Bloch, J., Craig, J., McIntyre, D.J., Adams, P.J., 1996.
799 Paleoenvironmental changes in the Cretaceous (Albian to Turonian) Colorado Group of
800 western Canada: microfossil, sedimentological and geochemical evidence. *Cretaceous*
801 *Research* 17, 311-365.

802 Seifert, W.K., Moldowan, J.M., 1978. Applications of steranes, terpanes and monoaromatics to
803 the maturation, migration and source of crude oils. *Geochimica et Cosmochimica Acta*
804 42, 77-95.

805 Seifert, W.K., Moldowan, J.M., 1986. Use of biological markers in petroleum exploration. In:
806 Johns, R.B. (Ed.), *Methods in Geochemistry and Geophysics*, Vol. 24, pp. 261-290.

807 Shanmugam, G., 1985. Significance of coniferous rain forests and related organic matter in
808 generating commercial quantities of oil, Gippsland Basin. *American Association of*
809 *Petroleum Geologists Bulletin* 69, 1241-1254.

810 Simons, D.-J. H., Kenig, F., 2001. Molecular fossil constraints on the water column structure of
811 the Cenomanian-Turonian Western Interior Seaway, USA. *Palaeogeography,*
812 *Palaeoclimatology, Palaeoecology* 169, 129-152.

813 Simons, D-J.H., Kenig, F., Schröder-Adams, C.J., 2003. An organic geochemical study of
814 Cenomanian-Turonian sediments from the Western Interior Seaway, Canada. *Organic*
815 *Geochemistry* 34, 1177-1198.

816 Sinninghe Damsté, J.S., Kenig, F., Koopmans, M.P., Koster, J., Schouten, S., Hayes, J.M., de
817 Leeuw, J.W., 1995. Evidence for gammacerane as an indicator of water column
818 stratification. *Geochimica et Cosmochimica Acta* 59, 1895-1900.

819 Stasiuk, L.D., Goodarzi, F., 1988. Organic petrology of Second White Speckled Shale,
820 Saskatchewan, Canada - A possible link between bituminite and biogenic gas? *Bulletin of*
821 *Canadian Petroleum Geology* 36, 397-406.

822 ten Haven, H. L., de Leeuw, J. W., Rullkötter, J., Sinninghe Damsté, J. S., 1987. Restricted
823 utility of pristane/phytane ratio as a palaeoenvironmental indicator. *Nature* 330, 641-643.

824 ten Haven, H.L., de Leeuw, J.W., Sinninghe Damsté, J.S., Schenck, P.A., Palmer, S.E.,
825 Zumbege, J.E., 1988. Application of biological markers in the recognition of
826 palaeohypersaline environments. In: Fleet, A.J., Kelts, K., Talbot, M.R (Eds.), *Lacustrine*
827 *Petroleum Source Rocks*, Geological Society Special Publication No. 40, Blackwell
828 Scientific Publications, pp. 123-130. Tissot, B., Califet-Debyser, Y., Deroo, G., Oudin,
829 J.L., 1971. Origin and evolution of hydrocarbons in early Toarcian shales, Paris Basin,
830 France. *American Association of Petroleum Geologists Bulletin* 55, 2177-2193.

831 Tissot, B.P., Welte, D.H., 1984. *Petroleum Formation and Occurrence*. Springer-Verlag, New
832 York, pp. 699.

833 Tu, Q., Schröder-Adams, C.J., Craig, J., 2007. A new lithostratigraphic framework for the
834 Cretaceous Colorado Group in the Cold Lake heavy oil area, east-central Alberta,
835 Canada. *Natural Resources Research* 16, 17-30.

836 Tyagi, A., Plint, A.G., McNeil, D.H., 2007. Correlation of physical surfaces, bentonites, and
837 biozones in the Cretaceous Colorado Group from the Alberta Foothills to southwest
838 Saskatchewan, and a revision of the Belle Fourche-Second White Specks formational
839 boundary. *Canadian Journal of Earth Sciences* 44, 871-888.

- 840 Vermeij, G.J., 1995. Economics, volcanoes, and Phanerozoic revolutions. *Paleobiology* 21, 125-
841 152.
- 842 Waples, D.W., Machihara, T., 1991. Biomarkers for geologists: a practical guide to the
843 application of steranes and triterpanes in petroleum geology. *American Association of*
844 *Petroleum Geologists Methods in Exploration*, No. 9, 19-40.
- 845

Figure captions

Fig. 1. Locations of the 7 studied cores from wells on a thermal maturity map of the Second White Specks Fm. in Alberta, Canada (modified after Creaney and Allan, 1990; Kwan and Mooney, 2010). Wells No. 1 to 7 – well numbers assigned for this study; UWI – Unique Well Identifier; T – township; W – range. The NW-SE and W-E cross-sections are shown in Fig. 2.

Fig 2. Cross-sections through west-central Alberta (**A**) from NW to SE and (**B**) from W to E showing the stratigraphy of the Belle Fourche (BF) and Second White Specks (SWS) Formations. “Base of Fish Scales” represents the base of the Fish Scales Formation. Distances between wells are not drawn to a scale. Positions of cores in wells are indicated by the black vertical bars (well locations are shown in Fig. 1). The well gamma-ray log (GR) in GAPI units (Gamma-ray, American Petroleum Institute; Hoppie et al., 1994) is shown in red. Stratigraphy adapted from Tu et al. (2007), Tyagi et al. (2007), and Schröder-Adams et al. (2012).

Fig. 3. Maceral composition (vol%) and measured vitrinite reflectance %Ro values for core samples from seven wells based on averaged values for samples from the Belle Fourche (BF) and Second White Specks (SWS) Formations in west-central Alberta. Wells No. 1 to 7- well number as shown on map (Fig. 1); UWI - Unique Well Identifier. The number of samples used for analyses in each well is given in Table 2. Alginite, amorphous organic matter (AOM), and other liptinites belong to the liptinite maceral group. Vitrinite and inertinite jointly represent terrigenous material. Solid bitumen is a secondary maceral typically formed after generation and expulsion of oil.

Fig. 4. Representative photomicrographs of macerals observed in polished blocks under reflected white and fluorescent light with an optical microscope using oil immersion. Pictures were taken on core samples from well No. 7, Second White Specks Fm., Alberta (Fig. 1), because they best represent the type and quality of organic matter found in studied mudstone/shale intervals from seven cores. Panels **E** and **F** show the same view with alginite on the far left representing part of *Tasmanites*. Abbreviations: **V** – vitrinite, **gV** – granular vitrinite, **OxV** – oxidized vitrinite, **RwV** – reworked vitrinite, **gSB** – granular solid bitumen, **mSB** – micronized solid bitumen, **foram** – foraminifera test, **P** – pyrite, **EZ** – elongated zone filled with μm -sized solid bitumen, **AOM** – amorphous organic matter, **Sp** – sporinite, **A** – alginite, **I** – inertinite.

Fig. 5. Changes in average values of geochemical parameters with increasing thermal maturity for samples from seven wells in west-central Alberta. Relationships between (**A**) original and present-day TOC values (TOC_o and TOC_{pd} , respectively) - total organic carbon, and (**B**) original and present-day HI values (HI_o and HI_{pd} , respectively) - hydrogen index relative to the transformation ratio (i.e. extent of conversion of organic carbon and hydrogen in kerogen to hydrocarbons) in each core. Well No. 1 to 7 - well number as shown on map (**Fig. 1**) and UWI - Unique Well Identifier listed in order of increasing maturity. Average values and number of samples used for the analyses are given in **Table 2**. Complete data sets are provided in **Tables S1, S2, and S4** as part of the supplementary materials.

Fig. 6. Mass chromatograms (m/z 99) showing distribution of *n*-alkanes and acyclic isoprenoids for representative samples from the Belle Fourche and Second White Specks Formations of different maturity levels: from (**A**) immature, (**B**) early mature, and (**C**) mature zones in west-central Alberta. %Ro avg. - average vitrinite reflectance value for samples in each core from a

888 given well; well No. - well number as shown on map (Fig. 1); C₁₇ - *n*-C₁₇ alkane, etc.; Pr -
889 pristane; Ph - phytane. Values and formulas of biomarker ratios are provided in Table 3A.

890 **Fig. 7.** Mass chromatograms (*m/z* 191) showing distributions of terpanes and hopanes for
891 representative samples from the Second White Specks Formation at different levels of maturity
892 from immature (**A**), early mature (**B**), and mature (**C**) zones in west-central Alberta. %Ro avg. -
893 average vitrinite reflectance value for samples in each core from a given well; Well No. - well
894 number as shown on map (Fig. 1). Values of ratios are provided in Table 3B. TR19-TR30 - C₁₉-
895 C₃₀ tricyclic terpanes; Ts - C₂₇ 18 α (H)-trisnorneohopane; Tm - C₂₇ 17 α (H)-trisnorhopane; H28 -
896 C₂₈ 17 α ,18 α ,21 β (H)-dinorhopane; H29 - C₂₉ 17 α (H),21 β (H)-norhopane; C29 Ts - C₂₉ Ts
897 18 α (H)-norneohopane; DH30 - C₃₀ 17 α (H)-diahopane; M29 - C₂₉ normoretane; OL - oleanane;
898 H30 - C₃₀ 17 α (H)-hopane; M30 - C₃₀ moretane; H31-H35 S+R - C₃₁-C₃₅ 22S+22R 17 α (H)-
899 hopanes; GAM - gammacerane.

900 **Fig. 8.** Distribution of 17 α (H),21 β (H)-hopane homologs from C₃₁ to C₃₅ (22S+22R) detected in
901 organic extracts of (**A**) samples from wells No. 3 to 7 and (**B**) samples from wells No. 1 and 2
902 (after Peters and Moldowan, 1991).

903 **Fig. 9.** Mass chromatograms (*m/z* 217) showing distributions of steranes and diasteranes for
904 representative samples from the Second White Specks Formation at different levels of maturity
905 from immature (**A**), early mature (**B**), and mature (**C**) zones in west-central Alberta. %Ro avg. -
906 average vitrinite reflectance value for samples in each core from a given well; Well No. - well
907 number as shown on map (Fig. 1). Values of ratios are provided in Table 3C.

Fig. 10. A cross-plot of present-day total sulfur (TS_{pd}) content against present-day total organic carbon (TOC_{pd}) content used as a general proxy for characterizing the paleoenvironment (after Berner and Raiswell, 1984; compare Adegoke et al., 2014) for samples from the Belle Fourche and Second White Specks Formations in west-central Alberta, Canada. Wells No. 1 to 7 - well number as shown on map (Fig. 1) and UWI - Unique Well Identifier listed in order of increasing maturity. Numbers of samples used for the analyses are given in Table 2. The complete data set is provided in Table S1 as part of the supplementary materials.

Fig. 11. Modified van Krevelen diagrams showing relationships between (**A**) the present-day hydrogen and oxygen index (HI_{pd} and OI_{pd} , respectively) values, and (**B**) the HI_{pd} and T_{max} values. The diagrams characterize kerogen type, oil/gas proneness and maturity level for samples from the Belle Fourche (indicated by red arrows) and Second White Specks Formations in west-central Alberta, Canada. Wells No. 1 to 7 - well number as shown on map (Fig. 1) and UWI - Unique Well Identifier are listed in order of increasing maturity. The cross-hatched area in panel **A** represents data points from Beaton et al. (2009) for core samples from well No. 3. Numbers of samples used for the analyses are given in Table 2. The complete data set is provided in Table S2 as part of the supplementary materials. Kerogen maturation paths on diagrams are drawn after Peters (1986) and Dembicki (2009).

Fig. 12. Relationship between C_{27} , C_{28} , and C_{29} $\alpha\alpha\alpha(H)$ -20R sterane compositions indicating a predominantly marine source of organic matter in samples from the Belle Fourche (indicated by red arrows) and Second White Specks Formations in Alberta Province, Canada. Wells No. 1 to 7 - well number as shown on map (Fig. 1) and UWI - Unique Well Identifier listed in order of

increasing maturity. Values of plotted data points are provided in Table 3C. Diagram modified from Huang and Meinschein (1979) and Adegoke et al. (2014).

Fig. 13. Correlation of vitrinite reflectance %Ro with biomarker indices based on hopanes and steranes. Each point represents average value of the maturity indicator for samples in each core from a given well. Values of biomarker-based thermal maturity indicators are given in Table 3B and C. Regression lines based on linear model with the equations and coefficient of determination (R^2) values are added to represent the strength of correlations.

Fig. 14. Cross-plot of the present-day total organic carbon (TOC_{pd}) content against values of Rock-Eval pyrolysis S2 peak (after Peters, 1986; Dembicki, 2009; compare Hakimi et al., 2013; Hakimi and Abdullah, 2014) showing organic matter richness (TOC-based) and generative source rock hydrocarbon potential (S2-based) for samples from the Belle Fourche and Second White Specks Formations in Alberta Province, Canada. Wells No. 1 to 7 - well number as shown on map (Fig. 1) and UWI - Unique Well Identifier. Refer to Table 2 for average values and numbers of samples used for analyses. The complete set of data is provided in Tables S1 and S2 as part of the supplementary materials.

Figure 1

A **Well No. 7**
100/06-36-63-04W6

NW

A. NW-SE Cross-section

Well No. 6
100/04-31-052-13W5

Well No. 5
100/13-20-051-14W5

Well No. 3
100/07-19-045-06W5

Well No. 1
102/10-12-028-21W4

A'
SE

Figure 2A

Figure 2B

Figure 3

A. Sample #15, white reflected light

B. Sample #15, white reflected light

C. Sample #7, white reflected light

D. Sample #11, fluorescent reflected light

E. Sample #13, white reflected light

F. Sample #13, fluorescent reflected light

G. Sample #18, white reflected light

H. Sample #19, white reflected light

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Table 1. Basic information of cores and samples collected from the Belle Fourche (BF) and Second White Specks (SWS) Formations in Alberta, Canada.

UWI	102/10-12-28- 21W4	100/13-34- 47-20W4	100/07-19-45- 06W5	102/12-31-39- 09W5	100/13-20-51-14W5	100/04-31-52- 13W5	100/06-36-63-04W6
Well No.	1	2	3	4	5	6	7
Latitude (NAD 83)	51.381352	53.102456	52.892376	52.40243	53.421051	53.530211	54.49385
Longitude (NAD 83)	-112.830195	-112.85312	-114.854086	-115.29322	-116.035363	-115.91245	-118.46806
Time of drilling	4/27/2004	6/14/2005	9/3/1979	7/1/2006	4/2/2003	12/12/2002	12/19/2009
Time of sample collection	3/12/2012	3/12/2012	6/14/2011	3/12/2012	3/12/2012	3/12/2012	3/24/2014
Core intervals (m)	1075.0-1084.0 and 1084.5-1093.5	843.0-851.6	1793.5-1871.0	2638.0-2658.0 and 2658.0-2679.1 and 2679.1-2697.1	2014.00-2023.55 and 2071.40-2080.40	1800.0-1818.9	1855.0-1873.0 and 1873.0-1891.0 and 1891.0-1909.0
Core recovered (m)	6.95+9.00	8.6	77.5	18.95+21.00+18.00	9.00+9.00	18.9	18.00+18.00+17.70
Formation included	SWS + BF	SWS	SWS + BF	SWS + BF	SWS + BF	SWS	SWS
Formation interval (m)	1063.0-1153.0	836.0-919.0	1754.0- >1890.0	2560.0-2771.0	1956.0-2169.0	1748.0-1943.0	1685.0-2103.0
Formation thickness (m)	90	78	>120	211	213	195	418
No. of samples collected	20	5	19	25	17	12	33

UWI - Unique Well Identifier; Well No. - well number as shown on map (Fig. 1).

NAD 83 - geographic coordinates based on the North American Datum 1983 earth model (World Geodetic System of 1984 or WGS 84; Ericksen, 1994).

SWS - Second White Specks Fm., BF – Belle Fourche Fm.

Formation interval (m) represents depth from the top of the Second White Specks Fm. to depth of the base of Fish Scales Formation as shown in Fig. 2.

Table 2. List of data for parameters based on organic petrography (vitrinite reflectance values %Ro and oil/ gas proneness) and geochemistry (TOC, TS, and Rock-Eval data) for samples from the Belle Fourche and Second White Specks Formations in west-central Alberta. Average values and ranges for samples from seven wells are arranged with regard to increasing maturity level. The transformation ratio, original total organic carbon (TOC_o) and original hydrogen index (HI_o) for selected samples were calculated for mature core samples from wells No. 3-7 according to Jarvie et al. (2007). The number of samples (n) used for analyses in each core is provided in parentheses.

Parameter	UWI	13-34-47-20W4	10-12-28-21W4	06-36-63-04W6	04-31-52-13W5	07-19-45-06W5	12-31-39-09W5	13-20-51-14W5
	Well No.	2	1	7	6	3	4	5
%Ro	average	0.42 (n=2)	0.43 (n=6)	0.65 (n=33)	0.78 (n=4)	0.79 (n=19)	0.85 (n=3)	0.89 (n=5)
	range	0.40-0.44	0.38-0.47	0.61-0.72	0.77-0.78	0.74-0.87	0.84-0.85	0.85-0.92
Original TOC _o (wt%)	average	n.a.	n.a.	5.34	4.15	3.84	3.48	3.90
	range			1.57-10.04	3.59-4.79	2.39-4.97	2.38-4.68	1.99-6.76
Present-day TOC _{pd} (wt%)	average	4.03 (n=5)	3.52 (n=20)	5.03 (n=33)	3.14 (n=12)	2.86 (n=19)	2.01 (n=25)	2.62 (n=17)
	range	2.02-5.23	1.59-5.23	1.44-10.04	2.69-3.58	1.74-3.62	0.15-3.16	1.46-4.52
Present-day TS _{pd} (wt%)	average	2.43	3.00	2.59 (n=8)	2.60	2.84	2.25	2.30
	range	2.17-3.16	2.25-4.16	0.93-3.99	2.13-3.32	1.11-4.61	0.13-3.20	0.94-4.62
Present-day TOC _{pd} /TS _{pd}	average	1.65	1.20	1.55 (n=8)	1.22	1.08	0.92	1.23
	range	0.93-2.33	0.63-2.15	1.09-1.77	1.07-1.40	0.56-1.57	0.58-1.19	0.92-2.39
T _{max} (°C)	average	421 (n=2)	421 (n=6)	434 (n=33)	441 (n=4)	441 (n=19)	447 (n=3)	447 (n=5)
	range	417-424	417-425	432-439	439-443	438-446	445-448	446-449
S1 (mg HC/g rock)	average	0.84	0.92	2.55	2.13	1.76	2.47	1.67
	range	0.57-1.10	0.53-1.28	0.40-4.92	1.75-2.73	1.03-2.66	1.42-4.16	1.18-2.26
S2 (mg HC/g rock)	average	15.74	13.07	21.65	7.69	3.81	2.61	3.62
	range	5.26-26.21	2.78-25.99	3.09-48.16	5.88-9.42	2.09-6.51	1.70-4.09	1.85-6.56
S3 (mg CO ₂ /g rock)	average	0.99	0.82	0.19	0.75	0.74	0.69	0.60
	range	0.81-1.16	0.46-1.12	0.10-0.39	0.70-0.87	0.60-0.92	0.59-0.83	0.50-0.70
Present-day OI _{pd} (mg CO ₂ / g TOC)	average	36	27	4	26	27	39	27
	range	26-46	14-39	2-4	20-32	19-48	33-44	12-51

Original HI _o (mg HC/g TOC)	average	n.a.	n.a.	460	445	394	443	447
	range			439-522	443-447	331-426	435-448	444-448
Present-day HI _{pd} (mg HC/g TOC)	average	439	368	421	254	132	139	137
	range	296-581	181-538	215-522	228-283	97-194	126-163	125-145
Transformation ratio (%)	average	n.a.	n.a.	12 (n=33)	56 (n=4)	75 (n=19)	79 (n=3)	79 (n=5)
	range			0-47	50-62	60-83	75-81	78-81
Oil proneness (vol%)	average	72	65	64	57	65	54	70
	range	50-70	55-75	53-74	54-63	10-76	39.5-69	35-90
Gas proneness (vol%)	average	18	29	25	29	20	14	12
	range	15-21	21-37	21-32	26-32	0-37	0.5-21	5-31

UWI – Unique Well Identifier; Well No. – well number as shown on map (Fig. 1). %Ro – average vitrinite reflectance value for samples from each well; TOC – total organic carbon; TS – total sulfur; T_{max} – temperature reached during maximum generation of hydrocarbons measured via S2 peak of Rock-Eval pyrolysis; S1 – free hydrocarbons emitted from rock without cracking of kerogen; S2 – residual hydrocarbons representing the remaining generative hydrocarbon potential; S3 – generated carbon dioxide; OI – oxygen index (= S3 × 100/ TOC); HI – hydrogen index (= S2 × 100/ TOC); Transformation ratio – transformation of carbon and hydrogen in original kerogen to hydrocarbons upon ongoing maturation; n.a. – calculations were not performed for immature samples in cores from wells No. 1 and 2. Oil and gas proneness data are derived from maceral composition; macerals from the liptinite group, including alginite, liptodetrinite and fluorescent amorphous organic matter (vol%) account for the oil-prone organic matter (by vol. %), whereas the sum of the non-fluorescent amorphous organic matter and vitrinite (vol%) accounts for the gas-prone organic matter (by vol%). Complete data are provided in Tables S1-S5 as part of the supplementary materials.

Table 3. Calculated ratios using peak areas in mass chromatograms for designated biomarker groups (**A**) *n*-alkanes and acyclic isoprenoids (*m/z* 99), (**B**) terpanes and hopanes (*m/z* 191), and (**C**) steranes (*m/z* 217) for selected samples from the Belle Fourche and Second White Specks formations in west-central Alberta. Concentrations of components in each biomarker group is given in ppm (based on the internal standard 5β-cholane).

Well No.	UWI	%Ro avg.	Sample #	Depth (m)	Formation	A. <i>n</i> -Alkanes and isoprenoids					B. Terpanes and hopanes							C. Steranes							
						Pr/Ph	CPI	Pr/C ₁₇	Ph/C ₁₈	Concn. (×10 ⁹ ppm)	Tm/Ts	H32 22S/(22S+R)	OL/H30	M30/H30	GA M/H30	GA M concn. (ppm)	Concn. (×10 ⁹ ppm)	C ₂₉ 20S/(20S+R)	(C ₂₁ +C ₂₂)/(C ₂₇ - ₂₉ R+S)	Dia/Reg Sterane	% C ₂₇ aaa R	% C ₂₈ aaa R	% C ₂₉ aaa R	Concn. (×10 ⁹ ppm)	sterane s/hopanes
2	13-34-47-20W4	0.42	5	851.25	SWS	1.7	1.1	1.5	1.7	1.12	1.80	0.37	0.10	0.25	0.09	100	1.09	0.18	0.03	0.61	25	43	32	3.92	3.6
1	10-12-28-21W4	0.43	5	1079.42	SWS	1.9	1.0	1.7	1.2	1.22	2.80	0.41	0.08	0.25	0.08	62	0.96	0.18	0.02	0.51	27	47	26	3.47	3.6
			12	1085.25	BF	1.2	1.0	1.8	1.8	0.83	2.44	0.43	0.13	0.21	0.06	47	0.87	0.17	0.03	0.39	27	42	32	2.90	3.3
7	06-36-63-04W6	0.65	14	1882.03	SWS	1.4	1.0	0.9	0.7	0.96	1.04	0.58	n.d.	0.14	0.07	82	0.33	0.47	0.22	0.82	32	38	30	0.30	0.9
			27	1902.27	SWS	1.5	1.0	1.0	0.7	1.05	0.66	0.58	n.d.	0.14	0.05	58	0.33	0.52	0.17	1.61	31	39	30	0.33	1.0
6	04-31-52-13W5	0.78	3	1802.60	SWS	1.6	1.0	1.0	0.7	1.72	0.31	0.58	0.06	0.12	0.08	35	0.48	0.51	0.29	2.55	29	36	35	0.46	1.0
			11	1817.03	SWS	1.6	1.0	0.9	0.7	2.22	0.31	0.59	0.06	0.11	0.09	38	0.49	0.46	0.38	2.20	30	35	35	0.47	1.0
3	07-19-45-06W5	0.79	7	1818.75	SWS	1.6	1.0	0.9	0.6	1.95	0.11	0.62	0.27	n.d.	0.14	6	0.08	0.53	0.28	3.38	28	36	37	0.24	2.8
			9	1822.60	SWS	1.7	1.0	0.8	0.5	2.60	0.12	0.62	0.37	n.d.	0.21	7	0.07	0.53	0.33	3.44	32	35	34	0.23	3.3
4	12-31-39-09W5	0.85	3	2646.07	SWS	0.9	1.0	0.8	0.9	2.29	0.18	0.60	0.25	0.19	0.28	6	0.04	0.57	1.89	4.53	34	38	27	0.09	2.7
			9	2656.03	SWS	0.8	1.0	0.6	0.8	2.05	0.30	0.62	0.24	0.24	0.19	5	0.04	0.50	1.26	2.12	37	36	27	0.08	2.1
			12	2667.90	BF	1.1	1.0	0.9	0.8	2.41	0.26	0.60	0.28	0.21	0.22	6	0.05	0.55	1.01	4.06	39	33	28	0.12	2.6
			25	2696.30	BF	1.2	1.0	0.7	0.7	1.93	0.06	n.d.	0.59	n.d.	n.d.	6	0.02	0.58	0.96	4.19	43	34	23	0.09	5.5
5	13-20-51-14W5	0.89	3	2017.58	SWS	1.8	1.0	0.7	0.4	1.76	0.11	0.60	0.29	n.d.	0.26	6	0.05	0.54	0.58	5.21	24	37	38	0.12	2.2
			8	2071.71	BF	1.8	1.0	0.5	0.3	1.58	0.09	0.58	0.47	n.d.	0.27	2	0.03	0.55	0.61	3.31	32	39	29	0.09	3.6

Well No. – well number as shown on map (Fig. 1); UWI - Unique Well Identifier.; %Ro avg. – average vitrinite reflectance value for samples in each core from a given well; SWS – Second White Specks Fm.; BF – Belle Fourche Fm.

A: Pr/Ph - pristane/phytane ratio (ten Haven et al., 1987); C₁₇ and C₁₈ - *n*-C₁₇ and *n*-C₁₈ alkanes.

CPI – carbon preference index, based on *n*-alkanes (formula by Hunt, 1979 provided in Marzi et al., 1993):

$$\text{CPI} = 0.5 \times (\sum (n\text{-C}_{25} - n\text{-C}_{33})_{\text{odd}} + \sum (n\text{-C}_{23} - n\text{-C}_{31})_{\text{odd}}) / \sum (n\text{-C}_{24} - n\text{-C}_{32})_{\text{even}};$$

Concn. ($\times 10^9$ ppm) – concentrations of *n*-alkanes in a range from *n*-C₁₃ to *n*-C₃₂ represented in Fig. 6.

B: Tm – C₂₇ 17 α (H)-trisnorhopane; Ts – C₂₇ 18 α (H)-trisnorneohopane; GAM – gammacerane; H30 – C₃₀ 17 α , 21 β (H)-hopane; OL – oleanane; H32 22S – C₃₂ 22S 17 α (H)-hopanes; H32 22R – C₃₂ 22R 17 α (H)-hopane; M30 – C₃₀ moretane; n.d. – not determined;

GAM concn. (ppm) – concentrations of gammacerane in each extract (peak of GAM is marked on Fig. 7);

Concn. ($\times 10^9$ ppm) – concentrations of all hopanoids (C₂₇ to C₃₅) represented in Fig. 7.

C: C₂₉ 20S - C₂₉ $\alpha\alpha\alpha$ (H)-20S; C₂₉ 20R - C₂₉ $\alpha\alpha\alpha$ (H)-20R sterane; (C₂₁+C₂₂)/(C₂₇-29 R+S) = (C₂₁ + C₂₂ sterane)/ $\sum$ (C₂₇-C₂₉ $\alpha\alpha\alpha$ (H)-20R+20S steranes); Dia/Reg Sterane = C₂₇ $\alpha\beta\alpha$ (H)-20S+20 R diasteranes/C₂₇ $\alpha\alpha\alpha$ (H)-20S+20R regular steranes; percentages of C₂₇, C₂₈, C₂₉ steranes given for $\alpha\alpha\alpha$ (H)-20R steranes configuration; steranes/hopanes - ratio of total steranes to total hopanes, each calculated as sum of peak areas for compounds in each biomarker group;

Concn. ($\times 10^9$ ppm) – concentrations of steranes in a range from C₂₇ to C₂₉ represented in Fig. 9.