Distribution, origin, and implications of hydrogen sulphide in unconventional reservoir rocks in Western Canada with insights into the stratigraphic zonation and lateral variability of producible hydrocarbon liquids

> Results of Research Final Report to Geoscience BC, 12-31-2021 (Geoscience BC Report 2022-06)

> > R. Marc Bustin

# Gareth Chalmers, Pablo Lacerda Silva, Amanda Bustin

Department of Earth, Ocean and Atmospheric Sciences

The University of British Columbia 2207 Main Mall #2020, Vancouver, BC V6T 1Z4





# Table of Contents

1.	Executive Summary24			
	1.1.	Prelu	de and Acknowledgements	26
	1.1.1	1. P	relude	26
	1.1.2	2. A	cknowledgements	26
2.	Introductio	on		28
	2.1.	Previ	ous Work	
3.	Geology ar	nd Geo	chemistry of the Doig and Montney Formations	
	3.1.	Abstr	act	
	3.2.	Intro	duction	32
	3.3.	Geol	ogical Background	
	3.4.	Resu	lts	35
	3.4.1	1. N	Iontney Formation	35
	3.	4.1.1.	Structure and Isochore	
	3.	4.1.2.	Thermal Maturity	
	3.	4.1.3.	Total Organic Carbon and Kerogen	
	3.	4.1.4.	Burial and Thermal History	
	3.	4.1.5.	Petroleum Generation	
	3.	4.1.6.	Thermochemical Sulphate Reduction and Gas Analyses	
	3.4.2	2. D	oig Formation	
	3.	4.2.1.	Structure and Isochore	
	3.	4.2.2.	Thermal Maturity	
	3.	4.2.3.	Total Organic Carbon and Kerogen	
	3.	4.2.4.	Burial and Thermal History	
	3.	4.2.5.	Petroleum Generation	
	3.	4.2.6.	Gas Analysis and Thermochemical Sulphate Reduction	
	3.5.	Discu	ission	
	3.6.	Sumr	mary	134
4.	Hydrocarbo	on Con	nposition Distribution in the Montney Formation	
	4.1.	Abstr	ract	

	4.2.	Introduction	135
	4.3.	Results	136
	4.4.	Discussion	140
	4.5.	Summary	141
5. Th	e Origins	s of the H2S Gas in the Montney Formation, British Columbia	143
	5.1.	Abstract	143
	5.2.	Introduction	143
	5.3.	Methodology	148
	5.3.1	1. XRD Mineralogical Composition	148
	5.3.2	2. Anhydrite, Pyrite and Organic Matter Separation	149
	5.4.	Results	150
	5.5.	Discussion	161
	5.6.	Summary	164
6. Dis Waters Water	stributior : Implica 166	n of Sulphate and Other Major Ions in Montney Completion, Produced and Forn ations for the In-Situ Formation of Hydrogen Sulphide and Origins of the Co 5	nation
	6.1.	Abstract	166

6.2.	Intro	oduction	167
6.3.	Met	thods	168
6.3.3	1.	Fluids	168
6.3.2	2. I	Produced water	170
6.3.3	3. /	Aging/Leachate/Connate Water/Speciation	171
6.4.	Res	ults	172
6.4.3	1.	Montney Formation Connate, Flowback and Produced Water Chemistry	172
6.4.2	2. 9	Sulphate	180
6.4.3	3. I	Insights from Barium Concentration	184
6.4.4	4. 9	Sulphate from Fluid – Rock Interactions	188
6.4.	5. \	Water/Leachate/Aging/Extraction Experiments	189
6.	.4.5.1.	. Well 1A	
6.	.4.5.2	. Well H1	192
6.	.4.5.3.	Well H2	195
6.	.4.5.4.	. Well B	

6.4	4.5.5. Well I - Doig	202
6.4.6	<ol> <li>Contribution of Oxidation of Pyrite to Sulphate Concentration in Flowback 205</li> </ol>	Water
6.4.7	7. Contribution of Sulphate from Completion or Drilling Fluid Additives	206
6.4.8 Subsequent	3. Comparison of Sulphate Concentration in Flowback and Produced Watt H <sub>2</sub> S and CO <sub>2</sub> in Produced Gas	ter and 207
6.4.9	9. Regional Distribution of Sulphate and other Major Ions - Implications	220
6.4.1	10. Structural Relationship	224
6.4.1	11. Produced Water Salinity	227
6.4	4.11.1. Implications of Regional Cl/Br Ratios	227
6.4	4.11.2. Sulphate in Solution	231
6.4	4.11.3. $H_2S$ in Solution and H2S in Produced Gas	235
6.4	4.11.4. Other Major Ions in Montney Produced Water	236
6.5.	Discussion and Conclusions	239
7. Comparativ Acid Gas Produc	ve Hydrogen Sulphide, Carbon Dioxide and Methane Adsorption Affinity: Implicati tion from the Montney and Doig Formations	on for 242
7.1.	Abstract	242
7.2.	Introduction	242
7.2.	Introduction Methods	242 243
7.2. 7.3. 7.4.	Introduction Methods Results	242 243 245
7.2. 7.3. 7.4. 7.4.1	Introduction Methods Results I. Desorption Data/Adsorption Capacity	242 243 245 245
7.2. 7.3. 7.4. 7.4.1 7.4.2	Introduction Methods Results 1. Desorption Data/Adsorption Capacity 2. Methane Adsorption Capacity	242 243 245 245 247
7.2. 7.3. 7.4. 7.4.1 7.4.2 7.4	Introduction Methods Results 1. Desorption Data/Adsorption Capacity 2. Methane Adsorption Capacity 4.2.1. Doig Formation	242 243 245 245 247 247
7.2. 7.3. 7.4. 7.4.1 7.4.2 7.4 7.4	Introduction Methods Results 1. Desorption Data/Adsorption Capacity 2. Methane Adsorption Capacity 4.2.1. Doig Formation 4.2.2. Montney Formation	242 243 245 245 247 247 249
7.2. 7.3. 7.4. 7.4.1 7.4.2 7.4 7.4 7.4	Introduction Methods Results 1. Desorption Data/Adsorption Capacity 2. Methane Adsorption Capacity 4.2.1. Doig Formation 4.2.2. Montney Formation 3. Hydrogen Sulphide Adsorption	242 243 245 245 247 247 249 249
7.2. 7.3. 7.4. 7.4.1 7.4.2 7.4 7.4 7.4.3 7.4.3	Introduction Methods Results 1. Desorption Data/Adsorption Capacity 2. Methane Adsorption Capacity 4.2.1. Doig Formation 4.2.2. Montney Formation 3. Hydrogen Sulphide Adsorption 4. Adsorption Affinity Contribution to Gas Portioning During Production	242 243 245 245 247 247 249 249 249
7.2. 7.3. 7.4. 7.4.1 7.4.2 7.4 7.4 7.4 7.4.3 7.4.4 7.5.	Introduction Methods Results 1. Desorption Data/Adsorption Capacity 2. Methane Adsorption Capacity 4.2.1. Doig Formation 4.2.2. Montney Formation 3. Hydrogen Sulphide Adsorption 4. Adsorption Affinity Contribution to Gas Portioning During Production Summary and Conclusions	242 243 245 245 247 247 247 249 249 249 263
7.2. 7.3. 7.4. 7.4.1 7.4.2 7.4 7.4 7.4 7.4.3 7.4.4 7.5. 8. Production Modelling 264	Introduction Methods Results Desorption Data/Adsorption Capacity Methane Adsorption Capacity 2. Methane Adsorption Capacity 4.2.1. Doig Formation 4.2.2. Montney Formation 4.2.2. Montney Formation 3. Hydrogen Sulphide Adsorption 4. Adsorption Affinity Contribution to Gas Portioning During Production Summary and Conclusions of Hydrogen Sulphide from the Montney Formation: Insights from Res	242 243 245 245 247 247 249 249 249 249 263 263
7.2. 7.3. 7.4. 7.4.1 7.4.2 7.4 7.4 7.4 7.4.3 7.4.4 7.5. 8. Production Modelling 264 8.1.	Introduction Methods Results 1. Desorption Data/Adsorption Capacity 2. Methane Adsorption Capacity 4.2.1. Doig Formation Capacity 4.2.2. Montney Formation 4.2.2. Montney Formation 3. Hydrogen Sulphide Adsorption 4. Adsorption Affinity Contribution to Gas Portioning During Production 5. Summary and Conclusions of Hydrogen Sulphide from the Montney Formation: Insights from Res 4. Abstract	242 243 245 245 245 247 247 249 249 263 264

 8.3.
 Model Parameters
 266

	8.4.	Resu	lts and Interpretation	
	8.5.	Sumr	nary and Conclusions	277
9.	Variation i	in Petr	rophysical Properties of the Montney and Doig Formations:	Implications for
Pro	duction of H	ydroca	rbon Liquids	
	9.1.	Abstr	act	279
	9.2.	Intro	duction	
	9.3.	Meth	nods	
	9.3.2	1. N	1ineralogy	
	9.3.2	2. P	orosity	
	9.3.3	3. V	/ettability, Surface, and Interfacial Tension	
	9.3.4	4. To	otal Organic Carbon and Source Rock Characterisation	
	9.3.5	5. C	apillary Pressure	
	9.3.6	5. P	ermeability	
	9.4.	Resu	lts	
	9.4.2	1. D	oig Formation	
	9.	4.1.1.	Mineralogy	
	9.	4.1.2.	Porosity and Pore Size Distribution	
	9.	4.1.3.	Permeability	
	9.	4.1.4.	Geologic Controls on Reservoir Properties	
	9.4.2	2. N	Iontney Formation	
	9.	4.2.1.	Dry Gas Window	
	9.	4.2.2.	Capillary Pressures	
	9.	4.2.3.	Production	
	9.	4.2.4.	Wet Gas in the Dry Gas Area	
	9.	4.2.5.	Wet Gas/Oil	
	9.	4.2.6.	Black Oil – Waskahigan	
	9.	4.2.7.	Porosity, Permeability and Capillary Pressure	
	9.	4.2.8.	Conventional Gas – Kahntah	
	9.4.3	3. V	ariability in Montney Reservoir Properties	
	9.	4.3.1.	Porosity and Permeability	
	9.	4.3.2.	Capillary Pressure	
	9.	4.3.3.	Other Considerations	

	9.5.	Di	iscussion and Conclusions	. 330
	9.5.1	1.	Doig Formation	. 330
	9.5.2	2.	Montney Formation	. 332
10.	Conclusions	s ai	nd Recommendations	. 333
11.	References			. 335
12.	Appendices	s		. 352

# List of Figures

Figure 3.1 - Location map and structure on top of the Montney Formation, as mapped by this study.

Figure 3.4 - Montney type log for area 2 (TVD = true vertical depth).

Figure 3.6 - Thickness distribution of the upper Montney Formation, as mapped by this study. ... 42

Figure 3.7 - Thickness distribution of the middle Montney Formation, as mapped by this study. . 43

Figure 3.8 - Thickness distribution of the lower Montney Formation, as mapped by this study. ... 44

Figure 3.9 - Distribution of the thermal maturity indicator Tmax on the Montney Formation. Changes in the maturation trends within the Fort St. John area (to cooler blue colours and lower maturity) is due to the Fort St. John Graben structures (see Figure 3.40) impacting the maturation Figure 3.14 - Kerogen activation energy distribution used in the Montney Formation basin model. Figure 3.15 - Burial history of the basin at a location immediately south of the Noel field in BC, highlighting the Montney Formation, and showing temperature, H<sub>2</sub>S yield, maturity, and transformation ratio as overlays (respectively from top to bottom). ......54 Figure 3.18 - Cross-section along stratigraphic dip of the basin, showing the burial at different times, highlighting the Montney Formation. Facies legend shown below. Figure 3.19 - Cross-section along stratigraphic strike of the basin, showing the burial at different 

Figure 3.21 - Petroleum generation of the source rocks simulated in the basin model, showing the onset and plateauing of generation
Figure 3.22 - Kerogen transformation ratio in the middle Montney Formation at 101 Ma
Figure 3.23 - Kerogen transformation ratio in the middle Montney Formation at 85 Ma
Figure 3.24 - Kerogen transformation ratio in the middle Montney Formation at 72 Ma
Figure 3.25 - Kerogen transformation ratio in the middle Montney Formation at 85 Ma6
Figure 3.26 - Present day kerogen transformation ratio in the middle Montney Formation
Figure 3.27 - Distribution of $H_2S$ yield from thermochemical sulphate reduction during petroleur generation in the Montney Formation.
Figure 3.28 - Petroleum and TSR $H_2S$ generation curves in the Montney Formation through geologi time
Figure 3.29 - Lower Montney Formation thermochemical sulphate reduction entry age map considering 120°C as the lower boundary7
Figure 3.30 - Upper Montney Formation thermochemical sulphate reduction exit age map considering 120°C as the lower boundary7
Figure 3.31 - Lower Montney Formation thermochemical sulphate reduction entry age map considering 100°C as the lower boundary7
Figure 3.32 - Lower Montney Formation thermochemical sulphate reduction exit age map considering 100°C as the lower boundary7
Figure 3.33 - Charlie Lake thermochemical sulphate reduction entry age map
Figure 3.34 - Charlie Lake thermochemical sulphate reduction exit age map
Figure 3.35 - Distribution of $H_2S$ on the entire Montney Formation, based on public data obtained from AER and BCOGC
Figure 3.36 - Distribution of $H_2S$ on the lower Montney Formation
Figure 3.37 - Distribution of $H_2S$ on the middle Montney Formation
Figure 3.38 - Distribution of $H_2S$ on the upper Montney Formation.

Figure 3.40 - Map of the first vertical derivative of the magnetic anomaly from Miles and Oneschuk (2016), showing discontinuities interpreted as faults, and Montney H<sub>2</sub>S contours displayed for reference. Fault interpretations indicate possible updip migration pathways for the H<sub>2</sub>S generated at greater depths.

Figure 3.44 - Distribution of gas dryness ratio on the entire Montney Formation
Figure 3.45 - Distribution of gas dryness ratio on the lower Montney Formation
Figure 3.46 - Distribution of gas dryness ratio on the middle Montney Formation90
Figure 3.47 - Distribution of gas dryness ratio on the upper Montney Formation $91$
Figure 3.48 - Distribution of thermal maturity in the Montney Formation and bubble map overlay of iC4/nC4 ratio
Figure 3.49 - Distribution of thermal maturity in the Montney Formation and bubble map overlay of iC5/nC5 ratio
Figure 3.50 - Distribution of CO $_2$ on the entire Montney Formation
Figure 3.51 - Distribution of CO $_2$ on the lower Montney Formation
Figure 3.52 - Distribution of $CO_2$ on the middle Montney Formation
Figure 3.53 - Distribution of $CO_2$ on the upper Montney Formation
Figure 3.54 - Cross-plot of the spatial distribution of $CO_2$ versus $H_2S$ in the Montney Formation, colored by the ratio between $H_2S$ and $CO_2$ , highlighting the correlation that exists only in the high $H_2S$ area (> 5%)
Figure 3.55 - Three-dimensional map showing the CO <sub>2</sub> gas concentrations for the Montney Formation across BC and Alberta
Figure 3.56 - Three-dimensional map showing the H <sub>2</sub> S gas concentrations for the Montney Formation across BC and Alberta
Figure 3.57 - Structure map of the top of the Doig Formation (Silva, 2021) $101$
Figure 3.58 - Thickness distribution of the Doig Phosphate Zone (Silva, 2021).

6	0 1		
Figure 3.59 - Thickness distribution	of the upper Doig Forma	ation (Silva, 2021)	

	Figure 3.60 - Cross-section of the Doig Formation along stratigraphic st	trike (Silva,	2021).	See Figure
3.57 f	or location			

Figure 3.61 - Cross-section of the Doig Formation along stratigraphic dip (Silva, 2021). See Figure 3.57 for location
Figure 3.62 - Doig thermal maturity Tmax distribution map (Silva, 2021)
Figure 3.63 - Total organic carbon content histogram for the Doig Formation $108$
Figure 3.64 - Total organic carbon distribution of the Doig Phosphate Zone (Silva, 2021) $110$
Figure 3.65 - Total organic carbon distribution of the upper Doig Formation (Silva, 2021) $111$
Figure 3.66 - Pseudo-van Krevelen plot of Doig Formation Rock-Eval analyses $113$
Figure 3.67 - Distribution of hydrogen index in the Doig Phosphate Zone (Silva, 2021) $114$
Figure 3.68 - Distribution of hydrogen index in the upper Doig Formation (Silva, 2021) $115$
Figure 3.69 - Type II kerogen activation energy distribution used in the Doig Formation basin model
Figure 3.70 - Type III kerogen activation energy distribution used in the Doig Formation basin model
Figure 3.71 - Maximum depth of burial of the Doig Phosphate Zone
Figure 3.72 - Kerogen transformation ratio in the Doig Phosphate Zone at 101 Ma $119$
Figure 3.73 - Kerogen transformation ratio in the Doig Phosphate Zone at 85 Ma $120$
Figure 3.74 - Kerogen transformation ratio in the Doig Phosphate Zone at 72 Ma $121$
Figure 3.75 - Kerogen transformation ratio in the Doig Phosphate Zone at 60 Ma $122$
Figure 3.76 - Kerogen transformation ratio in the Doig Phosphate Zone at 0 Ma $123$
Figure 3.77 - Distribution of $H_2S$ yield from thermochemical sulphate reduction during petroleum generation in the Doig Formation
Figure 3.78 - Map of age of entry in the thermochemical sulphate reduction zone of the Doig Phosphate Zone
Figure 3.79 - Map of age of exit of the thermochemical sulphate reduction zone of the upper Doig Formation
Figure 3.80 - Distribution of $H_2S$ in the Doig Formation
Figure 3.81 - Distribution of gas dryness ratio on the entire Doig Formation
Figure 3.82 - Distribution of CO $_2$ on the Doig Formation

Figure 4.1 - Cross plot of gas dryness and the iC4/nC4 ratio for all British Columbia Montney producers at the time of this report. The iC4/nC4 is used as a maturity indicator with the line of best fit representing the regional maturation trend from Euzen et al. (2021). An excess methane percentage is calculated from the deviation away from the expected gas composition of the regional maturation trend. Wells that have high excess methane (i.e., red colours) have a greater ex-situ (migrated) gas content compared to wells in the black symbols. Wells represented by black or green symbols have low ex-situ gas

Figure 4.2 - Cross plot of gas dryness and the iC4/nC4 ratio for all Alberta Montney producers at the time of this report. The iC4/nC4 is used as a maturity indicator with the line of best fit representing the regional maturation trend from Euzen et al. (2021). An excess methane percentage is calculated from the deviation away from the expected gas composition of the regional maturation trend. Wells that have a high excess methane (i.e., red colours) have a greater ex-situ gas content compared to wells in the black symbols. Wells represented by black or green symbols have low ex-situ gas contents and the hydrocarbons are the result of in-situ generation that is typical of a self-sourcing reservoir. The Alberta Montney producers have a greater contribution of migrated gas than the BC wells.

Figure 5.3 - Cross plot of sulphur and oxygen isotopes from anhydrite, pyrite, kerogen and  $H_2S$  gas from both Triassic and Devonian sources. Point data is the oxygen and sulphur isotopic data for anhydrite minerals for both Triassic and Devonian samples. Triassic sourced sulphur from anhydrite minerals all plot

Figure 5.4 - Distribution of sulphur isotopic ratios in the Montney Formation on the base map of H<sub>2</sub>S distribution. The sulphur isotopic ratio shows no trends across the area and has a narrow range of ratio from  $\delta^{34}$ S of 9 to 21‰ compared to the range of sulphur ratios from Devonian to the Triassic rocks.

Figure 5.5 - H<sub>2</sub>S formation models for sour Montney wells. A total of 218 mineral and organic matter samples were isotopically analysed with 120 H<sub>2</sub>S gas sampled also isotopically analysed. Diamond symbols represent the sulphur in the mineral form, prior to being converted to sulphate ions and used in the formation of H<sub>2</sub>S gas when in contact with hydrocarbons. Circle symbols represent the sulphur once converted to H<sub>2</sub>S gas. Model 1 represents an in-situ conversion which would be the conversion of anhydrite that is derived from the Montney Formation (i.e., syn-depositional anhydrite). This model is plausible as the Montney Formation does contain small amounts of anhydrite (< 5%). However, the  $H_2S$ distribution would be more consistent and the localised changes between sweet and sour lateral wells on the same pad would not be observed (i.e., Figure 3.39). Model 2 is structurally controlled, with anhydrite or sulphate ions derived from sulphate minerals with the Charlie Lake Formation migrating through local fracture/fault systems into the Montney Formation (prior to hydrocarbon charging and over-pressuring). H<sub>2</sub>S gas is generated once hydrocarbons are generated in the Montney Formation and encounter the sulphate ions. A similar model has been shown for migration of sulphate ions from the Charlie Lake and into the Halfway Formations (Sharma, 1969). Model 3 is a mixing of sulphur ions from Triassic and Devonian sources and structural controls would need to include a deeper connection with the Devonian source. This results in a heavier sulphur isotopic signature in the H<sub>2</sub>S compared to Model 2. Liseroudi et al. (2020) shows evidence that dissolved sulphate ions have migrated from the Devonian in to the 

Figure 5.6 - Scanning electron microscope images and energy dispersive X-ray spectroscopic (EDX) mapping showing the textural relationship between dolomite (D) and anhydrite (A) within the upper Montney Formation. Well Authorization # 30876 EDX maps show the concentration of magnesium (Mg) and calcium (Ca) in the dolomite minerals and the concentration of sulphur (S) and calcium (Ca) in the

Figure 5.7 - Mineralogical textures in the Charlie Lake formation. The Charlie Lake Formation shows both detrital anhydrite grains (white arrow; A) and evaporitic textures (black arrow; E). The detrital anhydrite grains are also associated with quartz grains (blue arrow; A). The anhydrite is determined by the high calcium (F) and high sulphur (H) contents. The evaporitic texture seen in (E) is similar to the nodular texture seen in Warren (2016) evaporites; dolomite anhydrite associations are interpreted as evaporites in the Charlie Lake Formation (Hunt and Ratcliffe, 1959). Very large dolomite grains also form in the evaporitic environment (E). The dolomite contains high magnesium (G) and calcium (F) contents.

Figure 5.8 - The Doig Formation that overlays the Montney Formation shows phosphatic nodules that are also rich in anhydrite, as illustrated by the high sulphur concentrations. The nodules are concentrated in calcium, sulphur and phosphate and are found associated with dolomite grains (blue arrows). Anhydrite-rich phosphatic nodules have also been observed in the Doig Formation by Desrocher (1997). This detrital texture for the anhydrite shows that the sulphate would need to be dissolved from the nodules and then migrated and deposited in the Montney Formation as a cement in fractures. ....160

Figure 6.1 - Samples for oxygen and hydrogen isotope analyses used for the mixing models, were prepared from a sub-sample of unheated, filtered fluid, and mixing it with activated charcoal for a minimum of 48 hours to remove organic compounds through adsorption, as the organics may interfere with the isotopic measurements. The sample was filtered a second time to remove the activated charcoal. The stable oxygen and hydrogen isotopic analyses were completed using an LGR<sup>®</sup> DLT-100 with an LC-PAL liquid autosampler. High salinity samples were diluted with deionized water prior to the analysis in order to prevent the salts present in the sample from precipitating and plugging the instrument tubing. ..... 169

Figure 6.4 - Flowback water TDS for the study sites plotted as a function of the cumulative volume of flowback collected (Owen, 2017). a) Site A wells – upper Montney Formation; b) Site B wells – upper Montney Formation; c) Site D wells – upper (well D-1 and well D-2) and middle (well D-3 and well D-4) Montney Formation; d) Site E and Site F wells – middle Montney Formation; e) Site G and Site H wells – middle (well G-1) and upper (well H-1) Montney Formation; f) Site I wells – lower Montney Formation.

Figure 6.5 - Relationship between major ions in the Montney Formation flowback water. a) Na-Cl plot; b) Ca-Mg plot. The linear relationship between the major ions suggests mixing between two endmembers – the injected hydraulic fracturing fluid with relatively low TDS and the high TDS formation water. The three samples with elevated Cl concentrations at site B are from well B-1 at the end of the

Figure 6.15 - Variation in SO<sub>4</sub> in flowback water (left plot) with cumulative flowback. Red dot is the produced water SO<sub>4</sub> after a minimum of one year of production. Right plot is CO<sub>2</sub> and H<sub>2</sub>S mole fraction of produced gas vs time of sample collection. H<sub>2</sub>S values that plot on the x-axis are where analyses were

made but the result at or below detection limit. The letter corresponds to the well location in Figure 6.1.

Figure 6.21 - Regional variation of concentration of H<sub>2</sub>S in Montney produced gas......226

Figure 6.25 - Dissolved SO $_4$ and Cl in Montney produced water. The red dot is modern (~2680 mg/l) and the dashed red line is a projected SET	seawater 232
Figure 6.26 - Variation in concentration of dissolved SO $_4$ with depth	232
Figure 6.27 - Concentration of SO $_4$ in Montney produced water	233
Figure 6.28 - Contours of SO4/CI molar ratio	234
Figure 6.29 - Relationship between $H_2S$ in solution and $H_2S$ in produced gas shown on log	-log scale. 235

Figure 8.1 - Regional distribution of hydrogen sulphide production from the Montney Formation.

Figure 8.5 - Map view of the layer containing the wellbore showing (left) the pressure distribution and (right) the mole fraction of  $H_2S$  in the reservoir after 50 years of production......272

Figure 8.6 - Gas mole fraction of  $CH_4$  and  $H_2S$  for models with TOC of 1% and 7% with  $H_2S$  concentrations of (a) 5%, (b) 15%, and (c) 1%, showing the cross-overs between  $CH_4$  and  $H_2S$ .....274

Figure 8.7 - Production rate of (a) H<sub>2</sub>S and (b) CH<sub>4</sub> for the six models......275

Figure 9.2 - Location of wellbores samples and analysed, and public data used in this study on a map of the Doig subcrop area and shaded relief topographic backdrop map, with main structural lineaments (after Berger et al., 2008) and outline of fields on which the Doig sampled wells are located.

Figure 9.4 - Photomicrographs of representative lithologies of the upper Doig Formation in planepolarized light. Porosity is blue in thin sections. Green box shows location of detailed image. Pie chart represents mineral volumes from XRD converted from weight using reference density values from Serra (1990) and normalized to include porosity and TOC content. (A) Sample TB1: siltstone with quartz (Qt), Kfeldspar (KF) and plagioclase grains with corroded borders, quartz overgrowth (QO), dolomite (Do) and siderite cement, interstitial pyrite (Py), and abundant intergranular porosity. (B) Sample CZ4: siltstone with grain dissolution and calcite and dolomite cementation and overlying laminated mudstone with quartz and feldspar grains in a clay (CI) matrix. (C) Sample HM2: very fine sandstone composed mostly of quartz grains with corroded borders, sparse apatite (Ap) grains, pervasive grain dissolution and interstitial dolomite cement. (D) Sample TG1: heterolithic laminated siltstone and mudstone with quartz, feldspar and sparse apatite grains, clay matrix, and calcite (Ca) and dolomite cement, as well as a calcite vein offset by a clay lamination (E) Sample CD9: bio-wackestone with quartz, and feldspar silt matrix, calcite, and dolomite cement, as well as almost complete dissolution of bioclasts, creating moldic porosity and partial filling by quartz. (F) Sample TG5: siltstone with quartz, feldspar, and sparse apatite grains, with calcite and dolomite cement, interlaminated with clay-rich laminae.............287

Figure 9.8 - Cross-plot of porosity versus absolute gas permeability at in-situ net confining stress, with marker colored by lithotypes of Gamero-Diaz (2012) based on mineralogy, size by common logarithm of median pore throat diameter from MICP and shape by plug orientation with respect to bedding. Lines of the relation between permeability and porosity based on the Kozeny-Carman equation for pore

Figure 9.9 - Cross-plots of common logarithm of permeability versus net confining stress for all core plugs at different stresses, for the various lithotypes of Gamero-Diaz (2012) and colored accordingly. Measurements of the same sample at different net confining stresses are represented by the same symbols and connected by a linear regression line. The slope of the line is proportional to the sensitivity of permeability to stress. The same symbols connected by a line represent the same sample measured at different stresses.

Figure 9.13 - Variation in weight percent mineralogy by XRD through the Montney Formation. .299

Figure 9.19 - Lily Pad wells, north Montney area. Note the condensate production in the 200D well.

Figure 9.21 - Plots of pore throat diameter vs porosity volume derived from MICP with the P10, P50 and P90 pore size provided for sample of varying depth in metres. The graphs show how the sample void volume is distributed amongst pores of indicated size. Corresponding well log provided in Figure 9.20.

Figure 9.23 - Variation in porosity, permeability, and mineralogy through the cored interval $309$
Figure 9.24 - Relationship between mineralogy and porosity. The trend line and correlation coefficient plotted is for quartz alone
Figure 9.25 - Gas-brine capillary pressure curves and corresponding saturation associated with the indicated pore throat size distribution
Figure 9.26 - Production data for the 13-26 well. The well has produced significant condensate and gas but with an associated consistently high water cut ( $\approx$ 70%)
Figure 9.27 - Gas composition plotted with the overlying Barnett Shale trend. Modified from Glemser et al. (2019)
Figure 9.28 - Presumed migration pathways of gas into the Ante Creek – Waskahigan pools based on gas iC4/nC4/methane ratios. Modified from Glemser et al. (2019)
Figure 9.29 - Variation in porosity, pore size (p10, p50 and p90 from MICP) and permeability in the upper Montney in the 103/13-23-63-24W5 well
Figure 9.30 – Cross-plot of porosity and permeability. Colors correspond to different Waskahigan wells. The green dots are the 13-23 well data plotted in Figure 9.29
Figure 9.31 - Upper Montney in Well 12-7-64-23W5 showing variation in lithology, mineralogy (XRD) and capillary pressure from MICP. Note the abundance of authigenic quartz and dolomites in the SEM images
Figure 9.32 - Variation in pore throat distribution (cumulative and incremental from MICP) of samples for the 12-7 well
Figure 9.33 - Variation in permeability with effectives stress following Dean Stark core plugs from the 12-7 well
Figure 9.34 - Oil-Water capillary pressure vs saturation of the wetting phase (brine) and pressure translated to height above the free water level
Figure 9.35 - Example of production profile of a Waskahigan well (4-7-64-23W4). The extreme water cuts are interpreted to reflect contribution from wet porous and permeable sands interbedded with sands with higher oil saturation
Figure 9.36 - Montney Formation- conventional reservoir in Kahntah. Capillary pressure of gas-brine vs saturation of wetting phase, and porosity and permeability, production history and well log
Figure 9.37 - Conventional Montney reservoir porosity and permeability vs the P10, P50 and P90 pore size diameter (pore throat) in nanometers
Figure 9.38 - Absolute porosity versus permeability of samples from the Montney and Doig formations. Only confined permeability data is shown, which has been normalized to an effective stress of 33 MPa (4800 psi) where possible. The colours correspond to different wells. The low porosity green dots are from the Doig Formation in the Graham strike area
Figure 9.39 - The variation of P50 pore throat diameter, in nanometers, from MICP with porosity.

Figure	e 9.40 - Variation in	permeability wit	h P50 pore:	throat	diameter	in nanometers	from	MCIP.
Permeability	y measured at effect	ive stress of 33 N	/IPa (4800 p	sia)				326

Figure 9.43 - Comparison of gas-brine capillary pressures in the upper most Montney facies at wells at Kahntah (left) and Karr (right). The dashed curves are from Kahntah and solid curves are from Karr.

# List of Tables

Table 3.1 - Parameters used in the estimation of total  $H_2S$  currently within the Montney Formation.

Table 5.1 - Mineralogy from X-ray diffraction and Rietveld analyses for of the 4 wells, WA# 30876,3944, 8183 and 29453.152

Table 6.2 - Summary of pH, conductivity, total alkalinity, TDS, and major ion concentrations in the flowback waters collected in the study. Data for wells at the same site and completed within the same member of the Montney Formation are grouped. For the TDS and the major ions, lower values for all wells are from earlier in the flowback period, while higher values are from later in the flowback period. .....176

Table 6.3 - Summary of the hydraulic fracturing fluid and formation water chemistry. The formation water chemistry is based on the median values for the produced water samples collected in the present study (sites A, B, and I) and produced waters from nearby wells with publicly available results (sites D-H).

Table 6.4 - Summary of proportions of formation water contributing to the flowback water for the conservative tracers used in the study. The minimum value is early in the flowback period, while the maximum value is late in the flowback period. A –  $\delta^{18}$ O values excluded as the values were interpreted to be contaminated by organics that were not removed by the activated charcoal treatment. B – isotopic values are potentially contaminated, as the mixing ratios calculated using the isotopes do not agree with those calculated using the CI concentrations.

Table 6.6 - Well H1. Measured chemistry of raw fluids and leachate following 7 days at 78 °C. EC. = conductivity. TDS= total dissolved solids, DO- dissolved oxygen. All compositional data is in mg/L......193

Table 6.8 - Well B. Measured chemistry of leachate following 7 days at 76 °C. EC.= conductivity. TDS = total dissolved solids, DO = dissolved oxygen. All compositional data is in mg/L......200

	Table 7.1 -	Langmuir	parameters	derived	from	type	curve	and curves	interpolated	to	other	тос
value	s based on t	ype curves										.256

Table 8.1 - The input parameters used during the modelling. The first Langmuir	pressure is for 1%
TOC and the second corresponds to 7% TOC	
Table 8.2 - Original gas (OGIP) and water in place (OWIP) (m <sup>3</sup> ) and original mass of	of $CH_4$ and $H_2S$ (kg)
absorbed in the model	

Table 9.2 - Upper - Interfacial tension between produced water and oil for various upper Montney.
Waskahigan wells. Lower variation in contact angle of produced oil and produced water on samples from
12-7 well

## 1. Executive Summary

Two of the major issues facing upstream and midstream operators and regulators in developing some unconventional reservoirs in Western Canada are the presence of trace to significant amounts of hydrogen sulphide (H<sub>2</sub>S) in produced gas and the seemingly inexplicable vertical/stratigraphic zonation and yield of producible hydrocarbon liquids.

The Doig and Montney formations are an unconventional to hybrid petroleum system that provide significant contributions to the national energy portfolio. For example, the Montney Formation provided a significant proportion (34%) of natural gas to the total Canadian gas production in 2017 (NEB, 2018). This petroleum system is complex with initial formation of petroleum being generated in deeper western areas where secondary cracking of the hydrocarbons to drier gases migrated updip and mixed with insitu, wetter petroleum in less mature areas to the east. The mixing of the petroleum from more mature sources changes the hydrocarbon composition and can reduce the confidence in the prediction of hydrocarbon composition based on its relationship to basin-scale maturation trend (i.e., Wood and Sanei, 2016). This is further complicated by regional structures, such as the Peace River Arch, Fort St John Graben, Hay River Fault Zone, and the Laurier Embayment areas that modify depositional and subsidence rates as well as the depth of burial that affects the regional maturation trends and the generation of hydrocarbons. Chapters 3 and 4 illustrate the workflow that is needed to understand complex interactions between basin evolution, regional structural activity, sedimentation patterns, total organic carbon content and type, maturation trends, as well as in-situ versus migrated hydrocarbon compositional trends to aid the prediction of the expected hydrocarbon composition. This prediction will help operators define the most efficient operations and development program to maximise profits and increase sustainability of the energy resource. Chapter 3 provides a workflow on mapping the essential elements to determine the petroleum system processes at play across the basin. Chapter 4 provides the workflow and tools needed to understand why hydrocarbon composition departs from the regional maturation correlation. Chapter 4 also illustrates the effective use of hydrocarbon geochemistry, particularly isomer ratios, to calculate an excess methane content (%), and when mapped, highlight areas that have seen migration of deeper, shorter-chained hydrocarbons (i.e., methane) into less mature areas.

Hydrogen sulphide ( $H_2S$ ) is a highly toxic, non-hydrocarbon gas found within some petroleum systems.  $H_2S$  gas is harmful to humans and the environment and, due to its highly corrosive characteristics, can increase operational costs as more expensive, sour specification infrastructure needs to be implemented. The  $H_2S$  distribution within the Montney Formation is highly variable. The majority of Montney producing wells are sweet gas (i.e., zero percent  $H_2S$ ); though more recently, operators have drilled sour Montney wells that can produce alongside sweet wells on the same multi-well pad. The concentration of  $H_2S$  is much lower in British Columbian Montney producers (< 1%) than is observed in Alberta Montney producers (> 1%) which can point to different processes at play. Researchers (i.e., Liseroudi et al., 2020) using sulphur isotopic data have concluded for Montney producing wells in Alberta that deep seated faults and fractures have provided conduits for sulphate and/or  $H_2S$  gas to migrate from deeper sulphur sources in the Devonian strata. Chapter 5 provides an effective workflow using sulphur isotopic, SEM and XRD analyses to understand the cause of souring in Montney producing wells in BC. This workflow has shown that the source of sulphur for the majority of British Columbian souring wells may have come from Triassic rocks; the Charlie Lake Formation is the likely source due to its close proximity and high concentration of anhydrite in its evaporite facies. The process is somewhat complex, and we present a geological model that suggests the sulphate-rich fluids have migrated from the Charlie Lake Formation prior to hydrocarbon generation in the Montney Formation and has concentrated in discrete zones due to precipitation in conduits like fracture and fault systems.

SEM analysis confirms massive anhydrite within the Montney Formation that is likely from infilled fractures. The anhydrite in the fractures is most likely the source of the sulphur that reacts with the generated hydrocarbons to form H<sub>2</sub>S gas. The model fits the observation of very discrete sour zones within the Montney Formation and both sweet and sour wells producing on the same multi-well pad in British Columbia (BC). The sulphur isotopic analysis from northeast British Columbia indicates that the sulphur isotopic range for Triassic anhydrite is the same as the  $H_2S$  sulphur that is produced from the Montney Formation. The deeper sources in the Devonian are enriched in <sup>34</sup>S and are not the likely source for sulphur. There are several wells that show a slightly heavier isotopic signature (18 to 20 ‰ <sup>34</sup>S) in the produced gas that are in close proximity to the deformation front and may have deep-seated faults that acted as a conduit for Devonian sulphur to migrate into the Montney Formation. The use of threedimensional seismic data is essential in any workflow but was not used in this study due to the nature of seismic acquisition by third party companies and the difficulty in obtaining these data for scientific studies such as this project. Chapter 5 provides a workflow that operators can follow that will aid the risk management of encountering sour wells when developing the Montney Formation. Operators will need access to three-dimensional seismic data that will provide maps on structural features which can then be overlain with the distribution of the Charlie Lake Formation. Combining these maps with the sulphate ion concentrations in connate water of the Montney Formation will provide a robust risk map for the souring potential across their development lands. In Chapter 6, the distribution of sulphate and other major ions in Montney and Doig formations flowback and produced waters are determined to provide insights into the origin and distribution of H<sub>2</sub>S in produced gas and nature of the connate water. The impact of fluidrock interactions of produced fluids is determined through the use of aging-leach experiments carried out at reservoir temperature, using surface area to volume ratios anticipated during completion. The sulphate content of most produced Montney waters generally ranges from 50 mg/L to about 300 mg/L, although many exceptions occur. The variation in sulphate concentrations in produced water and the coeval production of H<sub>2</sub>S and CO<sub>2</sub> gas are complex, and in many wells unclear. For some wells, there are trends of increasing or decreasing H<sub>2</sub>S and CO<sub>2</sub> gas production with time, while in other wells there are no consistent trends.

In Chapter 7, the sorption gas capacity is quantified for representative Doig and Montney mudstones. At reservoir conditions for a mudstone with 2-3% total organic carbon, the sorbed gas represents about 20% of the reservoir gas. Since H<sub>2</sub>S has five to six times the sorption affinity and capacity of methane, it is selectively retained in the sorbed state until later in the reservoir's life when the critical desorption pressure is reached. Due to much higher solubility of H<sub>2</sub>S in brines than CH<sub>4</sub>, ( $\approx$  10,000x), high water cuts during production will be associated with higher H<sub>2</sub>S concentrations if H<sub>2</sub>S is present in the system. In Chapter 8, the metrics derived in Chapter 7 are used to study the impact of varying gas contents

and initial concentrations of H<sub>2</sub>S on the producibility of H<sub>2</sub>S through a series of 3D reservoir models based on a Montney shale gas reservoir. The models consider the confounding impacts of gas storage (solution, free and sorbed) that are dynamic with production, and the impact of different gas diffusivities. In Chapter 9, the regional petrophysical properties of the Doig and Montney formations in Alberta and BC are investigated to determine the controls on the distribution and production of H<sub>2</sub>S and hydrocarbon liquids. Reservoir properties in the Doig and Montney formations are controlled by a complex interplay between depositional environment, diagenesis, and mechanical compaction. Using capillary pressures determined by mercury intrusion tests and wettability and interfacial tensions measured on Montney fluids, conventional and unconventional reservoir facies are readily differentiated. Upper Montney conventional reservoirs have low critical pressures and required a trap and seal to retain hydrocarbons whereas in the lateral continuous unconventional reservoirs, the reservoir is self-sealing due to high capillary pressures.

### 1.1. Prelude and Acknowledgements

#### 1.1.1. Prelude

Geoscience BC provided funding towards a three-year research study designed to determine the distribution and origin of H<sub>2</sub>S in unconventional reservoirs and producible liquid hydrocarbons. The study also supported, in part, by industry partners (EnCana/Ovintiv, Crew Energy, Saguaro, AGAT, Chevron Canada, Pacific Canbriam). The initial industry downturn beginning in 2018 and the COVID-19 pandemic beginning in March 2020 have had a continuing impact on the study, as initially proposed. COVID-19 has had a direct impact on the mental and physical health of some of the researchers involved in the study and has impacted the moral work habits of all. Nevertheless, the study progressed well in terms of meeting the broad objectives and anticipated deliverables as outlined in the original application. During the course of the study, two of industry partners (Saguaro and Canbriam) ceased to exist due to takeovers or mergers and Ovintiv divested many of their assets that were relevant to this study. The main impact of COVID-19 has been in the laboratory component of the study since both our UBC labs and third-party labs that we were using for isotope and petrophysical analyses were shuttered completely or operating at a fraction of capacity since March 2020. Additionally, the combination of closure or partial closure of the government core repositories and Provincial and UBC enforced travel and field work restrictions meant that access to samples for the graduate student research was constrained. The combined impact of the industry slowdown, company corporate changes, and COVID-19 has resulted in our industry partners being less engaged than was anticipated; however, we have managed to keep our partners informed and most have been forthcoming in providing in-kind support and intellectual guidance. In recognition of the impact of COVID-19 on the research, Geoscience BC extended the end date, unfunded, of the study to December 31, 2021.

#### 1.1.2. Acknowledgements

The studies reported and the students and other highly qualified people trained in preparing this report would not have been possible without the financial support of Geoscience BC, NSERC and our industry partners Chevron Canada, Ovitniv (EnCana), AGAT Laboratories, Crew Energy, Canbriam (Pacific

Canbriam Energy), Saguaro Resources (Tourmaline Oil) and RMB Earth Science Consultants. We also thank Progress Energy (Petronas Canada) and particularly Matthew Adams for logistical support and access to data and sharing of ideas. We are also indebted to Travis Hobbs of Ovitniv for access to data that would not have been otherwise accessible. R. Bustin thanks Tangle Creek for the opportunity to work on their Waskahigan Montney and permission to present and utilize some of the data. This study would not have been possible without software donations to UBC by Geologic (Geoscout), IHS and Schlumberger for which we thank them. We express our great thanks to CMG for the ongoing support of our research through access to their software and supporting engineers.

Significant contributions to the studies summarised in this report were made by the thesis research of Jennifer Owens, Andrea Sanlorenzo, Scott Hazel, Kris Mitchener, Mark LeMessurier, and Katherine Lazaruk.

This report was improved by some of the comments of three anonymous reviewers and by careful editing by Geoscience BC.

## 2. Introduction

Understanding and predicting the presence and amount of producible hydrogen sulphide (H<sub>2</sub>S) and hydrocarbon liquids is a critical aspect to the economic development of unconventional plays (i.e., Compton et al. 2017). In Western Canada, the presence of H<sub>2</sub>S and hydrocarbon liquids is a major consideration in valuing resources, reserves, and production, and in the design of mid-stream facilities (i.e., Adams, 2016). The lack of prior knowledge of the presence and abundance of H<sub>2</sub>S and hydrocarbon liquid yields results in operational inefficiencies and higher operating and capital expenditures. Additionally, H<sub>2</sub>S bearing produced gas (sour gas) is one of the most important environmental risks, hazards, and challenges as well as being a principal concern of stakeholders.

Important unconventional reservoirs in the Western Canadian Sedimentary Basin (WCSB), including the Montney and Doig formations, have no, to variable amounts of H<sub>2</sub>S and hydrocarbon liquids. Hydrogen sulphide in produced gas, even in trace amounts, impacts the economics of drilling, production, treatment, and marketing of gas and associated liquids. The occurrence of H<sub>2</sub>S in produced fluids is also one of the most important environmental hazards and risks to development. The aerial and stratigraphic distribution of H<sub>2</sub>S and hydrocarbon liquids in these unconventional reservoirs is complex and, in some areas, seemingly inexplicable. Additionally, during production, the gas may progressively sour, or if initially sour, may sweeten. In some areas there is a complex distinct stratigraphic zonation of H<sub>2</sub>S and hydrocarbon liquids from buoyancy and fluid gravity.

The origin, distribution, abundance, and producibility of reservoir H<sub>2</sub>S and hydrocarbon liquids in conventional and unconventional reservoirs in Western Canada is clearly complex (i.e., BC Oil and Gas Commission, 2008; Bustin and Bustin, 2016) and hence hard to predict. Based on studies and inferences to date, the origin of  $H_2S$  in many areas of the WCSB, superficially at least, is in part inexplicable;  $H_2S$  varies laterally, stratigraphically, and during production. In some areas, H<sub>2</sub>S is high enough that specialised sour drilling, production, and mid-stream facilities are required, whereas in other areas the abundance of H<sub>2</sub>S is low enough that it can be treated (sweetened) at the well site, while in other areas, H<sub>2</sub>S is absent. The amount of H<sub>2</sub>S in the produced fluids may also change with time; the produced gas might be initially sweet and the gas may progressively sour through production, or the reverse may occur; the initial production may be sour and the gas will sweeten through time. It is anticipated that the origin of the  $H_2S$  may include: migration from thermal-chemical sulphate reduction (TSR) from deeper formations (or when the reservoir was at higher paleotemperature), bacterial sulphate reduction, cracking of sulphur rich kerogen, and potential oxidation of sulphate or break down of drilling and completion additives (Goldstein and Aizenshtat, 1994; Mougin et al., 2007; Hubbard et al., 2014; Pirzadeh et al. 2014). Thus, understanding and predicting the distribution of  $H_2S$  requires a multifaceted approach that includes the study of basin thermal and structural history, organic- and inorganic-chemistry of the source rocks, reservoirs, migration pathways and fluids, as well as an understanding of diffusion, solution, and adsorption of H<sub>2</sub>S.

In the Montney and Doig formations, although the spatial variation in hydrocarbon liquids is in general predictable from regional maturation trends (Bustin and Bustin, 2016; Euzen et al., 2021 and many others), in detail the variation in producible hydrocarbon liquids in many areas is exceedingly complex.

Most notably in the Montney Formation there are pools where hydrocarbon liquids and gases are complex, vertically stratified, and their distribution does not conform to hydrocarbon gravity, creating unique challenges in optimizing completions and production. In some areas, the H<sub>2</sub>S distribution mimics the hydrocarbon liquid stratification, suggesting a related causality.

In order to predict the distribution and abundance as well as to anticipate production rates of H<sub>2</sub>S and hydrocarbon liquids in produced fluids from unconventional reservoirs, a multi-faceted, multi-year study has been undertaken with support from Geoscience BC, NSERC and industry partners. The study was designed with milestones designed to meet both short-term and longer-term exploration and development needs of industry and for environmental management. The purpose of the study was to aid in understanding and predicting the distribution of sour gas and hydrocarbon liquids, which in turn will help industry focus exploration through identification of sweet spots, and better plan upstream and midstream development that is compatible with anticipated produced fluid composition. One of the aspirations of the study was to integrate our work with colleagues working on a parallel study of the genomics of the introduced or indigenous sulphate-reducing bacteria, however, the colleagues' study did not materialize.

This study met our objectives, but we have not answered all the questions to our satisfaction. The problem is exceedingly complex with confounding variables at play. We trust that our results, which will be detailed in forthcoming papers and presentations as well as this report, will motivate and assist others to continue to unravel the very complex distribution and producibility of H<sub>2</sub>S and liquid hydrocarbons. We hope the study can assist the Crown in providing stewardship of the resources and for evaluating and mitigating the environmental impact of sour gas and liquids development. The authors would be pleased to present an overview of the study to stakeholders in the study area who are concerned about the risks and hazards, when such a presentation becomes possible.

This report is divided into seven major sections corresponding to the main deliverables of the study. We have also appended some critical data, and published papers that provide greater depth on some elements related to the study. Our deliverables in chapters 3, 4 and 5 include detailed mapping of produced gases and liquids and isotopic analysis together with maps of H<sub>2</sub>S distribution and abundance. These chapters describe the generation and migration of gases and liquids. Chapter 6 discusses the distribution of sulphate and major ion distribution mainly for the Montney Formation. Chapter 7 describes the sorbed gas capacity of different gases on the Montney and Doig formations and the potential importance of sorption differential production of H<sub>2</sub>S and other gases. In Chapter 9, we describe the petrophysical properties of the Montney and Doig formations in attempt to better understand the productivity of different zones and distribution and production of liquid hydrocarbons, H<sub>2</sub>S and carbon dioxide (CO<sub>2</sub>).

#### 2.1. Previous Work

The formation of H<sub>2</sub>S in conventional reservoirs and oil sands processing has been exhaustively studied. There are numerous review papers including the excellent articles by Machel (2001) and Marriott et al. (2016). Hydrogen sulphide can originate from the reservoir biomass (and additives during drilling and completion) or from sulphate containing minerals via microbial sulphate reduction (MSR) or thermochemical sulphate reduction (TSR). Numerous papers have addressed H<sub>2</sub>S distribution in the Paleozoic strata in the WCSB including the classic review paper by Hutcheon et al. (1995).

There is very little public data on H<sub>2</sub>S in unconventional shale petroleum systems. Hydrogen sulphide however, does occur in important amounts in unconventional resources including the Eagle Ford, Permian, Wolfcamp, and Duvernay formations. Some recent notable studies include those of Dubois et al. (2014) on the spurious distribution of H<sub>2</sub>S in some Eagle Ford shale wells, Chalmer's (2016) study on souring of Duvernay wells in Alberta and the theoretical studies by Xia and Ellis (2016, 2017) on mudstones of the Permian Basin. The recent studies by Xia and Ellis (2016, 2017) on the Permian Basin are excellent and include many of the types of modelling techniques that will be utilised in this study.

The importance of H<sub>2</sub>S and its economic impact and risk to development of unconventional shale reservoirs in Western Canada is well documented in company reports (i.e., Seven Generations Energy, 2020; NGI, 2017), investor presentations, the press (The Globe and Mail, 2009; Seeking Alpha, 2017), and reports by regulators (BC Government, 2005, 2016). As operators continue to expand their developments away from core areas in B.C, there is now a realization that sour risking needs to be part of their workflows to help mitigate any souring of the Montney play as even minor contamination (i.e., ppm) will need to be treated before entering pipeline infrastructure. This report contains workflows that can be adopted by operators looking to derisk their acreage as they begin developing unrisked lands in terms of souring potential.

Research is limited on the changes in hydrocarbon composition across the entire Montney Formation play area. The composition of hydrocarbons varies both spatially and stratigraphically with liquids-rich hydrocarbons found in all stratigraphic zones, but in discrete locations (Euzen et al., 2021). Kirste et al. (1997) used dry gas index (DGI) to map the distribution of hydrocarbon composition for the Montney Formation. On a regional scale, the hydrocarbon composition follows the maturation trends with the driest gas compositions (methane rich) found in areas that have experienced the deepest burial and highest reservoir temperatures (Kirste et al., 1997). More detailed research has been conducted on the second and third order variations in hydrocarbon composition that are at the scale of operator's acreages. Wood and Sanei (2016) utilised the isomer ratio of butane (i.e.,  $iC_4/nC_4$ ) to highlight the migration of methane from deeper sections of the Montney Formation (proximal to deformation front) to the wetter areas to the east. The authors speculate that the methane has migrated along localised lithological changes in the Montney Formation; however, they have not petrophysically examined these areas. The geochemical fingerprint of hydrocarbons appears to be a powerful tool that can help unravel the complexities due to the degree of mixing of in-situ and ex-situ hydrocarbons. More research is needed to determine the role petrophysical changes have on the zonation of hydrocarbon composition. This report will utilise these novel techniques to examine distributions of hydrocarbons across the entire Montney Formation play area.

# 3. Geology and Geochemistry of the Doig and Montney Formations

## 3.1. Abstract

The geology and geochemistry of the Doig and Montney formations were investigated for both Alberta and British Columbia play areas. Key parameters for understanding a complex petroleum system like the Montney-Doig play include changes in thickness, depth of burial, mass balance calculations, timing and magnitudes of paleotemperature exposure, as well as kerogen concentration and types to determine the distribution of hydrocarbon composition, H<sub>2</sub>S concentrations and CO<sub>2</sub> concentrations. Results show that there are first-, second- and third- order variations in the maturation patterns, caused by heat flow patterns and varying amounts of eroded section, which impact the hydrocarbon composition. The compositional changes in produced fluids are also impacted by migration of shorter-chained hydrocarbons (i.e., methane) from deeper, more mature areas proximal to the deformation front. Hydrogen sulphide is observed to be laterally discontinuous and found in discrete zones or pockets. The location of higher concentrations of H<sub>2</sub>S in the Montney do not align with the sulphate-rich facies of the Charlie Lake Formation but can be seen to underlie areas of higher sulphate ion concentrations in the formation water. There is some alignment between  $CO_2$  and  $H_2S$  in the Montney, particularly south of Dawson Creek, however the cross-plot of CO<sub>2</sub> and H<sub>2</sub>S illustrates some deviation away from any correlation and there must be other processes at play (i.e., decomposition of kerogen or carbonate dissolution).

### 3.2. Introduction

In recent years, exploration and development has focused on the gas shale-tight gas hybrid play of the Lower Triassic Montney and Doig formations in northeastern British Columbia. For Triassic strata in the Alberta Basin, conventional oil in place is estimated at 800 million barrels and gas in-place estimated at nearly 10 TCF (Edwards et al., 1994). Unconventional gas in-place estimates are between 220 and 342 TCF (Silva, 2021) for the Doig Formation and between 3,197 and 5,405 TCF for the Montney Formation (NEB, 2013). Gas recoveries have been estimated from decline curve analysis for the upper Montney play in Dawson Creek area to be an average of 4.7 BCF per well for a ten-year period (Burke and Nevison, 2011).

Hydrocarbon composition in the Montney Formation not only varies in the first order, following the regional maturation trends of the Triassic across the Western Canadian Sedimentary Basin, but are also impacted on a higher frequency by changes in paleo-heat flow, migration along higher permeability fairways and large structural elements like the Fort St. John Graben (Bustin and Bustin, 2016; Wood and Sanei, 2016; Euzen et al., 2021). To better understand the hydrocarbon compositional changes, i.e., drier gas zones versus liquids-rich gas zones, the mapping of geochemical variations in the produced hydrocarbons has shown promise in distinguishing between in-situ generation of hydrocarbon in a true

unconventional reservoir and the mixing the hydrocarbon from both in-situ and ex-situ generation of hydrocarbons (Wood and Sanei, 2016; Euzen et al., 2021).

As production increases from the Montney Formation in British Columbia, more wells are coproducing non-hydrocarbon gases like H<sub>2</sub>S and CO<sub>2</sub> (Kirste et al., 1997). The distribution of these nonhydrocarbon gases can be inexplicable with multi-well pads showing both sweet and sour gas production. This report has investigated the potential processes to why the Montney Formation has such localised changes in the sweet and sour gas distribution across the Montney play in British Columbia.

### 3.3. Geological Background

The Montney, Doig and Halfway formations were long considered to have been deposited along a passive continental margin and consist of a westward thickening, siliciclastic, prograding wedge (Edwards *et al.*, 1994; Davies, 1997; Walsh *et al.*, 2006; Dixon, 2009; Furlong et al., 2018). More recently, a tectonically influenced model for the deposition during the Middle Triassic (Golding et al., 2015), and forearc basin configuration starting during the Early Triassic and persisting through the Middle Triassic (Rohais et al., 2016) have been proposed.

The Montney, Doig and Halfway formations represent the first and second of three transgressiveregressive (T-R) cycles that deposited the Triassic strata in northeastern British Columbia (Gibson and Barclay, 1989; Edwards et al., 1994). The depositional setting for the Montney and Doig formations is described as an open shelf marine environment (Edwards et al., 1994). The palaeoenvironmental setting for the Halfway Formation is considered as barrier island shoreface clastics and coquinas (Edwards et al, 1994). Palaeogeographic reconstruction for Triassic sedimentation suggests a palaeoshoreline that prograded during sea level regressions to just east of the Fort St. John and the Alberta/BC border (Kent, 1994). During this time, shallow shelf muds covered the eastern part of the basin with deeper marine muds deposited to the west.

The Montney Formation unconformably overlies Carboniferous or Permian strata and consists of variable amounts of interbedded mudstone, siltstone, and sandstone. Strata of the Montney Formation developed during the first of three major transgression-regression cycles. Within British Columbia, Dixon (2000) subdivided the Montney Formation into the lower siltstone-sandstone and the upper mudstone members based on lithostratigraphy. Members are separated by a basin-wide unconformity that developed due to tectonic uplift of the basin margin (Dixon, 2009). The mudstone member is absent within Alberta and progressively becomes thicker (up to 159 m) towards the foothills of British Columbia to the west (Dixon, 2000).

North of the study area, Utting et al. (2005) subdivided the Montney Formation into two T-R couplets which correlate with the siltstone-sandstone and mudstone members of Dixon (2000). The upper Montney mudstone member is more organic-rich and radioactive than the lower Montney siltstone-sandstone member (Dixon, 2000). The Montney Formation was deposited within an inner to distal shelf setting (Edwards et al., 1994) which varied from tempestites in distal shelf to mudstones and deltaic/shoreline sandstones at the eastern margin (Edwards *et al.*, 1994). More recently, the Montney Formation has been subdivided based on sequence stratigraphic analyses and consists of an upper,

middle, and lower units (Davies et al., 2018). These subdivisions more or less correlate with the siltstonesandstone and mudstone members by Dixon (2000). This project has used the subdivisions of Davies et al. (2018) to identify any stratigraphic differences in H<sub>2</sub>S and hydrocarbon composition distributions.

On the western portion of the basin, the offshore to lower shoreface sediments of the Sunset Prairie Formation lie unconformably on the Montney Formation (Furlong et al., 2018). Where the Sunset Prairie Formation is absent, the Doig Formation rests directly on the Montney. The lower contact of the Doig Formation with the Montney and with the Sunset Prairie formations is also unconformable (Golding et al., 2015; Furlong et al., 2018). The Doig, Halfway and Charlie Lake formations correspond to the second T-R cycle. The Doig Formation thickens southwestwards from the eastern zero edge towards the foothills to a maximum thickness of 229 m in the Hudson Hope low region southwest of Fort St. John. In this study, to simplify descriptions and comparisons, the Doig Formation is subdivided into Doig A, B and C based on lithological differences and is similar to the informal subdivisions by Davies (1997): the lowermost phosphate zone (Doig A), middle siltstone (Doig B); and the upper-regressive coarsening-upward sequence (Doig C). Doig A is a highly radioactive unit that consists of phosphatic nodules and granules within argillaceous siltstone, interbedded with calcareous siltstone and dark-grey shale (Riediger et al., 1990). Doig B is medium to dark grey argillaceous siltstone and shale which locally contains a thick shoreface sandstone (up to 25 m; Evoy, 1998). Doig C varies from siltstone to fine sandstone, and near the upper boundary it transitions from the argillaceous Doig sandstone informal unit to the overlying cleaner Halfway Formation sandstone (Evoy, 1998).

The Doig Formation was deposited in a distal to mid shelf setting during a marine transgression. The Doig A and B were deposited in a distal shelf distal shelf setting with the Doig B sandstone being interpreted as deltaic to shoreface environment (Harris and Bustin, 2000). Doig C is interpreted to have been deposited in a proximal shelf to lower shoreface environment. The arid conditions that prevailed during the Triassic and consequent lack of chemical weathering is reflected in the low clay content and narrow range of grain size of the Doig Formation (Zonneveld et al., 2011; Crombez et al., 2014). The Doig Formation is overlain by the prograding beach barrier sandstones of the Halfway Formation. The thickness of the Halfway Formation is less than 60 m within the Farrell area of the foothills and, similarly to the Doig Formation, the Halfway Formation tapers out towards the east into central Alberta (Edwards et al., 1994). The Halfway Formation consists of predominantly quartz arenite with dolomite and anhydrite cements and locally important coquinas (Edwards et al., 1994; Dixon, 2008).

Diagenetic processes are important influences on reservoir quality of the Doig and Montney formations. Dolomite, ankerite, calcite, quartz and anhydrite are common cements within the Montney Formation in west-central Alberta (Davies et al., 1997). The Doig B sandstone contains a combination of calcite, quartz, dolomite, and anhydrite cements (Harris and Bustin, 2000). Interpretation of the paragenesis of the Doig sandstone, shows late diagenetic secondary porosity (inter- and intragranular and moldic) formed by dissolution of earlier calcite cement and quartz framework grains (Harris and Bustin, 2000).

Structural features located within the study area consist of asymmetrical pull-apart grabens with failed arms, shallow fault systems that developed during the Laramide thrusting and deeper basement

faults that follow the basement terranes (Berger et al., 2008; Figure 3.40 this study). Graben faults within the Peace River Embayment were active during the Triassic, which affected the deposition of the Montney and Doig formations. It has been argued that structural lineaments exert some control on the location of sweet spots in the conventional and unconventional Montney and Doig plays, through the formation of localized thickened sections and migration pathways (Berger et al., 2009).

### 3.4. Results

The results have been sub-divided into Montney and Doig Formations, which include the structure, thickness (isochore), organic geochemistry, maturation trends, basin analysis, hydrocarbon and associated gases geochemistry and composition. The results are discussed to provide information on how the Montney and Doig formations generated hydrocarbons and non-hydrocarbon gases. This will aid operators in the development of this prolific energy resource of Canada.

#### 3.4.1. Montney Formation

#### 3.4.1.1. Structure and Isochore

The Montney structure and isochore were mapped from well logs obtained from geoLOGIC's Geoscout software, based on stratigraphic picks of Davies et al., (1998). The subcrop area of the Montney Formation to the northwest of the fold and thrust belt forms an elongated belt extending over a maximum of 250 km and dipping to the southwest (Figure 3.1). The top and base structures of the Montney Formation are sub-parallel and follow the general southwesterly dip trend of the Phanerozoic in the basin (Figure 3.1). The present-day subsea elevations of the top of the Montney Formation range from 200 m in the northeastern part of the subcrop, near the border between British Columbia and Alberta, to 3,200 m along the southwestern limit of the deformation front. The structure on top of the Montney Formation is significantly shallower to the northwest of the Fort St. John Graben, where it forms a plateau immediately west of Fort St. John, that does not exceed 1,500 m of subsea elevation.

The isochore thickness of the Montney Formation generally increases towards the deformation front (Figure 3.2). However, there is an increase in the thickness south of the Fort St. John area due to the active subsidence of the Fort St. John Graben structure during the Triassic. Thickness remains consistent in most parts of the basin, with the exception of the areas north of latitude 57° and west of longitude 122° which may be due to large-scale structural features related to the Laurier Embayment (Berger et al., 2008; Figure 3.41, this study). Four areas are shown in Figure 3.1 that show the change in the lithological characteristics of the Montney Formation over the entire play area and this is illustrated by the type logs for areas 1-3 Figure 3.2 to Figure 3.5.

The thickness of the upper Montney Formation, as defined on the type logs in Figure 3.2 to Figure 3.5, indicate that significant thickness (greater than 50 m) is limited to the proximity of the deformation front and within the Fort St. John Graben areas (Figure 3.6). The upper Montney is either very thin or absent in the majority of Alberta. The majority of the Montney Formation thickness is within the middle Montney, which ranges from 50 to 250 m across most of the British Columbia and Alberta play areas

(Figure 3.7). The thickest part of the middle Montney is west of Fort St. John and Grand Prairie and runs parallel to the deformation front. The middle Montney thins towards the subcrop to the east, towards Peace River and High Prairie. The lower Montney thickness varies between 120 and 0 m. Similar to the upper Montney, the lower Montney is absent or very thin in Alberta with the exception of localised depocentres (Figure 3.8). The lower Montney also thins towards the eastern margins of the Montney Formation subcrop area in Alberta.


## **Upper Montney Top Structure**

Figure 3.1 - Location map and structure on top of the Montney Formation, as mapped by this study.



### **Total Montney Thickness**

Figure 3.2 - Thickness distribution of the Montney Formation, as mapped by this study. The impact of the Fort St. John Graben (see Figure 3.40 and Figure 3.41) is shown by the localised thickening of the Montney Formation in the Fort St. John and Dawson Creek areas (red and orange shaded contours).



Figure 3.3 - Montney type log for area 1 (TVD = true vertical depth, GR = gamma ray, AT60 = deep resistivity).

	200C078C094H0500			
Halfway	TVD 1:1817	Gamma	Density	Resistivity
	1362 1380	W) Hay ( Jos	A Martin	James Con
Doig	1420 1420	ally provide the	And and a second second	A MAN
Upper Montney	1460		hours	My m
Middle Montney	1500	and fulling the	المالية وماليب بال	and the second second
	1540	disting in the		Come Print, og
	1580	- Z	an mark	and a
Lower Montney	1600 1620	الدهر الاكاسانيد يبدرون وال		14 Denserver and a faith
	1660 1680 1700	All the Red Store and	MARAN CANADA	man have
Belloy	1720	E	huke	

Figure 3.4 - Montney type log for area 2 (TVD = true vertical depth).



Figure 3.5 - Montney type log for area 3 (MD = measured depth, GR = gamma ray, RHOZ = bulk density).



# **Upper Montney Thickness**

Figure 3.6 - Thickness distribution of the upper Montney Formation, as mapped by this study.



# **Middle Montney Thickness**

Figure 3.7 - Thickness distribution of the middle Montney Formation, as mapped by this study.



# **Lower Montney Thickness**

Figure 3.8 - Thickness distribution of the lower Montney Formation, as mapped by this study.

### 3.4.1.2. Thermal Maturity

The thermal maturity indicator, Tmax (Espitalie, 1977), was mapped for the Montney Formation. Tmax values were obtained from the public domain and reviewed for consistency within each well and for regional agreement. Data outside of the reasonable range expected for Tmax between 400 to 550 °C was discarded. South of Dawson Creek, in the overmature area, Tmax measurements are unreliable, and converted vitrinite reflectance data from Wood and Sanei (2016) were used instead. In the south corner of the subcrop area, around Hinton, data are sparse, and the map is based on vitrinite reflectance data published by the Alberta Energy Regulator (Rokosh et al., 2012) was used as a guide. A vitrinite reflectance to Tmax correlation based on Petersen (2002) was used.

The regional trend of thermal maturity is generally subparallel to the basin axis, increasing to the southwest towards the eastern limit of the deformation front (Figure 3.9). Thermal maturity trend deflections from the current depth of burial, such as the overmature areas south of Dawson Creek and in the southern edge, around Hinton, are caused by second and third-order controls, such as variable amounts of eroded section, variations in the heat flow patterns as well as large structural features like the Fort St. John Graben (Euzen et al., 2021). Maturity trends impact the hydrocarbon composition of the Montney Formation and the ability for  $H_2S$  to generate by thermochemical sulphate reduction (TSR) reactions (if sulphate is present in reservoir), as well as the thermal limitations to bacterial sulphate reduction (BSR) process (pasteurization temperatures, < ~80 °C).



**Montney Thermal Maturity Tmax** 

Figure 3.9 - Distribution of the thermal maturity indicator Tmax on the Montney Formation. Changes in the maturation trends within the Fort St. John area (to cooler blue colours and lower maturity) is due to the Fort St. John Graben structures (see Figure 3.40) impacting the maturation process.

### 3.4.1.3. Total Organic Carbon and Kerogen

The total organic carbon (TOC) content in the Montney Formation ranges from 0.1 to 12%, with a 10th percentile of 0.4%, a median of 1.2% and a 90th percentile of 2.7% (Figure 3.10). These statistics are based on ten thousand Rock-Eval analyses from the public domain (Riediger, 1990; Snowdon, 1997; Fowler and Snowdon, 1998; Fowler and Snowdon, 2001; Faraj et al., 2002; Ibrahimbas and Riediger, 2004; Fowler et al., 2007; Walsh and McPhail, 2007; Chalmers and Bustin, 2012; Rokosh et al., 2012; Ferri et al., 2013; Romero-Sarmiento et al., 2016). The geographic distribution of TOC suggests higher organic richness against the western thrust and fold belt boundary (Figure 3.11), where the upper Montney Formation is thicker and has higher gamma ray and higher resistivity. Along the eastern edge, particularly in the southeast, there are areas of higher TOC content, which are likely due to the low thermal maturity in these regions, and consequently lower kerogen transformation ratios (i.e., present day TOC content remains higher due to lower transformation to hydrocarbons). The geographic distribution of TOC content, however, is based on point data from sample analysis, and therefore is biased according to more heavily sampled locations and stratigraphic intervals.

The Montney Formation is predominantly composed of kerogen Type II and III, with a hydrogen index of up to 750 mg HC/g TOC (Figure 3.12). The Montney Formation median HI is 38 mg/g TOC, with a 10th to 90th percentile range between 11 and 207 mg/g TOC, while the median OI is 18 mg/g TOC, with a 10th to 90th percentile range between 6 and 52 mg/g TOC. The HI decreases in a trend that approximately follows thermal maturity, from 460 mg HC/g near the eastern edge, to less than 20 mg HC/g in the overmature central western and southwestern regions (Figure 3.13). A kerogen reaction kinetics model (Figure 3.14) was created based on an average of kerogen Types II and III from the Doig Formation, as described in detail in Silva and Bustin (2020). The median activation energy is 52 kcal/mol, with a pre-exponential factor of  $1.81 \times 10^{25}$ /Ma.

The combination of higher TOC content and lower HI content along the western edge adjacent to the deformation front indicates that this area would have generated the largest volumes of hydrocarbons in the Montney Formation, and at some stage or over several stages during the generation of these hydrocarbons, the volumes would have been too large to be retained by the self-sourcing reservoir and migrated up dip to other parts of the Montney Formation in the east, forming a more conventional hydrocarbon system (i.e., oil-water contact).



Figure 3.10 - Total organic carbon (TOC) content histogram for the Montney Formation.



# **Total Montney Total Organic Carbon**

Figure 3.11 - Total organic carbon distribution of the Montney Formation.



Figure 3.12 - Pseudo-van Krevelen plot of Montney Formation Rock-Eval analyses.



# **Total Montney Hydrogen Index**

Figure 3.13 - Distribution of hydrogen index in the Montney Formation.



Figure 3.14 - Kerogen activation energy distribution used in the Montney Formation basin model.

### 3.4.1.4. Burial and Thermal History

A reconstruction of the burial and thermal history of the Montney Formation was conducted through basin modelling using the Schlumberger PetroMod software. Publicly available regional heat flow data (Majorowicz et al., 2005; Tuya Terra Geo Corp and Geothermal Management Company, 2016) were used to map present-day heat flow. The post-Laramide heat flow distribution (60 Ma) was calculated as 90% of the present-day heat flow, based on estimates by Bachu and Cao (1992). A constant heat flow of 55 mW/m2 was assumed for the Cambrian, based on an average for the North American continent (Allen and Allen, 1990).

The burial history is divisible into seven chronological phases with similar net subsidence rates (Figure 3.15; Silva, 2021). The first phase, ranging from the Cambrian to the Middle Devonian, is characterized by very low subsidence rates in the order of 3 m/Ma. During this time, sedimentation was limited to the northern part of the basin with little to no net deposition in the south. In the second phase,

from the Upper Devonian through the Mississippian, subsidence rate associated with the development of a carbonate platform increased to a maximum of 30 m/Ma. The highest subsidence rates in this interval are in the north of the study area, with thinning of strata towards the south.

In the third phase, after an uplift during the Pennsylvanian, sedimentation resumed from the Permian through most of the Early Cretaceous at steady but relatively low rates of between 3 and 6 m/Ma. A few erosional unconformities with generally less than 200 m of missing section, and hiatuses occur throughout this period across the entire region, but with very little impact to depth of burial. During this time, significant localized variations in relative subsidence rates occurred. With the collapse of the Peace River Arch and the Dawson Creek Graben Complex faults reactivation in the Triassic (Brack et al., 1987; Barclay et al., 1990; Davies, 1997; Eaton et al., 1999), the Peace River Embayment becomes the depocentre; net subsidence rates in the western central part of the basin are twice as high as towards the northern, southern, and eastern edges. In the Peace River Embayment depocentre, subsidence rates during the Triassic are as high as 15 m/Ma.

The fourth phase occurred during the Albian stage of Early Cretaceous, during the deposition of the Mannville and Fort St. John Groups, when the entire region subsided at much increased rates of 50 to 90 m/Ma. During this stage of the foreland, subsidence rates were relatively uniform across the region. In the fifth phase, during the earlier stages of Late Cretaceous the locus of sedimentation switched to the south, which continued subsiding at similar rates, while the north part of the basin was starved of sediments. In the sixth phase, between the Late Cretaceous and the Paleogene, the entire region underwent a marked further increase in burial rates associated with the foreland subsidence. Net subsidence rates in this phase vary from 140 m/Ma in the northern and eastern edges of the study area to 390 m/Ma in the southwest. In the last phase, the basin has undergone exhumation at rates of 50 to 80 m/Ma, starting in the Paleogene with the post-Laramide uplift to Quaternary isostatic rebound from the removal of the ice sheets that covered much of the North America until the end of the Pleistocene.

The maximum paleo-burial depth of the Montney Formation throughout the basin history is located south of Dawson Creek, near the eastern limit of the thrust and fold belt in British Columbia. In this region, the base of the Montney Formation reached a depth of 8,600 m (Figure 3.16 and Figure 3.17), prior to 60 Ma, when the post-Laramide event began uplifting these strata to its present-day depth of 3,500 m. The maximum temperature of the Montney Formation during this time ranged from 100 to 235°C, according to depth of overburden and regional variations in heat flow. The depocentre of the basin migrated southeast during the Late Cretaceous and Paleogene, towards its present location in central-western Alberta (Figure 3.18, Figure 3.19 and Figure 3.20).



Figure 3.15 - Burial history of the basin at a location immediately south of the Noel field in BC, highlighting the Montney Formation, and showing temperature,  $H_2S$  yield, maturity, and transformation ratio as overlays (respectively from top to bottom).



### Lower Montney Maximum Burial Depth

Figure 3.16 - Maximum depth of burial of the lower Montney Formation.



### **Upper Montney Maximum Burial Depth**

Figure 3.17 - Maximum depth of burial of the upper Montney Formation.



Figure 3.18 - Cross-section along stratigraphic dip of the basin, showing the burial at different times, highlighting the Montney Formation. Facies legend shown below.



Figure 3.19 - Cross-section along stratigraphic strike of the basin, showing the burial at different times, highlighting the Montney Formation. Facies legend shown below.





### 3.4.1.5. Petroleum Generation

The onset of hydrocarbon generation in the studied area of the Western Canadian Sedimentary Basin (WCSB) occurred in the Pennsylvanian, when the Paleozoic Duvernay and Exshaw source rocks entered the oil window (Figure 3.21). Although they entered the generation window during the Pennsylvanian, the Duvernay and Exshaw formations did not reach peak hydrocarbon generation until the end of the Early Cretaceous, due to the low subsidence rates between the end of the Paleozoic and the end of the Jurassic, which resulted from the migration of the basin depocentre after the collapse of the Peace River Arch. The Triassic Doig and Montney formations started generating hydrocarbons at 101 Ma (Figure 3.22), and the Jurassic Gordondale Member, at 94 Ma. The Cretaceous source rocks of the Wilrich Member, Shaftesbury Formation and Colorado Group entered the oil window at 85, 72 and 60 Ma, respectively. The Montney Formation reached peak oil generation along most of the western boundary adjacent to the fold and thrust belt, at 85 Ma (Figure 3.23). From the end of Cretaceous to Paleocene, between 72 and 60 Ma, due to the rapid foreland subsidence in the southwest, wet gas generation in the Montney Formation started throughout most of southwest, and dry gas started in the deepest areas (Figure 3.24 and Figure 3.25). During the Eocene, at approximately 50 Ma, a portion of the Montney Formation in the southwest reached the late dry gas window, with complete kerogen transformation ratio (Figure 3.26) before thermal maturation was frozen by the rapid uplift and exhumation of Paleogene sediments.



Figure 3.21 - Petroleum generation of the source rocks simulated in the basin model, showing the onset and plateauing of generation.



### Middle Montney Transformation Ratio 101 Ma

Figure 3.22 - Kerogen transformation ratio in the middle Montney Formation at 101 Ma.



### Middle Montney Transformation Ratio 85 Ma

Figure 3.23 - Kerogen transformation ratio in the middle Montney Formation at 85 Ma.



### Middle Montney Transformation Ratio 72 Ma

Figure 3.24 - Kerogen transformation ratio in the middle Montney Formation at 72 Ma.



### Middle Montney Transformation Ratio 60 Ma

Figure 3.25 - Kerogen transformation ratio in the middle Montney Formation at 85 Ma.



### Middle Montney Transformation Ratio 0 Ma

Figure 3.26 - Present day kerogen transformation ratio in the middle Montney Formation.

### 3.4.1.6. Thermochemical Sulphate Reduction and Gas Analyses

The potential for thermochemical sulphate reduction (TSR)  $H_2S$  generation in the Montney Formation was assessed through basin modelling. Two sources of sulphur were considered, seawater and generated petroleum. A sulphate (SO<sub>4</sub>) content of the average seawater for the Montney pore water, and 1% sulphate by weight of sulphur in petroleum were assumed. The central western and southwestern portions of the Montney Formation are at higher risk of H<sub>2</sub>S generation by TSR from generated petroleum (Figure 3.27). Based on a lower temperature threshold for TSR of 120 °C (Goldstein and Aizenshtat, 1994; Mougin et al., 2007), the lower Montney Formation entered the TSR phase in its central western portion (located at the centre of the Peace River Embayment) by approximately 100 Ma (Figure 3.28 and Figure 3.29), although it did not start generating significant quantities of H<sub>2</sub>S until 72 Ma. The southwest entered the TSR phase later, at approximately 85 Ma. The TSR generation region expanded relatively slowly until 75 Ma, and then abruptly in the southwest until 70 Ma, as the focus of deposition and subsidence shifted south. The entirety of the lower Montney Formation was within the TSR zone by 60 Ma. As Paleogene sediments were eroded and the basin uplifted, the eastern half of the Montney Formation area remained in the TSR for less than 40 Ma (Figure 3.30). Exhumation rates were lower in the southwest, where the Montney Formation had entered the TSR between 75 and 95 Ma, and so the Montney Formation did not exit the TSR zone in this region until at least 20 Ma. Progressively deeper strata exited the TSR region towards the southwest, where a relatively small area currently remains at temperatures above 120°C. When considering a lower temperature threshold for TSR of 100°C, the western half of the Montney subcrop area entered the TSR phase by 80 Ma and remained for at least 60 Ma until 20 Ma before present (Figure 3.31 and Figure 3.32).

A mass balance comparison of present-day H<sub>2</sub>S estimated from the Montney Formation gas analyses and the total H<sub>2</sub>S yield estimated by thermal sulphate reduction suggests that thermal sulphate reduction can account for all of the H<sub>2</sub>S currently found in the Montney Formation. The total mass of H<sub>2</sub>S estimated to have been generated by thermal sulphate reduction is 2.10x10<sup>16</sup> g, assuming 1 wt.% sulphur content in petroleum and a sulphate concentration of seawater (0.0282 mol/m<sup>3</sup>) in connate water. For the present-day H<sub>2</sub>S volume, a reservoir volumetric model of the Montney Formation was constructed using the structure maps, assuming an average porosity of 2% and an average gas saturation of 50%. Gross rock volume and hydrocarbon pore volumes were estimated from the model, and an estimate of total H<sub>2</sub>S mass was made using the gas analysis maps (Table 3.1). The total  $H_2S$  mass of 6.88x10<sup>14</sup> g estimated by this method, is thirty times lower than the mass of H<sub>2</sub>S estimated to have been generated by thermal sulphate reduction in the Montney Formation. On the other hand, the estimated mass of sulphur held in pyrite in the Montney Formation is 7.02x10<sup>17</sup> g, assuming 2% pyrite by weight, an average matrix density of 2.68 g/cm<sup>3</sup> and 2% average porosity. This mass is much larger (by a factor of 35) than the mass of sulphur estimated to have been generated in the form of H<sub>2</sub>S during TSR (6.88x10<sup>14</sup> g; i.e., 94% of the mass of TSR-generated H<sub>2</sub>S). This suggests pyrite acted as a major sink for sulphur generated through thermal reduction of organic matter and sulphate in connate water, and that there was likely another source for the sulphur in the  $H_2S$  currently found in the Montney Formation. The chapter on the origin of  $H_2S$  gas in the Montney Formation will examine the potential sources of sulphur in anhydrite from the Muskeg, Doig and Charlie Lake formations.

Anhydrite from the Charlie Lake Formation is potential source of sulphate for the hydrogen sulphide found in the Montney Formation reservoir. The Charlie Lake Formation first entered the TSR zone at 90 Ma in the southwest region, south of Dawson Creek (Figure 3.33) and was progressively buried under the 120°C isotherm towards the southwest until reaching the maximum depth of burial at 60 Ma. During the uplifting associated with the removal of the Paleogene section, progressively deeper sections were uplifted above the TSR zone. The southwestern portion of the Charlie Lake, where evaporite facies are more abundant, remained below the 120°C thermocline until 30 Ma, for a total of 50 Ma (Figure 3.34). This area approximately coincides with the area where higher concentrations of hydrogen sulphide are found in the Montney Formation (Figure 3.35). Assuming a 120°C threshold for the reduction of inorganic sulphate, it is plausible that anhydrite from the Charlie Lake was at least partially responsible for souring in the Montney Formation.

The H<sub>2</sub>S gas distribution in the Montney Formation was mapped from public data obtained from the British Columbia Oil and Gas Commission (BCOGC) and the Alberta Energy Regulator (AER). The distribution is complex and represented by many bullseye patterns across the play areas due to its localised distribution (Figure 3.35), which implies that souring of the Montney Formation is due to structural or stratigraphic control. There are many areas of the Montney Formation that have produced sweet hydrocarbons in Alberta and British Columbia, and there are locations that have not been tested yet as illustrated by the lack of cross symbols in Figure 3.35 in some areas. The highest concentrations of H<sub>2</sub>S from Montney Formation production and downhole samples are found in the more central location north and west of Grande Prairie (Figure 3.35 to Figure 3.38), instead of in the southwestern region that remained longer in the TSR zone which would have, in theory, potentially generated greater amounts of H<sub>2</sub>S. This may imply, for areas of higher H<sub>2</sub>S gas concentrations in Alberta, that the gas has migrated laterally, from the deeper and hotter regions where it was generated, to its present location or from deeper, older H<sub>2</sub>S sources like in the Devonian strata. Liseroudi et al. (2020) interpreted that high H<sub>2</sub>S concentrations in Alberta Montney producers was due to migration of deeper Devonian sources of H<sub>2</sub>S gas. Furthermore, the mapping of TSR potential assumes that there is a uniform supply of sulphate for the production of H<sub>2</sub>S across the play area in the Montney Formation, which does not seem to be the case; otherwise, there would be more consistent souring of the Montney Formation as operators drill and produce their wells. In fact, there are multi-well pads that can have sweet and sour wells within hundreds of metres of each other (Figure 3.39). This indicates very localised differences in the sulphate concentrations in the Montney Formation and can only be explained by structural controls of sulphate ion or H<sub>2</sub>S gas migration.

The majority of sour gas in the Doig Formation is found in the regions north of Fort St. John and east of Dawson Creek (Figure 3.80), updip of the area with significant potential TSR generated gas. If the source of the Doig Formation H<sub>2</sub>S is TSR from Triassic strata, this implies that H<sub>2</sub>S migrated updip from the area that actively generated H<sub>2</sub>S between 95 and 75 Ma through the network of faults that connect these areas or has been sourced from anhydrite within the DPZ which contains anhydrite within phosphatic nodules (Figure 5.8). During the time of most active TSR, only approximately a quarter of the total amount of hydrocarbons generated from the Doig Formation had been generated, most of which had not undergone secondary migration by that time.



### **Montney Petroleum Generation H2S Yield**

Figure 3.27 - Distribution of  $H_2S$  yield from thermochemical sulphate reduction during petroleum generation in the Montney Formation.



Figure 3.28 - Petroleum and TSR H<sub>2</sub>S generation curves in the Montney Formation through geologic time.

Table 3.1 - Parameters used in the est	imation of total H	$H_2S$ currently v	within the I	Vontney
For	rmation.			

Gross rock volume (m <sup>3</sup> )	2.35x10 <sup>13</sup>
Hydrocarbon pore volume @ NTP (m <sup>3</sup> )	3.35x10 <sup>13</sup>
H <sub>2</sub> S volume (m <sup>3</sup> )	4.52x10 <sup>11</sup>
H <sub>2</sub> S molar volume (mols)	2.02x10 <sup>13</sup>
H <sub>2</sub> S mass (g)	6.88x10 <sup>14</sup>



### Lower Montney Thermochemical Sulphate Reduction Entry

Figure 3.29 - Lower Montney Formation thermochemical sulphate reduction entry age map, considering 120°C as the lower boundary.



### **Upper Montney Thermochemical Sulphate Reduction Exit Age**

Figure 3.30 - Upper Montney Formation thermochemical sulphate reduction exit age map, considering 120°C as the lower boundary.



Lower Montney TSR (100 °C) Entry Age

Figure 3.31 - Lower Montney Formation thermochemical sulphate reduction entry age map, considering 100°C as the lower boundary.


## Lower Montney TSR (100 °C) Exit Age

Figure 3.32 - Lower Montney Formation thermochemical sulphate reduction exit age map, considering 100°C as the lower boundary.



#### Charlie Lake Thermochemical Sulphate Reduction Entry Age

Figure 3.33 - Charlie Lake thermochemical sulphate reduction entry age map.



#### Charlie Lake Thermochemical Sulphate Reduction Exit Age

Figure 3.34 - Charlie Lake thermochemical sulphate reduction exit age map.



#### **Total Montney H2S**

Figure 3.35 - Distribution of  $H_2S$  on the entire Montney Formation, based on public data obtained from AER and BCOGC.

#### **Lower Montney H2S**



Figure 3.36 - Distribution of  $H_2S$  on the lower Montney Formation.

### **Middle Montney H2S**



Figure 3.37 - Distribution of  $H_2S$  on the middle Montney Formation.

#### **Upper Montney H2S**



Figure 3.38 - Distribution of  $H_2S$  on the upper Montney Formation.



Figure 3.39 - Sweet and sour wells on multi-well pads in the British Columbia Montney Formation play area. The distribution of Montney Formation sour production can be inexplicable with sweet and sour wells occurring in adjacent horizontal wells that are only hundreds of metres away. This observation indicates that the H<sub>2</sub>S within the Montney Formation needs to have a structural control with either the migration of sulphate from overlying or underlying anhydrite source or by migration of H<sub>2</sub>S gas.

Migration of sulphate is thought to be through fault networks, from either the overlying evaporites of the Charlie Lake Formation or from underlying strata (i.e., Devonian Muskeg Formation). Possible migration pathways through structural lineaments connecting the deeper parts of the basin to the areas of high H<sub>2</sub>S can be seen in Figure 3.40 and Figure 3.41. This will be further explored with isotopic analyses in the chapter of the origins of H<sub>2</sub>S gas below. The sulphate ion concentration measured from the formation water of Triassic strata (Figure 3.42; Kirste et al., 1997) shows the sulphate ions have migrated along strike or updip away from the Charlie Lake anhydrite source. The sulphate ion has been removed from the anhydrite by solution processes and migrated into the central part of the basin (Figure 3.42). The sulphate has also been seen to have migrate out of the Charlie Lake Formation and into the Halfway and Doig Formations (i.e., Sharma, 1965; Harris, 2000) as well as into the Montney Formation (this study, see

chapter on origins of  $H_2S$  gas below). This indicates that it may not be just the current location of the overlying Charlie Lake (Figure 3.43) that poses the largest risk to souring in the Montney Formation, but potentially the distribution of sulphate in the formation water that has migrated along strike or updip, as seen in Figure 3.42.



Figure 3.40 - Map of the first vertical derivative of the magnetic anomaly from Miles and Oneschuk (2016), showing discontinuities interpreted as faults, and Montney H<sub>2</sub>S contours displayed for reference. Fault interpretations indicate possible updip migration pathways for the H<sub>2</sub>S generated at greater depths.



### **Montney and Doig Structural Elements**

Figure 3.41 - Structural elements that may have an influence on the Doig and Montney formations across the Western Canada Sedimentary Basin (Silva, 2021).



Figure 3.42 - The sulphate ion concentration in formation water in Triassic strata that shows the occurrence of sulphate solution migrating along strike and updip from the anhydrite formation; this corresponds well with the locations of  $H_2S$  with produced fluids of the Montney Formation (modified from Kirste et al., 1997).



**Montney H2S and Charlie Lake Anhydrite Facies** 

Figure 3.43 - Distribution of  $H_2S$  on the entire Montney Formation and overlay of anhydrite facies from the Charlie Lake Formation. It is the distribution of the sulphate ions (Figure 3.42) from solution processes on the Charlie Lake that is responsible for the  $H_2S$  distribution and not the location of the anhydrite itself as the sulphate in the formation water has migrated updip from the Charlie Lake Formation.

The gas dryness ratio ( $C1/\Sigma C1-C5$ ) is the methane fraction divided by the sum of the total methane to pentane hydrocarbon fraction, inclusive, of each gas sample. The gas dryness ratio decreases from almost completely dry gas in the overmature central-western and southwestern areas of British Columbia, to between 0.6 and 0.8 across the central part of the basin, increasing again towards the east, to above 0.9 (Figure 3.44). The gas wetness increases in areas within the hydrocarbon generation window of oil (Tmax between 445 and 460 °C). However, there are some discrepancies in the relationship between gas dryness and maturation across the Montney Formation, and this is further explored in the chapter on hydrocarbon composition below. The zone of dry gas in the deepest part of the basin reflects the overmaturity in this region (Tmax higher than 490°C). Secondary cracking of wetter gases and longchained hydrocarbons occur in this region and produce large volumes of methane. The same gas dryness pattern is observed when mapping the upper, middle, and lower Montney Formation subzones individually (Figure 3.45 to Figure 3.47). The zone of relatively higher gas wetness ratio located between the Triassic subcrop edge and the deformation front flanked on both sides by dry gas regions has been noted for Triassic reservoirs in the WCSB by Desrocher (1997). The author suggested this distribution pattern may be caused by mixing of updip migrated of thermally generated gas at greater depths containing higher alkanes, with shallower biogenic gas. Alternatively, gases generated by oil-prone sapropelic, and gas-prone humic kerogens may also be mixed to create a complex distribution. Further discussion can be found in the chapter on hydrocarbon distribution in the Montney Formation below.

The iC4/nC4 isomer ratio for butane (Figure 3.48) and the iC5/nC5 isomer ratio of pentane (Figure 3.49) were mapped for the Montney Formation in both British Columbia and Alberta. These geochemical signatures are used as a proxy for maturation processes and the ratio should increase with increasing maturity of the reservoir fluids (Wood and Sanei, 2016; Euzen et al., 2021). In most cases, the ratio iC4/nC4 ratio increases towards the deformation front (Figure 3.48) as indicated by the symbols becoming larger and lighter blue and green colours. Some data points have ratios greater than five and may be due to erroneous readings or other geological processes. Further investigation into these anomalies is needed. The ratio between the isomers iC5/nC5 of pentane shows similar trends (Figure 3.49) with increasing ratio with towards the deformation front. These two isomer ratios (iC4/nC4 and iC5/nC5) of produced hydrocarbons reflect the overall trend of increasing maturation towards the deformation front and show that the in-situ generation of hydrocarbon in a self-sourced reservoir is the dominant process of hydrocarbon generation in the Montney Formation. Areas that show migration of drier hydrocarbon from more mature areas to wetter hydrocarbon areas are further discussed in the chapter on hydrocarbon composition of the Montney Formation below.

Distribution of CO<sub>2</sub> is distinct from H<sub>2</sub>S; higher concentrations of CO<sub>2</sub> (>2%) are restricted to the deeper parts of the basin (Figure 3.50 to Figure 3.53), where it reaches up to 18%. The origin of CO<sub>2</sub> in sedimentary basins without metamorphic or volcanic episodes could be related to dissolution of carbonate minerals during diagenesis, a by-product from H<sub>2</sub>S generation or breakdown of Type III kerogen. When comparing the distribution of H<sub>2</sub>S and CO<sub>2</sub> in the Montney Formation, there is a log-linear correlation for regions with a high ratio (>5) of H<sub>2</sub>S to CO<sub>2</sub> (Figure 3.54). These regions are located around the Grande Prairie area, where the H<sub>2</sub>S concentrations are more elevated (Figure 3.54 to Figure 3.56). This area is also flanked to the northwest and southeast by areas of elevated CO<sub>2</sub> and low H<sub>2</sub>S. Considering the

cogeneration of  $CO_2$  and  $H_2S$  through reduction of sulphate in anhydrite, there may have been either updip migration of the  $H_2S$  generated in the high  $CO_2$  southwest and northwest areas; or the  $CO_2$  in those areas is not associated with thermal sulphate reduction, but instead due to decomposition of kerogen or limestone dissolution.



### **Total Montney Gas Dryness Ratio**

Figure 3.44 - Distribution of gas dryness ratio on the entire Montney Formation.



## Lower Montney Gas Dryness Ratio

Figure 3.45 - Distribution of gas dryness ratio on the lower Montney Formation.



## Middle Montney Gas Dryness Ratio

Figure 3.46 - Distribution of gas dryness ratio on the middle Montney Formation.



## **Upper Montney Gas Dryness Ratio**

Figure 3.47 - Distribution of gas dryness ratio on the upper Montney Formation.



### Montney Thermal Maturity Tmax and iC4/nC4 Ratio

Figure 3.48 - Distribution of thermal maturity in the Montney Formation and bubble map overlay of iC4/nC4 ratio.



## Montney Thermal Maturity Tmax and iC5/nC5 Ratio

Figure 3.49 - Distribution of thermal maturity in the Montney Formation and bubble map overlay of iC5/nC5 ratio.



## **Total Montney Carbon Dioxide**

Figure 3.50 - Distribution of CO<sub>2</sub> on the entire Montney Formation.



## Lower Montney Carbon Dioxide

Figure 3.51 - Distribution of CO<sub>2</sub> on the lower Montney Formation.



## **Middle Montney Carbon Dioxide**

Figure 3.52 - Distribution of  $CO_2$  on the middle Montney Formation.



## **Upper Montney Carbon Dioxide**

Figure 3.53 - Distribution of  $CO_2$  on the upper Montney Formation.



Figure 3.54 - Cross-plot of the spatial distribution of  $CO_2$  versus  $H_2S$  in the Montney Formation, colored by the ratio between  $H_2S$  and  $CO_2$ , highlighting the correlation that exists only in the high  $H_2S$  area (> 5%).



Figure 3.55 - Three-dimensional map showing the  $CO_2$  gas concentrations for the Montney Formation across BC and Alberta.



Figure 3.56 - Three-dimensional map showing the  $H_2S$  gas concentrations for the Montney Formation across BC and Alberta.

#### 3.4.2. Doig Formation

#### 3.4.2.1. Structure and Isochore

The subcrop area of the Doig Formation to the northeast of the fold and thrust belt forms an elongated belt extending over a maximum of 180 km and dipping to the southwest (Figure 3.57). The top and base structures of the Doig Formation are sub-parallel and follow the general southwesterly dip trend of the Phanerozoic in the basin. The present-day subsea elevations of the top of the Doig range from 200 m in the northeastern part of the subcrop, near the border between British Columbia and Alberta, to 2,700 m along the southwestern limit of the deformation front (Figure 3.57). The structure to the top of the Doig Formation is significantly shallower to the northwest of the Fort St. John Graben, where it forms a plateau immediately west of Fort St. John, that does not exceed 1,500 m of subsea elevation. This shallowing of the strata has reduced the maturation over this area.

The upper Doig Formation and the Doig Phosphate Zone (DPZ) were mapped separately for this study (after Silva, 2021), based on well logs obtained from geoLOGIC's Geoscout software. Overall, the Doig Formation thickens southwestwards from the eastern zero edge towards the deformation front to a maximum thickness of 229 m in the Hudson Hope low region southwest of Fort St. John. Besides thinning towards the eastern edge, the Doig Formation also thins towards the north and south. In the northeastern edge, the Doig Formation and the overlying Halfway Formation are eroded by the Late Triassic Coplin unconformity. On the southeastern edge, the entire Triassic interval is erosionally thinned by a pre-Jurassic unconformity and the Doig Formation is overlain directly by Fernie Group strata. The isochore maps of the DPZ, upper Doig Formation and Halfway Formation display distinct patterns and trends in the distribution and orientation of depocentres (Figure 3.58 to Figure 3.61). The DPZ has a mean thickness of 22 m, abruptly thickening to a maximum thickness of 89 m in the Hudson Hope low region, southwest of Fort St. John. The upper Doig Formation has a mean thickness of 46 m and a maximum thickness of 185 m, also in the Hudson Hope low area. The cross-sections show the variability of the Doig Formation in both strike (Figure 3.60) and dip (Figure 3.61) orientations. The increased thickness within the strikeorientated cross-section is due to increased accommodation space in the Fort St. John Graben that was active during the deposition of the Doig and Montney formations.

### **Doig Top Structure**



Figure 3.57 - Structure map of the top of the Doig Formation (Silva, 2021).



#### **Doig Phosphate Zone Thickness**

Figure 3.58 - Thickness distribution of the Doig Phosphate Zone (Silva, 2021).

# **Upper Doig Thickness**



Figure 3.59 - Thickness distribution of the upper Doig Formation (Silva, 2021).



Figure 3.60 - Cross-section of the Doig Formation along stratigraphic strike (Silva, 2021). See Figure 3.57 for location.



Figure 3.61 - Cross-section of the Doig Formation along stratigraphic dip (Silva, 2021). See Figure 3.57 for location.

#### 3.4.2.2. Thermal Maturity

The thermal maturity indicator, Tmax (Espitalie, 1977), was mapped for the Montney Formation. Tmax values were obtained from the public domain and reviewed for consistency within each well and for regional agreement. Data outside of the reasonable range expected for Tmax between 400 to 550 °C was discarded. The regional trend of thermal maturity is generally subparallel to the basin axis and approximately follows the contour lines of the current depth of burial, increasing to the southwest towards the eastern limit of the deformation front (Figure 3.62). The hydrocarbon generation windows are interpreted based on a mixture of kerogens Type II and III, following the boundaries from Dow (1977)

for Type II, and Petersen (2002) for Type III kerogen. Approximately 80% of the total subcrop area, including the region of Grande Prairie in western Alberta and the regions of Fort St. John and Dawson Creek in northeastern British Columbia, is currently in the immature to late oil window of hydrocarbon generation (Tmax between 435 and 470 °C), depending on whether Kerogen Type II or Type III is assumed. The westernmost 20% of the subcrop area is in the wet to dry gas generation window (Tmax between 470 and 525 °C). If kerogen Type II is assumed, only slightly over 1% of the area has reached the dry gas windows (Tmax higher than 525 °C). For Type III kerogen the dry gas window reaches about 10% of the subcrop area 10% (Tmax higher than 490 °C).



## **Doig Thermal Maturity Tmax**

Figure 3.62 - Doig thermal maturity Tmax distribution map (Silva, 2021).

#### 3.4.2.3. Total Organic Carbon and Kerogen

The total organic carbon (TOC) content in the Doig Formation ranges from 0.1 to 12%, with a 10th percentile of 0.4%, a median of 1.7% and a 90th percentile of 4.3% (Figure 3.63). The upper Doig Formation has a median TOC of 1.3 wt.% and a 10th to 90th percentile range between 0.4 and 2.9 wt.%, whereas the DPZ has a median of 2.7 wt.% and a 10th to 90th percentile range between 1.1 and 6 wt.%. The maximum TOC in the upper Doig Formation is 8.4 wt.%, while in the DPZ the TOC content reaches 12.19 wt.%. These statistics are based on 2,600 Rock-Eval analyses from the public domain (Riediger, 1990; Snowdon, 1997; Fowler and Snowdon, 1998; Fowler and Snowdon, 2001; Faraj et al., 2002; Ibrahimbas and Riediger, 2004; Fowler et al., 2007; Walsh and McPhail, 2007; Chalmers and Bustin, 2012; Rokosh et al., 2012; Ferri et al., 2013; Romero-Sarmiento et al., 2016).



Figure 3.63 - Total organic carbon content histogram for the Doig Formation.

For the Doig Formation, well log-derived TOC content curves were calculated for over 840 wells, according to the method outlined by Carpentier et al. (1991), with coefficients calibrated to the laboratory analyses. The mean well log-derived TOC in the DPZ exceeds 2 wt.% in most of the subcrop area (Figure 3.64). The highest mean TOC values are 3.5% and occur in the DPZ northwest of Fort St. John. Other areas where the DPZ has a relatively high average TOC are to the southwest of Fort St. John near the deformation edge, and northwest of Grande Prairie, where the average TOC exceeds 3 wt.%. The lowest average TOC values in the DPZ are found in the central portion of the basin around Dawson Creek, and in the southwestern limit, where the average TOC is between 1 and 2 wt.%. In the DPZ, the areas of relatively high TOC overlap with the western depocentres and the relatively thicker section in the northwest, while the low TOC area in the central part corresponds to a region where the DPZ is anomalously thin. In the upper Doig Formation, high average TOC values of up to 2.5 wt.% are concentrated in areas along the
eastern edge arranged linearly parallel to the basin axis, as well as in the northwest of the subcrop area, where the upper Doig Formation is relatively thin (Figure 3.65). Elsewhere in the upper Doig Formation, including in the western depocentre, the average TOC content is typically between 1 and 1.5 wt.%.



## **Doig Phosphate Total Organic Carbon**

Figure 3.64 - Total organic carbon distribution of the Doig Phosphate Zone (Silva, 2021).



## **Upper Doig Total Organic Carbon**

Figure 3.65 - Total organic carbon distribution of the upper Doig Formation (Silva, 2021).

Original (restored) concentration of organic matter (Peters et al., 2005; Silva, 2021, Appendix K) is substantially higher in the DPZ than in the upper Doig Formation, which is interpreted to be a result of upwelling along the western margin of the WCSB. A linear trend of higher concentration of original TOC content subparallel to the long axis of the subcrop area highlights an elongated zone of enhanced organic productivity and preservation extending through the basin centre. The position and orientation of this axis may correspond to the centre of the marine basin, while the highest concentrations of original organic matter found in the northern part of the basin are related to the connection to an open marine environment to the north.

The kerogen types in the Doig Formation are of Types II and III (Figure 3.66). Kerogen Type III is less abundant in the DPZ, which is predominantly composed of kerogen Type II and II/III. The 10<sup>th</sup> to 90<sup>th</sup> percentile range for HI lies between 12 and 232 mg HC/g. There is a trend of decreasing HI towards the deformation front, similar to the trend of increasing thermal maturity. This trend occurs in both the DPZ and the upper Doig Formation (Figure 3.67 and Figure 3.68), as a result of hydrocarbon generation. Discrepancies between thermal maturity and HI trends are caused by local variations in kerogen composition impacting the initial HI distribution. Slight differences in the kerogen composition between the DPZ and the upper Doig Formation are also reflected in the HI distribution. The average HI in the DPZ decreases rapidly from approximately 360 mg HC/g TOC in the early oil generation window near the zero edge to 80 mg HC/g TOC at the onset of the wet gas generation window (Tmax of 470 °C), reaching 40 mg HC/g TOC adjacently to the western deformation edge. In the upper Doig Formation, the HI range is narrower, and the rate of decrease is less steep. Near the zero edge, where the HI is highest, the upper Doig Formation mean HI does not exceed 300 mg HC/g TOC, progressively decreasing to 20 mg HC/g TOC in the deepest and most mature part of the basin to the southwest.

Kerogen reaction kinetics models were created for kerogen Types II (Figure 3.69) and III (Figure 3.70) from the Doig Formation, as described in detail in Silva and Bustin (2020) and included in Appendix C of this report. Kerogen Type II has a median activation energy of 51.4 kcal/mol and a pre-exponential factor of 2.799×10<sup>27</sup>/Ma, while kerogen Type III has a median activation energy of 53.6 kcal/mol and a pre-exponential factor of 3.338×10<sup>28</sup>/Ma.



Figure 3.66 - Pseudo-van Krevelen plot of Doig Formation Rock-Eval analyses.



# **Doig Phosphate Hydrogen Index**

Figure 3.67 - Distribution of hydrogen index in the Doig Phosphate Zone (Silva, 2021).



# **Upper Doig Hydrogen Index**

Figure 3.68 - Distribution of hydrogen index in the upper Doig Formation (Silva, 2021).



Figure 3.69 - Type II kerogen activation energy distribution used in the Doig Formation basin model.



Figure 3.70 - Type III kerogen activation energy distribution used in the Doig Formation basin model.

#### 3.4.2.4. Burial and Thermal History

A reconstruction of the burial and thermal history of the Montney Formation was conducted through basin modelling using the Schlumberger PetroMod software. Publicly available regional heat flow data (Majorowicz et al., 2005; Tuya Terra Geo Corp and Geothermal Management Company, 2016) were used as to map present-day heat flow. The post-Laramide heat flow distribution (60 Ma) was calculated as 90% of the present-day heat flow, based on estimates by Bachu and Cao (1992). A constant heat flow of 55 mW/m<sup>2</sup> was assumed for the Cambrian, based on an average for the North American continent (Allen and Allen, 1990).

The maximum depth of burial reached by the Doig Phosphate Zone ranges from 8,480 m in the southwest to 3,070 m near the present-day subcrop edge (Figure 3.71). The maximum temperatures experienced by the Doig Formation in these locations were 250°C and 100°C, respectively, which is significantly higher than present-day temperatures, ranging from 131°C to 30°C.

#### 3.4.2.5. Petroleum Generation

Generation of oil in the Doig Formation started at the end of the Early Cretaceous at 101 Ma (Figure 3.72). Towards the end of the Cretaceous, rates of burial and petroleum generation increased rapidly. The Doig Formation reached peak oil generation along most of the western boundary adjacent to the fold and thrust belt, at 85 Ma (Figure 3.73). From the end of Cretaceous to Paleocene, between 72 and 60 Ma, due to the rapid foreland subsidence in the southwest, wet gas generation in the Doig Formation started throughout most of the southwest, and dry gas started in the deepest areas (Figure 3.74 and Figure 3.75). During the Eocene, at approximately 50 Ma, a small portion of the Doig Formation in the southwest reached the late dry gas window before thermal maturation was frozen to approximately present-day levels (Figure 3.76), by the rapid uplift and exhumation of Paleogene sediments.



# **Doig Phosphate Maximum Burial Depth**

Figure 3.71 - Maximum depth of burial of the Doig Phosphate Zone.



**Doig Phosphate Transformation Ratio 101 Ma** 

Figure 3.72 - Kerogen transformation ratio in the Doig Phosphate Zone at 101 Ma.



**Doig Phosphate Transformation Ratio 85 Ma** 

Figure 3.73 - Kerogen transformation ratio in the Doig Phosphate Zone at 85 Ma.



# **Doig Phosphate Transformation Ratio 72 Ma**

Figure 3.74 - Kerogen transformation ratio in the Doig Phosphate Zone at 72 Ma



## **Doig Phosphate Transformation Ratio 60 Ma**

Figure 3.75 - Kerogen transformation ratio in the Doig Phosphate Zone at 60 Ma.



## **Doig Phosphate Transformation Ratio 0 Ma**

Figure 3.76 - Kerogen transformation ratio in the Doig Phosphate Zone at 0 Ma.

#### 3.4.2.6. Gas Analysis and Thermochemical Sulphate Reduction

The potential for thermochemical sulphate reduction (TSR) H<sub>2</sub>S generation in the Doig Formation was assessed through basin modelling. The southwestern portion of the Doig Formation is at higher risk of H<sub>2</sub>S generation by TSR from generated petroleum (Figure 3.77). Based on a lower temperature threshold for TSR of 120°C (Goldstein and Aizenshtat, 1994; Mougin et al., 2007), the central western portion of the Doig Formation entered the TSR phase by approximately 90 Ma (Figure 3.78), at which time this area was located at the depocentre of the Fort St. John Graben. The TSR generation region expanded southeast until 75 Ma, as during that time, subsidence was more dominant in the southern area. From 75 to 60 Ma, the TSR region quickly extended east, covering almost the entire extent of the Doig Formation. As the Paleogene sediments were eroded and the basin uplifted, most of the eastern area of the Doig Formation remained in the TSR for less than 35 Ma (Figure 3.79). Exhumation rates were lower in the southwest, where the Doig Formation had entered the TSR by 75 Ma and did not exit it until 20 Ma. Progressively deeper strata exited the TSR region towards the southwest, where a very small area currently remains at temperatures slightly above 120°C. Portions of the southwestern region have stayed within the TSR region for a total of up to 80 Ma. The present-day concentration of H<sub>2</sub>S in the Doig Formation is higher in the region west of Grande Prairie, reaching nearly 2%. This area coincides with the elevated H2S in the Montney (Figure 3.80). Unlike the Montney, the Doig Formation, however, has high concentrations of H<sub>2</sub>S, in excess of 12%, in the area north of Fort St. John.



## **Doig Petroleum Generation H2S Yield**

Figure 3.77 - Distribution of  $H_2S$  yield from thermochemical sulphate reduction during petroleum generation in the Doig Formation.



**Doig Phophate Thermochemical Sulphate Reduction Entry Age** 

Figure 3.78 - Map of age of entry in the thermochemical sulphate reduction zone of the Doig Phosphate Zone.



## **Doig Phosphate Thermochemical Sulphate Reduction Exit Age**

Figure 3.79 - Map of age of exit of the thermochemical sulphate reduction zone of the upper Doig Formation.

Doig H2S



Figure 3.80 - Distribution of  $H_2S$  in the Doig Formation.

The Doig Formation gas dryness decreases from the early mature eastern edge towards the west (up to a minimum ratio of 0.7) in an arcuate belt extending from near Grande Prairie to northwest of Fort St. John (Figure 3.81). Southwest of this belt the gas dryness ratio increases again, reaching unity in the zone of dry gas southwest of Dawson Creek. The zone of lower gas dryness ratio is approximately coincident with the hydrocarbon generation window of oil (Tmax between 445 and 465 °C). The zone of dry gas in the deepest part of the basin correlates with and reflects the high degree of maturity, corresponding to the overmature hydrocarbon generation window for Type III kerogen (Tmax higher than 490 °C). The limited production data from the Doig Formation is in agreement with the thermal maturity and gas wetness maps and reveals an area with higher volumes of produced liquids that follows the same trend of maturity and gas wetness ratio.

There is partial overlap between the distributions of  $CO_2$  and  $H_2S$  in the Doig Formation (Figure 3.82). Relatively high concentrations of  $CO_2$  occur in the deeper portions of the central western and southwestern border, along the fold and thrust belt boundary, but also occur where the Doig Formation is relatively shallow, around Fort St. John. The highest concentrations of  $CO_2$  found in the Doig Formation are lower than 5%, which is much less than the  $CO_2$  concentrations in the Montney Formation gas.



## **Total Doig Gas Dryness Ratio**

Figure 3.81 - Distribution of gas dryness ratio on the entire Doig Formation.

# **Doig Carbon Dioxide**



Figure 3.82 - Distribution of  $CO_2$  on the Doig Formation.

#### 3.5. Discussion

The Montney and Doig formations show an increase in thickness and organic maturation towards the deformation front in the west of the WCSB. The gas dryness also generally increases towards the deformation front, corresponding to increasing thermal maturity on a broad scale. There are some localised variations, such as the Fort St. John Graben, that affect the general maturation trend (increasing maturity towards the west), and consequently the hydrocarbon composition (higher concentration of longer-chained hydrocarbons). These structural controls can be observed in the structure maps (Figure 3.1 and Figure 3.57). The Fort St. John Graben area shows higher thermal maturity and increased thickness in both the Montney and Doig formations, compared to the area north of the graben. Structures like the Fort St. John Graben, the Hay River fault zone and the Laurier Embayment had a profound effect on the depositional and maturation patterns of the Triassic strata (Euzen et al., 2021; Berger et al., 2008; Figure 3.40 and Figure 3.41, this study).

The thickness of the Doig Formation and the upper, middle, and lower Montney Formation vary significantly across the basin. The upper Doig Formation and DPZ both increase in thickness towards the deformation front and thin towards eastern Alberta. The DPZ is much thinner than the upper Doig Formation with the latter being greatly affected by the Fort St. John Graben (increased thickness). The upper Montney is thicker in the west, close to the deformation front, and it pinches out towards eastern Alberta. The middle and lower Montney units are thickest within the central portion of the play area and thin towards the deformation front and east towards the craton.

The total organic carbon content of the Montney increases towards the deformation front, as this area was further offshore, where both the generation and preservation of organic matter tend to be higher. The nearshore environments also received greater volumes of clastic material that could dilute the TOC contents. The TOC distribution for the DPZ is also similar to the Montney Formation. The upper Doig Formation shows an increase in the TOC content in the middle of the play area, possibly due its optimal location regarding the trade-off between dilution by clastic sedimentation and the oxidation of organic matter due to the redox potential of the bottom water (less oxidation of organic matter) away from the nearshore environments. The HI for both the Montney and Doig formations correlates with the maturation trends with decreasing HI content in the remaining kerogen towards the deformation front; this trend also correlates with the transformation ratios from the basin models, indicating that a greater portion of the kerogen is transformed into hydrocarbon in the deeper parts of the basin that experienced greater temperatures over a longer time period than the eastern portion of the basin.

The modeled H<sub>2</sub>S generation by TSR also shows similar patterns to the hydrocarbon generation, with higher volumes of H<sub>2</sub>S being generated along the deformation fronts (Figure 3.27 and Figure 3.77). The TSR-generated H<sub>2</sub>S gas model assumes that the Doig and Montney formations contain a uniform amount of sulphate in the pore water and sulphur in the generated petroleum. Studies have shown the Montney Formation has very low organic sulphur content in the organic matter (Ibrahimbas and Riediger, 2004), and this may not be the case. The following chapter on origins of H<sub>2</sub>S gas in the Montney indicates the anhydrite within the overlying Charlie Lake may be the source of sulphate, which would have migrated downward into the Montney Formation through fracture networks in localised concentrations; this would

also be a better fit to the observations of localised sour wells adjacent to sweet wells (Figure 3.39). The model highlights areas of the Montney Formation that have experienced paleotemperatures above 120°C, which combined with the knowledge of the location of the overlying Charlie Lake Formation evaporites (i.e., Figure 3.43) provides a risk assessment to areas that have not been drilled; however, as shown by the distribution of sulphate ions in the formation water of the Triassic strata (Figure 3.42; Kirste et al., 1997) appears to overlap with the H<sub>2</sub>S distribution in the Montney Formation. Updip migration of sulphate ions prior to hydrocarbon generation, instead of migration of H<sub>2</sub>S, is invoked to explain the discrepancy between the areas of highest H<sub>2</sub>S content in the Montney, and the location of Charlie Lake evaporites, as well as the areas of highest H<sub>2</sub>S yield from TSR as predicted by the basin modelling. The location of structural conduits is paramount to explaining the distribution of H<sub>2</sub>S, as the sulphate from the Charlie Lake source must have migrated through fault networks into the Montney Formation. Therefore, risking would need to be performed by operators using three-dimensional seismic data to identifies fracture and fault systems that may have allowed sulphate migration and hydrogen sulphide generation.

Another significant non-hydrocarbon gas found within the Montney and Doig formations is carbon dioxide. Kirste et al. (1997) observed that higher concentrations of  $CO_2$  and  $H_2S$  occur within the same pools across BC. The generation of  $CO_2$  in hydrocarbon reservoirs can be from the decomposition of limestone, certain types of kerogen, or as a by-product of  $H_2S$  production (see equation below; Hunt, 1996).

1.33 CH<sub>2</sub> + 0.66 H<sub>2</sub>O + SO<sub>4</sub><sup>2-</sup> > H<sub>2</sub>S + CO<sub>2</sub> + 2 OH<sup>-</sup> (1)

There is a correlation between increasing concentration of  $CO_2$  with increasing concentrations of  $H_2S$  when the concentration levels are above 5% (Figure 3.54); however, the distribution of  $H_2S$  does not directly overlap with the  $CO_2$  concentrations (Figure 3.55 and Figure 3.56), which suggests the  $CO_2$  may not be just a by-product of the  $H_2S$  generation. Further research into the sources of  $CO_2$  using isotope geochemistry will be needed to understand the  $CO_2$  distribution.

Kirste et al. (1997) suggests that there are three pools in British Columbia that show a positive correlation between increasing  $CO_2$  and increasing  $H_2S$  concentrations, suggesting the  $CO_2$  is related to the generation of the  $H_2S$ , as shown in equation 1 above. Similarly, this study shows that there is an increase in  $CO_2$  concentration south of Dawson Creek (Figure 3.52 and Figure 3.53) and a concomitant increase in  $H_2S$  concentration (Figure 3.43), which may indicate a connection in the generation of  $CO_2$  as a by-product of the  $H_2S$  generated as noted by Kirste et al. (1997). However as shown by the cross-plot of  $CO_2$  and  $H_2S$  (Figure 3.54) there are locations that have high  $CO_2$  and low  $H_2S$  gas and either the  $CO_2$  gas has migrated from downdip, or other processes are at play.

#### 3.6. Summary

This chapter has shown the importance of mapping the key geological and geochemical parameters to understand the processes involved within a complex petroleum system like the Montney and Doig formations. The project investigated changes in thickness, depth of burial, mass balance calculations, timing and magnitudes of paleotemperature exposure, as well as kerogen concentration and types to determine the distribution of hydrocarbon composition, H<sub>2</sub>S concentrations and CO<sub>2</sub> concentrations.

Regional maturation trends follow the general WCSB geometries and increase with the depth of burial. There are second- and third-order variations that are due to structural features like the Fort St. John Graben, Hay River fault zone and the Laurier Embayment area (Berger et al., 2008; Figure 3.40, this study). These structures impact the thickness of the Doig and Montney formations as well as the maturation patterns. The changes in maturation patterns (i.e., lower maturity across the graben structures) impact the hydrocarbon composition of the Montney Formation. Preferential migration of methane along these structural features may have also occurred and this has impacted the gas dryness distribution. This is explored in more detail in the chapter on gas hydrocarbon composition of the Montney Formation below.

The H<sub>2</sub>S concentration is discontinuous and is found in discrete pockets (as bullseyes in Figure 3.35 to Figure 3.38; Figure 3.80) within both the Montney and Doig formations. The location of the H<sub>2</sub>S measured in the Montney Formation producers does not align with locations of potential H<sub>2</sub>S generation based on basin modelling. High concentrations of H<sub>2</sub>S also does not coincide with the potential sources of sulphate from the Charlie Lake evaporite facies (Figure 3.43). The reason the H<sub>2</sub>S gas is further updip may not be due to migration of the gas itself, but instead, due to updip migration of anhydrite sulphate in solution which entered discrete locations of the Montney Formation via fractures and faults. The sulphate ion concentration map by Kirste et al. (1997) illustrates the distribution of the sulphate and its potential to be found within the Montney Formation (also dependent on regional and local structures). A H<sub>2</sub>S risking map would include the overlay maps of the sulphate ion concentration, paleotemperature and structures.

The distribution of the  $CO_2$  does show some alignment with the  $H_2S$  concentration, particularly around the area south of Dawson Creek; however, the cross-plot of  $CO_2$  and  $H_2S$  concentrations illustrates that the  $CO_2$  is not only being sourced from the generation of  $H_2S$  but is either sourced from other processes (i.e., decomposition of kerogen or carbonate dissolution) or is generated in deeper sour pools and migrated into the Montney Formation play areas. Deeper Devonian-aged sour pools may be responsible for some of the sour Montney producers in Alberta (Liseroudi et al., 2020).

# 4. Hydrocarbon Composition Distribution in the Montney Formation

## 4.1. Abstract

The geochemistry of produced fluids is a valuable tool in the exploration and development of a complex petroleum system like the Montney Formation. The use of isomer ratio calculations for butane and pentane in combination of the excess methane percentage is a powerful tool to highlight areas of the Montney Formation play area that has seen migration of hydrocarbons from deeper, more mature areas to the west. Methane has migrated along structural elements like the Fort St John Graben as well as areas that have seen changes in higher permeability lithologies. Excess methane percentage calculations highlight changes in hydrocarbon compositions in an unconventional petroleum system that have seen fluid mixing from hydrocarbon migration. The British Columbia Montney play appears to have hydrocarbon composition that reflects an in-situ generation, while the Montney play in Alberta has a higher proportion of its hydrocarbon volumes from migrated hydrocarbons. The technique of calculating excess methane percentage provides a better understanding of the hydrocarbon system for better drilling planning and optimizing operations for increase production efficiency.

#### 4.2. Introduction

Variability in the liquids and gas ratios of the Montney Formation is due to trends on first-, secondand third-orders of scale of variation (as explained below), and when superimposed, create a complex hydrocarbon composition distribution (Bustin and Bustin, 2016; Euzen et al., 2021; Figure 3.44, this study). Maturation of the organic matter is the key driver of the hydrocarbon composition in self-sourcing reservoirs, with an increase in gas dryness as source-reservoir rocks are buried more deeply and experience greater temperatures over geological time. This is a first-order variation, which is on a basin wide scale and shows an increase in organic matter maturation from the interior plains towards the deformation front (disturbed belt) in the southwest (Figure 3.9). Similar observations have been made by the BC Oil and Gas Commission (BC OGC, 2012). The second- and third-order variations are due to either: 1) regional to local changes in heat flow; 2) fault/fracture structures (i.e., Euzen et al., 2021); or 3) possibly an artifact created due to the lack of well/data control (Bustin and Bustin, 2016). These second- and thirdorder factors create perturbations of less mature and more mature areas within the broader increasing maturation trend towards the southwest. These subtle differences in the maturation trends have an impact on the hydrocarbon composition within the Montney Formation as seen with the gas dryness ratio of the entire Montney Formation, and its subunits lower, middle and upper Montney Formation maps (Figure 3.44 to Figure 3.47). However, some of the trends in gas dryness cannot be explained by organic maturation trends alone, and some areas show higher or lower gas dryness than what would be expected for their degree of maturity. These may be either due to the migration of deeper, shorter-chained

hydrocarbons (i.e., drier gas content) through basin structures (Desrocher, 1997; Euzen et al., 2021) or changes in lithologies/facies (Wood and Sanei, 2016). Euzen et al. (2021) suggests that the Fort St. John Graben structures have provided pathways for drier gas compositions to migrate into areas that are regionally wetter (i.e., C2+ hydrocarbons). To highlight areas that have a mixture of in-situ and migrated hydrocarbons within the Montney Formation reservoir, the calculation of an excess methane percentage for wells based on their isomer ratios is used (Wood and Sanei, 2016; Euzen et al., 2020). The isomer ratio of butane (iC4/nC4) and pentane (iC5/nC5) can be used as a maturation indicator and any deviation of the gas composition from the regional maturation trend can be calculated as a percentage of excess methane content, indicating that an area has experienced migration of drier, more mature gas into the area. This has been highlighted by Wood and Sanei (2016) and more recently by Euzen et al. (2021).

#### 4.3. Results

A total of 11,331 gas compositional samples from production and well tests were analysed from the Montney Formation in both British Columbia and Alberta. This study has generated cross-plots of iC4/nC4 isomer ratio of butane versus the gas dryness for British Columbia (Figure 4.1) and Alberta (Figure 4.2). Gas dryness is the ratio between the methane fraction and the sum of all the hydrocarbon fractions between methane and pentane, inclusive, for each sampled well. The regional maturation polynomial regression line from Euzen et al. (2021) was used to determine the gas dryness percentage for each well based on its maturation level determined by the butane isomer ratio (Figure 4.1). The deviation from the calculated gas dryness based on the regression was determined as an excess methane percentage and subdivided into nine categories of excess methane (< 1%; 1-2%; 2-3%; 4-5%; 6-7%; 8-10%; 11-12%; and 12%+). The distribution of excess methane across British Columbia and Alberta is shown in Figure 4.3 and Figure 4.4. The Alberta Montney producers have a greater contribution of migrated gas than the British Columbian Montney wells that have gas compositions with a lower influence of migrated hydrocarbons and is more typical of unconventional self-sourcing reservoirs.



Montney Producers in B.C.: Gas Dryness versus iC4/nC4 Ratio

Figure 4.1 - Cross plot of gas dryness and the iC4/nC4 ratio for all British Columbia Montney producers at the time of this report. The iC4/nC4 is used as a maturity indicator with the line of best fit representing the regional maturation trend from Euzen et al. (2021). An excess methane percentage is calculated from the deviation away from the expected gas composition of the regional maturation trend. Wells that have high excess methane (i.e., red colours) have a greater ex-situ (migrated) gas content compared to wells in the black symbols. Wells represented by black or green symbols have low ex-situ gas contents and the hydrocarbons are the result of in-situ generation that is typical of a self-sourcing reservoir.



Figure 4.2 - Cross plot of gas dryness and the iC4/nC4 ratio for all Alberta Montney producers at the time of this report. The iC4/nC4 is used as a maturity indicator with the line of best fit representing the regional maturation trend from Euzen et al. (2021). An excess methane percentage is calculated from the deviation away from the expected gas composition of the regional maturation trend. Wells that have a high excess methane (i.e., red colours) have a greater ex-situ gas content compared to wells in the black symbols. Wells represented by black or green symbols have low ex-situ gas contents and the hydrocarbons are the result of in-situ generation that is typical of a self-sourcing reservoir. The Alberta Montney producers have a greater contribution of migrated gas than the BC wells.



#### Montney Excess Methane and Gas Dryness Ratio

Figure 4.3 - The excess methane percentage (symbols) for Montney Producers in BC and Alberta. The excess methane percentage is the calculated increase percentage of methane based on the iC4/nC4 ratio regional maturation trend of Euzen et al. (2021). The methane gas dryness percentage is also shown as contour lines. Contour interval is 0.025 (i.e., 2.5%). Darker colours are indicative of hydrocarbon compositions that are aligned with the regional maturation trends across the basin and probably self-sourced hydrocarbons or very limited migration distances. The larger orange and red symbols indicate locations that have the hydrocarbon composition not aligned with regional maturation trends and there is a larger component of migrated hydrocarbons in the reservoir. This is well illustrated by the Montney in eastern Alberta that is a more conventional petroleum system.



## **Montney Excess Methane and Gas Dryness Ratio**

Figure 4.4 - Expanded view of the Fort St John to Grand Prairie areas that are the focus of the Wood and Sanei (2016) and Euzen et al., (2021) studies. Black-dashed lines with arrows indicate the direction of more mature, drier gas (higher methane content) that has migrated updip from the BC/Alberta boundary into less mature, more liquids-rich sections of the Montney Alberta play area.

#### 4.4. Discussion

The hydrocarbon composition of the Montney Formation is complex due to two processes occurring within the system. One process is in-situ generation and storage of hydrocarbons within an unconventional self-sourced reservoir, as illustrated by the low excess methane percentages in the northeast of British Columbia (Figure 4.3). The other process is the migration of shorter-chain hydrocarbons like methane, from more mature zones in the west and moving updip towards the eastern portion of the Montney play areas (assuming minimal local migration processes). This is illustrated by the higher excess methane percentages in the Alberta play areas in Figure 4.3 and Figure 4.4. Migration updip is also controlled by lineaments and lithologic changes in the Montney Formation. Changes into higher permeability lithologies are highlighted by Wood and Sanei (2016) and are shown by the black dashed lines in Figure 4.4. It is important to note that these trends appear well defined due to the bias of operators selecting areas to drill based on higher permeabilities (fractured, faults, lithological changes). Additional

infill drilling along the flanks of these fairways would confirm the reason(s) drier hydrocarbon composition has migrated in this region. Changes highlighted by the excess methane percentage across the regional play area can also be due to lineaments like the Fort St. John Graben structures (Euzen et al., 2021). Not only do the lineaments pose a pathway for fluid migration, but they also impacted the maturation trends across the area. The lower maturation trends across the graben area have impacted the hydrocarbon generation and in-situ composition of the Montney self-sourcing reservoir system. This is illustrated by the changes in maturation trends (Figure 3.9) in the area of the Fort St. John Graben (Figure 5 of Euzen et al., 2021 and Berger et al. 2008; Figure 3.40 this study).

Euzen et al. (2021) show two main areas of hydrocarbon migration from the downdip portions of the Montney Formation in the western play area to the eastern sections (Figure 4.5). Euzen et al. (2021) used gas dryness maps to infer these migration patterns. The excess methane mapping of the entire Montney Formation does show this migration pattern in the southern area (Area B) around Dawson Creek. Area A does not appear in our excess methane percentage mapping and methane migration may not be the reason for the drier gas contents in Area A, but a higher maturation was experienced in these areas as shown by Figure 3.9. This may be due to higher palaeoheat flow in the area. The gas dryness map (Figure 3.44) in this study does not show a significant migration of drier gas towards the east in Area A, like it does in Area B. This study does not draw the same conclusions as Euzen et al., 2021 for the migration of significant volumes of drier gas in the Area A of Figure 4.5.

The pattern of drier hydrocarbon composition interfingering into the wetter gas regions of Area B (Figure 3.44 and Figure 4.5) can been seen in the lower, middle and upper sections of the Montney Formation (Figure 3.44 to Figure 3.47). This suggests that the increase in gas dryness is more than just a local lithological variation, as it spans the entire Montney Formation and is not just concentrated in one of the stratigraphic units. The results of the mapping of gas dryness by upper, middle, and lower Montney Formation subunits indicate that there are probably structural elements that impact all parts of the Montney (i.e., localised faults), instead of simply lithological variations in the Montney Formation, as suggested by Wood and Sanei (2016).

#### 4.5. Summary

Hydrocarbon geochemistry is a valuable tool in the exploration and production of the Montney Formation. The composition varies, not only due to regional maturation trends, but also due to updip migration of shorter-chain hydrocarbons (i.e., methane) along structures and changes in lithology. Regional maturation is also affected by a large graben structure in the Fort St. John area and the change in maturation patterns has impacted the hydrocarbon composition across this area.

Excess methane percentage calculations can provide granularity to changes in hydrocarbon compositions from play areas that contain self-sourced hydrocarbons with little to no migration, to play areas that contain a mixture of self-sourced and migrated hydrocarbons. This technique provides a useful tool for understanding the hydrocarbon system, planning drilling campaigns, adjusting hydrocarbon production during market changes and optimizing operations for increase production efficiency.



Figure 4.5 - Migration patterns in the Montney Formation in relation to the depositional environments (modified from Euzen et al. 2021). Two areas of migration of hydrocarbons from deeper down dip areas that contain shorter chained hydrocarbons are highlighted Area A and Area B.

# 5. The Origins of the H2S Gas in the Montney Formation, British Columbia

## 5.1. Abstract

The sources of sulphur were investigated for souring Montney Formation producing wells. The distribution of H<sub>2</sub>S gas is inexplicable and can occur together with sweet wells on the same multi-well pad. This chapter illustrates the use of sulphur and oxygen isotopic analyses coupled together with SEM-EDX and XRD analyses to determine the most likely source of sulphur of the H<sub>2</sub>S gas. The Montney Formation in British Columbia can contain small discrete amounts of sulphur in the form of anhydrite as shown by XRD and SEM-EDX results. Sulphur isotopic analyses indicate that the most likely source of sulphur is from the Triassic rocks, in particular, the Charlie Lake Formation due to: 1) its close proximity; 2) its high concentration of anhydrite [i.e., 18-42%]; and 3) the evidence that dissolved sulphate ions migrated within the groundwater in fractures and precipitated as anhydrite into the Halfway Formation (Sharma, 1969) and into the Montney Formation (Desrocher et al., 2001). The isotopic signature shows the sulphur isotopic ratio of the anhydrite in the Montney Formation is in the same range as the sulphur within the H<sub>2</sub>S gas and is a lighter ratio than what is found in Devonian anhydrite and H<sub>2</sub>S gas. Government agencies and operators in British Columbia should map the Charlie Lake distribution, together with the structural elements from three-dimensional seismic and sulphate ion concentrations in the connate water to reduce the risk of encountering unexpected souring.

#### 5.2. Introduction

The Triassic Montney Formation is a large unconventional gas play in Western Canada (Figure 5.1) and contributed a significant proportion (34%) of natural gas to the total Canadian gas production in 2017 (NEB, 2018). As operators expand from core development areas, a greater proportion of producing wells in the Montney Formation is found to contain non-hydrocarbon gases such as hydrogen sulphide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>). Over 25% of Montney producing wells have tested or produced greater than 0.01% (100 ppm) of H<sub>2</sub>S gas. This gas impacts the economics and health and safety of petroleum operations. Even in trace amounts (i.e., ppm), H<sub>2</sub>S in produced hydrocarbons impacts the economics of drilling, production, treatment, and marketing of these hydrocarbons. The presence of H<sub>2</sub>S gas within produced fluids is also one of the most dangerous environmental hazards and risks to gas resource development.

The distribution of H<sub>2</sub>S varies markedly across Montney gas play areas in British Columbia and Alberta (i.e., Figure 24 in Kirste et al., 1997; Desrocher et al., 2004; Figure 3.35 to Figure 3.38 in this study). The distribution can be inexplicable and there can be many different mechanisms of H<sub>2</sub>S gas formation. For example, H<sub>2</sub>S in petroleum systems can develop by, 1) bacterial sulphate reduction [BSR]; 2) thermal sulphate reduction [TSR]; 3) kerogen cracking; and 4) sulphide oxidation and/or decomposition of surfactants used for well completions. Understanding H<sub>2</sub>S distribution is further complicated by the fact

that the gas can be produced in-situ within the Montney reservoir or may have migrated as either  $H_2S$  gas or as sulphate ions from above or below through more permeable beds or fracture networks.

Hydrogen sulphide is generated when sulphate present within the reservoir comes into contact with hydrocarbons and goes through a chemical reduction process that is catalysed by either microbial communities below 60-90°C (Machel, 1987; Hubbard et al., 2014) or by abiotic thermochemical processes above 90°C (Machel, 2001). TSR develops when petroleum reservoirs are at temperatures of 100-140°C (Machel, 2001) and the required temperature to catalyse the TSR reaction can vary due the gas diffusion rates, gas types present, catalysts involved, wettability and permeability of the reservoir (Machel, 2001). Reactive sulphates are needed in the reaction process, which include dissolved sulphates within the pore water from ancient seawater, evaporative brines or the dissolution and migration of anhydrite or other sulphate-rich minerals. Reactive organic compounds also need to be within the reservoir, and this includes organic matter, crude oil, microbial methane, or thermogenic gas/condensate.


Figure 5.1 - Location map for the four wells (red stars) that were analysed to determine the sources of sulphur and the origins of the hydrogen sulphide in British Columbia. In addition, the sulphur isotopic analyses from other studies have been included in this report with a total of 218 mineral and organic matter samples analysed (see Appendix A). The Well Authorization number for the four wells are also shown on the map. Orange circles represent towns, and the small black lines are horizontal wells that produce the Montney Formation in British Columbia and Alberta (as of October, 2019). The structure to the top of the Montney Formation (TVD, subsea, metres) is also shown as blue dash lines.

The sulphur isotopic composition varies across the WCSB because: 1) it is either generated via the BSR or TSR pathway or; 2) the sulphate source is from different aged seawater (i.e., Triassic versus Devonian). It has been observed that the sulphur isotopic ratio for BSR generated H<sub>2</sub>S gas is less positive than sulphur derived from TSR generated H<sub>2</sub>S (i.e., -30%; Hubbard et al., 2014). For example, Desrocher et al. (2004) found the Doig Formation anhydrite to be 26.3‰ while H<sub>2</sub>S gas generated by BSR (using this Doig Formation anhydrite) found in the Halfway Formation reservoir has a sulphur isotopic signature of only 6.3‰. The change in isotopic signature is due to fractionation, as the lighter sulphur isotope is used first by microorganisms, which break the slightly weaker bonds of lighter sulphur isotopes (Hubbard et al., 2014). There is no preferential use of different sulphur isotopes in TSR generated H<sub>2</sub>S gas and this will result in the sulphur signature in the gas being the same as the source of the sulphur. An exception to this case is when the reservoir contains organic sulphur that can fractionate during TSR (i.e., Meshoulam et al., 2016). In this study, the Montney Formation contains none to very low concentrations (<1 ppm) of organic sulphur. Desrocher et al. (2004) observe that the anhydrite of the Charlie Lake Formation has a similar sulphur isotopic signature to the H<sub>2</sub>S found in the Montney Formation in the west central Alberta Basin, which indicates that the H<sub>2</sub>S was generated via TSR processes. However, there is a difference in the original source of the sulphur (i.e., Triassic and Devonian seawater; Figure 5.2) and this will be reflected in the TSR generated H<sub>2</sub>S gas in the reservoir. Figure 5.2 shows that the sulphur isotopic range for Triassic seawater is between 10-20‰, and the oxygen isotopic signature is between 12-16‰, compared to a sulphur signature of 16-28‰ and an oxygen isotopic signature between 12-18‰ for Devonian seawater. This means that anhydrite formed during each of these geological periods will have specific sulphur and oxygen isotopic fingerprints, which will result in distinct TSR-generated  $H_2S$  gas.

The complex distribution of H<sub>2</sub>S in Triassic rocks was first identified by Kirste et al. (1999). Kirste et al. (1997), when examining formation water chemistry from Drill stem test (DST) data, observed higher dissolved sulphate ion concentrations in areas that are overlain by anhydrite-rich Charlie Lake Formation. This observation indicates that there is fluid communication between the Doig, Halfway and Montney formations and they act as a single unit (Kirste et al., 1997). This paper provided the first evidence that anhydrite may have migrated from the anhydrite-rich Charlie Lake formation into the Halfway, Doig, Montney formations below. Migration would have been through faults and fracture networks. The Doig Formation also contains anhydrite from primary sources (see below).

Anhydrite, the likely sulphur source in TSR souring in the WCSB, can be readily found in Triassic, Mississippian and Devonian rocks within the WCSB. Primary depositional anhydrite is observed in the Triassic Charlie Lake and Doig formations (Hunt and Ratcliffe, 1959; Desrocher, 1997; Desrocher et al., 2001; Zonneveld et al., 2004) as well as in the Mississippian Debolt, Banff and Shunda formations. Only secondary anhydrite in the form of pore, vug and fracture fill has been observed in the Montney Formation (Davies, 1997; Davies et al. 1997; Liseroudi et al., 2020) as well as in the Halfway Formation and the sandstone of the Doig Formation (Sharma, 1965; Harris, 2000). The Charlie Lake Formation can contain thick layers of evaporitic anhydrite (Hunt and Ratcliffe, 1959, Zonneveld et al., 2004). The Doig Formation is also a potential source of sulphate via anhydrite associated with phosphatic nodules (Desrocher, 1997; Desrocher et al., 2001) as well as pore cements in the Doig sandstone (Harris, 2000). Desrocher (1997)

suggests the dissolved sulphate has moved from the Charlie Lake into the Montney Formation in areas where the Doig/Halfway subcrop is absent and there is direct contact between the Charlie Lake and Montney formations towards the eastern part of the basin. It is further suggested that sulphate ions migrate along an unconformity surface in the centre of Montney (Markhasin, 1997) via fluid migration (Desrocher 1997). Sulphate recycling via solution and redeposition as secondary cements has also been observed in the Halfway Formation, and the origins of the sulphate were interpreted to be from the overlying Charlie Lake Formation (Sharma, 1969).



Figure 5.2 - The changes in sulphur isotopic signature of sulphur (i.e., anhydrite) through geological time. Note the Devonian sulphur isotopic ratio is heavier than the Triassic isotopic ratio and this difference is used to identify the sources of sulphur in the H<sub>2</sub>S of the Montney Formation. The isotopic ratios are also shown for this study and there is a clear difference in isotopic ratios for sulphur (anhydrite) between the Triassic and Devonian sources. Modified after Newton and Bottrell (2007).

The Montney Formation contains varying amounts of anhydrite (Davies, 1997; Davies et al. 1997; Liseroudi et al., 2020) which is more common and concentrated in Alberta than in British Columbia

(Liseroudi et al., 2020). Liseroudi et al. (2020) suggests that this is the reason the Montney Formation has higher H<sub>2</sub>S concentration in Alberta than in British Columbia. In Alberta, Davies (1997) observed anhydrite cements within the coquinas of the Montney Formation as well as a mineral replacement of fish fossils. Anhydrite is observed as either fine crystalline anhydrite cements in British Columbia or as coarse crystalline, vug and fracture fill cements in Alberta (Liseroudi et al., 2020). Geochemical analyses by Liseroudi et al. (2020) suggest the anhydrite within the Montney Formation in western Alberta is sourced from the deeper Devonian rocks via deep seated faults/structures; however, no interpretation was given for the anhydrite within the Montney Formation in British Columbia. Many operators believe the same processes that are responsible for the souring of the Montney Formation in western Alberta are also occurring in British Columbia where the H<sub>2</sub>S gas generated in deeper sour pools has migrated up through structures into the Montney Formation. The exact mechanism(s) for souring of the Montney Formation, particularly in British Columbia, is/are still not well understood.

This project investigates the sources of sulphur that contribute to the formation of hydrogen sulphide in the Montney Formation in British Columbia, in order to reduce the uncertainty regarding the encountering of hydrogen sulphide during drilling and production operations. Four wells in the province are the focus of the research, which include, Well Authorization numbers 30876, 3944, 8183 and 29453 (Figure 5.1). In addition, sulphur isotopic analyses of minerals and organic matter have been included to provide a total of 218 samples (see appendix A). The isotopic ratio of sulphur within the H<sub>2</sub>S gas can be used to identify the sources of the sulphur, as the isotopic ratio of sulphur sources varies according to H<sub>2</sub>S formation processes (thermochemical vs bacterial sulphate reduction), and the geological period according to changes in sulphate ratios in seawater over geological time (i.e., Triassic versus Devonian sulphates; Figure 5.2). The authors utilise this variation in sulphur isotopic ratios to determine the sources of the hydrogen sulphide in the Montney Formation in British Columbia. These data together with textural analyses (SEM-EDS) are used to develop a model for H<sub>2</sub>S formation, which can provide recommendations to future well planning in the Montney Formation.

# 5.3. Methodology

#### 5.3.1. XRD Mineralogical Composition

A total of 59 drill cuttings samples were analysed for mineralogical composition using XRD analyses and Rietveld analysis (Table 5.1). Crushed samples (<250 mm) were mixed with ethanol, hand-ground with mortar and pestle, and then smear-mounted on glass slides. A normal-focus cobalt X-ray tube was used on a Siemens<sup>®</sup> Diffraktometer D5000 at 40 kV and 40 mA. The mineral composition was quantified (Munson et al., 2016) by Rietveld analysis (Rietveld, 1967) using the Bruker AXS Topas<sup>®</sup> V3.0 software.

#### 5.3.2. Anhydrite, Pyrite and Organic Matter Separation

Anhydrite was chemically separated from a total of 37 samples from 4 wells. The bulk drill-cutting samples were crushed to a particle size finer than 60 mesh sieve, and chemical separation of anhydrite was performed by adding 5% (mass) of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) solution to dissolve anhydrite/gypsum from the samples. The mixture was acidified by adding hydrochloric acid until the pH dropped below 4.0, filtered, and then 10% (mass) of Barium dichloride dihydrate (BaCl<sub>2</sub>.2H<sub>2</sub>O) was added to precipitate barite (BaSO<sub>4</sub>). The precipitate contains the original sulphur and oxygen (as SO<sub>4</sub>) from the anhydrite. Once the barite is dried, the concentrates were sent to the Jan Veizer Stable Isotope Laboratory at the University of Ottawa. The sulphur and oxygen isotopic ratios that were measured are the average ratios for all anhydrite present in the formation. An additional 181 samples were used from a variety of studies (see Appendix A).

To test if sulphur could be sourced from organic matter or pyrite, a selection of Montney Formation samples was processed to concentrate kerogen (n = 5) and pyrite (n = 3). Silicates are removed from the samples by concentrated hydrofluoric acid within a fume hood. The mixture is filtered, and the solid residue is treated with hydrochloric acid (conc.) to remove carbonates. This is repeated until no reaction occurs. The residual solid contains both kerogen and pyrite as these components do not react with hydrofluoric acid or hydrochloric acid. The kerogen and pyrite are physically separated in heavy liquids with densities of 1.2 g/cc and 3.5 g/cc, respectively. Kerogen is collected as a float within the 1.2 g/ cm<sup>3</sup> heavy liquid and the pyrite in concentrated in the sink portion of the 3.5 g/cm<sup>3</sup> heavy liquid. As kerogen and pyrite can be finely associated, the pyrite is treated with concentrated hydrogen peroxide to remove any finely intermingled kerogen. The kerogen and pyrite concentrates were then sent to Jan Veizer Stable Isotope Laboratory at University of Ottawa for sulphur isotopic analyses.

The  $H_2S$  sampling for this study was performed by Stratum Reservoir, LLC (Calgary, AB) at the request of operators, and sent to Stratum Reservoir's Isotech Laboratory in Champaign, Illinois, USA. This is a specialised procedure due to the toxic nature of the  $H_2S$  gas that can only be performed by this company or by the University of Calgary. A total of 120 sulphur isotopic samples from  $H_2S$  gas in the Montney Formation were used in this study that includes the 69 samples from this study (see Appendix B).

A total of 29 drill cutting samples were analysed from Well Authorization numbers 30876, 3944, 8183 and 29453 (Figure 5.1). These samples are a sub-sample of the anhydrite mineral separation samples. Twenty-nine thick sections were cut and polished to a thickness of 30  $\mu$ m. Back-scattered electron microscopy (BSEM) was performed on selected samples. BSEM analysis and photomicrographs were acquired using a scanning electron microscope (SEM) with an accelerating voltage of 20 keV and at a working distance between 10 and 11 mm. Elemental identification was obtained using an energy-dispersive spectrometer (EDX), which allowed identification of the chemical composition of mineral phases by their X-ray spectra using Bruker Espirits V1.9 software with an accelerating voltage of 20 keV.

## 5.4. Results

The sulphur and oxygen isotopic ratios for anhydrite minerals for Triassic and Devonian samples are shown in Figure 5.3. Sulphur isotopic ratios for anhydrite for Triassic rocks range between 8.9 and 20.98‰ (Appendix A), and their spatial distribution is shown in Figure 5.4. The dashed boxes in Figure 5.3 illustrate the sulphur isotopic ranges for  $H_2S$  gas (red dashed box, n= 120) and kerogen (grey dashed box; n= 6), as these molecules do not have oxygen attached, or in the case of kerogen, the oxygen values are not relevant as the oxygen may not have formed with the sulphur. Pyrite results (n = 3) for the sulphur ratio range between 2.9 and 49.9‰ which covers the entire range of the cross-plot and therefore no dashed box is added.

The sulphur isotopic data for H<sub>2</sub>S gas are shown in Appendix B. Sulphur ranges between 9.3 and 17.4‰ with one outlier of 20.9‰ for the Montney Formation. There are no stratigraphic differences observed in the data (i.e., upper, middle, lower Montney; Figure 5.9) and there is no regional trend across the play area (Figure 5.4). The box and whisker plots for the sulphur isotopic ratio ranges seen within the upper, middle, and lower Montney Formation shows no significant difference in the sulphur isotopes (Figure 5.9). Sulphur ranges between 10.9 and 19.3‰ for H<sub>2</sub>S gas in Devonian-aged formations. There are no stratigraphic differences observed within the Devonian samples. Hutcheon (1999) had similar observations for Devonian-aged formations in WCSB. Hutcheon (1999) measured  $\delta$ 34S values between 14 and 26‰ for Devonian rocks in the Alberta basin.

XRD analyses show that the Triassic Charlie Lake Formation contains the highest proportions of anhydrite (Table 5.1). The Halfway, Doig, Montney and Belloy formations also contain anhydrite but at much lower concentrations than the Charlie Lake Formation.

SEM and EDX analyses of the Charlie Lake and Montney formations are shown in Figure 5.6 to Figure 5.8. As indicated by the XRD results, the Charlie Lake Formation contains a greater percentage of anhydrite than the Montney Formation. The anhydrite concentration in the Montney Formation is less than 2% by weight. The anhydrite in the Montney Formation is observed by SEM as a massive texture, as a diagenetic cement filling around fine-grained dolomite, or as part of a fracture fill with a dolomite and anhydrite phase (Figure 5.6). The anhydrite does not show detrital or evaporitic textures, which is observed with the Charlie Lake Formation (Figure 5.7). No massive anhydrite was observed in Charlie Lake Formation samples, but were observed as a diagenetic cement between dolomite grains. As these samples are drill cuttings collected during drilling operations, there is a potential that the anhydrite observed in the Montney Formation, is due to cave-in from the overlying Charlie Lake Formation. However, there was no massive anhydrite associated with the fine-grained dolomite observed in the Charlie Lake Formation, which is observed in the Montney Formation. SEM-EDX analysis of the Doig Formation indicates the nodules that are present are enriched in apatite and anhydrite (Figure 5.8) and the anhydrite does exist as primary depositional texture in the Doig Formation as observed by Desrocher (1997) and Desrocher et al. (2001).



Figure 5.3 - Cross plot of sulphur and oxygen isotopes from anhydrite, pyrite, kerogen and H<sub>2</sub>S gas from both Triassic and Devonian sources. Point data is the oxygen and sulphur isotopic data for anhydrite minerals for both Triassic and Devonian samples. Triassic sourced sulphur from anhydrite minerals all plot within the green box and are 34-depleted compared to the Devonian sourced sulphur (34-enriched) from anhydrite (blue box). Samples from the Muskeg Formation in this project (purple circles) have the isotopically lightest Devonian sulphur/oxygen anhydrite and with the

two samples from the Doig and Halfway formations have created a transitional zone between the two data sets (i.e., 18-20 ‰). Yellow points are from published data for the Devonian sulphate minerals. Concentrated pyrite samples (n = 3) have been separated from Montney Formation and are not plotted on this graph as the range of sulphur isotopic results is too broad. Concentrated kerogen samples (n = 5) are from the Montney Formation and are represented by the grey dashed box as the oxygen data is not necessarily associated with the organic sulphur and therefore not included in the plot. The isotopic sulphur data from the H<sub>2</sub>S gas are also represented by dashed boxes (red = Montney H<sub>2</sub>S gas; Blue and blue shaded = Devonian H<sub>2</sub>S gas) as the H<sub>2</sub>S gas has no oxygen data associated with the sulphur. Montney H<sub>2</sub>S gas is isotopically lighter compared to Devonian H<sub>2</sub>S and each data set divided by geological age reflecting a similar isotopic range as the anhydrite mineral from each geological age. These results indicate the sulphur of the Montney H<sub>2</sub>S is sourced from Triassic anhydrite or from a mixture of Triassic and Devonian anhydrite sources if 34-enriched (i.e.,  $\delta^{34}$ S is 17-21 ‰ CDT)

Sample ID	Well Authorization Number	Formation	Depth (m)	Anhydrite	Gypsum	Pyrite	Quartz	Dolomite	Calcite	Illite/Muscovite 1M	Chlorite	Apatite (fluor-)	Albite	Microcline	Orthoclase
	30876	Charlie Lake - Boundary													
PBN-1		Lake	1392	42.6	0.3	0.0	9.1	36.5	1.7	2.5	0.0	0.0	1.5	0.0	6.0
PBN-2	30876	Charlie Lake - Coplin	1430	19.9	0.1	0.0	11.5	50.8	3.8	3.0	0.0	0.0	1.3	0.0	9.6
PBN-3	30876	Charlie Lake N. Pine	1467	21.7	0.0	0.0	14.6	39.7	3.7	5.6	2.4	0.0	5.8	6.6	0.0
PBN-4	30876	Charlie Lake - Artex	1542	18.6	0.0	0.0	13.1	39.6	9.6	6.6	2.2	0.0	2.8	7.5	0.0
PBN-5	30876	Halfway	1597	0.4	0.1	0.8	65.5	18.6	3.7	1.6	0.0	0.0	1.2	8.0	0.0

Table 5.1 - Mineralogy from X-ray diffraction and Rietveld analyses for of the 4 wells, WA# 30876, 3944, 8183 and 29453.

PBN-6	30876	Doig Silt	1642	0.4	0.0	1.2	31.5	20.3	29.8	1.4	0.0	7.0	1.6	7.0	0.0
PBN-7	30876	Doig Shale	1722	0.7	0.0	1.5	21.5	22.4	18.0	9.2	0.2	5.9	3.7	17.0	0.0
PBN-8	30876	Doig Phosphate	1757	0.3	0.0	2.4	19.7	19.2	33.2	3.6	0.0	7.3	1.4	12.9	0.0
PBN-9	30876	Upper Montney	1770	0.9	0.0	1.7	33.9	17.3	14.9	3.2	0.0	2.5	3.7	4.7	17.2
PBN-10	30876	Upper Montney	1790	1.0	0.0	2.2	26.7	20.1	6.7	4.5	0.0	0.3	2.0	5.4	31.0
PBN-11	30876	Upper Montney	1815	0.9	0.0	1.8	27.8	18.8	3.2	5.9	1.1	0.0	2.3	5.9	32.2
PBN-12	30876	Upper Montney	1857	0.6	0.0	2.4	30.9	18.3	6.4	6.4	1.8	0.0	2.1	5.3	26.0
PBN-13	30876	Lower Montney	1972	0.6	0.0	2.6	25.8	15.8	6.8	6.8	3.0	0.0	1.8	7.0	29.9
PBN-14	30876	Belloy	2073	0.6	1.7	0.5	9.4	82.4	3.3	0.0	0.5	0.0	0.5	1.1	0.0
CL Upper 5570	3944	Charlie Lake	1698	17.6	1.6	0.0	11.4	39.9	0.3	19.4	2.3	0.0	7.7	0.0	0.0
CL 5620-5640	3944	Charlie Lake	1713	22.0	1.8	0.0	8.2	45.0	0.6	16.3	1.2	0.0	4.9	0.0	0.0
CL 5650-5850	3944	Charlie Lake	1722	16.9	1.8	0.0	15.2	35.5	4.6	18.9	1.7	0.0	5.4	0.0	0.0
Cl Base 6010- 6130	3944	Charlie Lake	1832	5.9	1.3	0.0	18.9	41.8	7.5	18.3	1.7	0.0	4.7	0.0	0.0
Halfway 6280 Single	3944	Halfway	1914	0.7	0.0	0.0	44.6	18.8	22.5	10.1	0.0	0.0	3.4	0.0	0.0
Halfway 6130- 6400	3944	Halfway	1914	3.3	0.0	0.0	44.7	29.4	2.7	11.7	0.2	0.0	7.9	0.0	0.0
Doig Silt 6400- 6570	3944	Doig Silt	1951	3.7	2.6	0.0	40.1	21.0	0.0	21.6	0.0	1.3	9.7	0.0	0.0
UM 6870- 7250	3944	UM	2094	1.0	0.0	1.7	30.5	15.7	7.7	23.9	1.8	0.8	16.9	0.0	0.0
UM 7180	3944	UM	2189	1.9	0.0	1.3	33.0	24.4	7.7	16.7	0.0	1.3	13.7	0.0	0.0
MM 7670	3944	MM	2338	1.5	0.0	1.2	36.6	18.2	5.6	16.3	7.4	1.3	11.9	0.0	0.0

LM 7930	3944	LM	2417	0.4	0.0	2.7	30.3	10.7	3.7	38.1	5.6	0.0	8.7	0.0	0.0
Belloy 8040	3944	Belloy	2451	0.0	0.0	1.5	48.6	9.8	32.5	32.5	0.1	0.0	3.3	0.0	0.0
Debolt 8180	3944	Debolt	2493	0.0	0.0	0.0	4.4	0.0	95.4	0.0	0.0	0.0	0.2	0.0	0.0
Debolt 8110- 8190	3944	Debolt	2472	0.0	0.0	0.0	2.7	0.0	97.2	0.0	0.0	0.0	0.1	0.0	0.0
8183-1425	8183	Charlie Lake	1425	5.6	0.0	0.0	19.1	37.1	0.0	29.3	6.4	0.0	2.6	0.0	0.0
8183-1480	8183	Charlie Lake	1480	1.2	0.0	0.0	45.3	16.2	6.6	18.4	0.7	0.0	11.7	0.0	0.0
8183-1510- 1550	8183	Halfway	1530	0.3	0.0	0.0	57.1	17.0	1.3	14.5	0.8	0.0	9.0	0.0	0.0
8183-1560- 1610	8183	Doig	1585	0.7	0.0	1.3	24.8	22.4	15.3	23.2	0.0	4.0	8.3	0.0	0.0
8183-1675	8183	Upper Montney	1675	0.7	0.0	2.1	24.3	18.9	22.1	22.4	1.0	0.0	6.2	0.0	0.0
8183-1720- 1780	8183	Middle Montney	1750	1.3	0.0	2.0	29.0	16.2	14.6	23.0	4.2	0.0	7.6	0.0	0.0
8183-1785- 1870	8183	Lower Montney	1827	0.2	0.0	2.7	33.1	14.3	4.2	33.3	8.4	0.0	3.8	0.0	0.0
8183-1875	8183	Belloy	1875	0.4	0.0	2.8	27.5	9.1	2.8	36.0	5.4	2.0	14.2	0.0	0.0
8183-1915	8183	Debolt	1915	0.4	0.0	0.0	2.2	3.7	77.8	15.6	0.1	0.0	0.2	0.0	0.0
8183-2130	8183	Debolt	2130	0.1	0.0	0.0	5.1	4.4	72.0	18.2	0.0	0.0	0.2	0.0	0.0
8183-2270	8183	Debolt	2270	0.0	0.0	0.0	12.6	5.5	56.5	23.8	0.5	0.0	0.5	0.0	0.0
8183-2690	8183	Debolt	2690	0.2	0.0	0.0	6.6	4.6	73.7	12.2	2.3	0.0	0.5	0.0	0.0
8183-2855	8183	Debolt	2855	0.2	0.0	0.0	17.8	7.2	36.4	25.6	11.6	1.2	0.0	0.0	0.0
8183-2935	8183	Debolt	2935	0.2	0.0	0.0	23.8	5.0	12.4	36.0	21.5	0.0	1.1	0.0	0.0
8183-3055	8183	Debolt	3055	0.3	0.0	1.6	14.3	8.9	0.3	40.9	29.4	0.0	4.2	0.0	0.0
8183-3302	8183	Slave Point	3302	0.0	0.0	1.4	10.4	54.4	17.8	15.1	0.5	0.0	0.4	0.0	0.0
8183-3342	8183	Slave Point	3342	0.0	0.0	0.6	16.2	41.6	14.3	26.1	0.6	0.0	0.7	0.0	0.0
8183-3326	8183	Slave Point	3326	0.3	0.0	0.0	16.9	5.0	0.9	34.8	26.6	0.0	15.4	0.0	0.0

8183-3400	8183	Slave Point	3400	0.1	0.0	0.5	3.0	10.4	69.3	15.9	0.6	0.0	0.3	0.0	0.0
8183-3490	8183	Muskeg	3490	45.3	4.6	0.3	5.2	35.6	2.4	4.5	1.1	0.0	1.0	0.0	0.0
8183-3495	8183	Muskeg	3495	9.8	1.5	0.3	7.5	72.0	3.0	4.8	0.4	0.0	0.8	0.0	0.0
8183-3500	8183	Muskeg	3500	41.9	5.4	0.2	5.7	32.8	7.9	4.7	0.5	0.0	0.9	0.0	0.0
8183-3505	8183	Muskeg	3505	32.1	5.6	0.3	4.9	51.2	2.3	2.7	0.2	0.0	0.7	0.0	0.0
CL 1590-1700	29453	Charlie Lake	1590	6.4	0.0	0.0	10.7	34.3	22.7	21.8	0.9	0.0	3.2	0.0	0.0
CL 1805-1873	29453	Charlie Lake	1805	9.8	0.0	0.0	12.9	39.1	5.6	28.6	1.1	0.0	3.0	0.0	0.0
Halfway 1880- 1890	29453	Halfway	1880	1.0	0.0	0.7	56.3	10.9	6.1	24.1	0.2	0.0	0.8	0.0	0.0
Doig Silt	29453	Doig Silt	1888	3.1	0.0	0.6	34.8	12.1	11.7	21.7	0.8	6.4	8.9	0.0	0.0
Doig Sh 1940- 2004	29453	Doig Shale	1940	3.0	0.0	1.2	16.6	14.3	25.6	24.3	1.5	4.5	9.0	0.0	0.0
UM 2004- 2140	29453	UM	2004	1.3	0.0	1.2	32.1	22.5	8.9	28.0	0.2	0.0	5.8	0.0	0.0
MM 2140- 2250	29453	ММ	2140	2.9	0.0	1.5	28.9	22.2	5.6	29.2	0.4	0.0	8.3	0.0	0.0
LM 2250-2320	29453	LM	2250	1.6	0.0	1.2	29.1	15.9	6.5	31.0	8.2	0.0	6.5	0.0	0.0
Hz LM 2330	29453	Hz Leg (LM)	2330	1.1	0.0	0.8	23.7	20.9	5.7	33.7	7.4	0.0	6.8	0.0	0.0



Montney Hydrogen Sulphide and Sulphur Isotopic Ratio

Figure 5.4 - Distribution of sulphur isotopic ratios in the Montney Formation on the base map of  $H_2S$  distribution. The sulphur isotopic ratio shows no trends across the area and has a narrow range of ratio from  $\delta^{34}S$  of 9 to 21‰ compared to the range of sulphur ratios from Devonian to the Triassic rocks.



Figure 5.5 - H<sub>2</sub>S formation models for sour Montney wells. A total of 218 mineral and organic matter samples were isotopically analysed with 120 H<sub>2</sub>S gas sampled also isotopically analysed. Diamond symbols represent the sulphur in the mineral form, prior to being converted to sulphate ions and used in the formation of H<sub>2</sub>S gas when in contact with hydrocarbons. Circle symbols represent the sulphur once converted to H<sub>2</sub>S gas. Model 1 represents an in-situ conversion which would be the conversion of anhydrite that is derived from the Montney Formation (i.e., syn-depositional anhydrite). This model is plausible as the Montney Formation does contain small amounts of anhydrite (< 5%). However, the H<sub>2</sub>S distribution would be more consistent and the localised changes between sweet and sour lateral wells on the same pad would not be observed (i.e., Figure 3.39). Model 2 is structurally controlled, with anhydrite or sulphate ions derived from sulphate minerals with the Charlie Lake Formation migrating through local fracture/fault systems into the Montney Formation (prior to hydrocarbon charging and over-pressuring). H<sub>2</sub>S gas is generated once hydrocarbons are generated in the Montney Formation and encounter the sulphate ions. A similar model has been shown for migration of sulphate ions from the Charlie Lake and into the Halfway Formations (Sharma, 1969). Model 3 is a mixing of sulphur ions from Triassic and Devonian sources and structural controls would need to include a deeper connection with the Devonian source. This results in a heavier sulphur isotopic signature in the H<sub>2</sub>S compared to Model 2. Liseroudi et al. (2020) shows evidence that dissolved sulphate ions have migrated from the Devonian in to the Montney Formation within the Alberta Montney play area.



Figure 5.6 - Scanning electron microscope images and energy dispersive X-ray spectroscopic (EDX) mapping showing the textural relationship between dolomite (D) and anhydrite (A) within the upper Montney Formation. Well Authorization # 30876 EDX maps show the concentration of magnesium (Mg) and calcium (Ca) in the dolomite minerals and the concentration of sulphur (S) and calcium (Ca) in the anhydrite minerals. The textural relationship shows the replacement of dolomite by anhydrite as either a fracture fill or diagenetic cement, infilling around dolomite grains (black arrow; E).



Figure 5.7 - Mineralogical textures in the Charlie Lake formation. The Charlie Lake Formation shows both detrital anhydrite grains (white arrow; A) and evaporitic textures (black arrow; E). The detrital anhydrite grains are also associated with quartz grains (blue arrow; A). The anhydrite is determined by the high calcium (F) and high sulphur (H) contents. The evaporitic texture seen in (E) is similar to the nodular texture seen in Warren (2016) evaporites; dolomite anhydrite associations are interpreted as evaporites in the Charlie Lake Formation (Hunt and Ratcliffe, 1959). Very large dolomite grains also form in the evaporitic environment (E). The dolomite contains high magnesium (G) and calcium (F) contents. Well Authorization # 30876.



Figure 5.8 - The Doig Formation that overlays the Montney Formation shows phosphatic nodules that are also rich in anhydrite, as illustrated by the high sulphur concentrations. The nodules are concentrated in calcium, sulphur and phosphate and are found associated with dolomite grains (blue arrows). Anhydrite-rich phosphatic nodules have also been observed in the Doig Formation by Desrocher (1997). This detrital texture for the anhydrite shows that the sulphate would need to be dissolved from the nodules and then migrated and deposited in the Montney Formation as a cement in fractures.



Figure 5.9 - The sulphur isotopic ratio range for the upper, middle, and lower Montney Formation from this study (n = 60). The box and whisker plot indicates that there is no significant difference between the isotopic signatures of these informal units. See Appendix B for details on samples.

## 5.5. Discussion

The isotopic signatures of the H<sub>2</sub>S gas in the Montney Formation in British Columbia range between 9.3 and 20.9‰. This range is similar to the sulphur isotopic ratios for Triassic anhydrite, which range between 8.9 and 20.98‰ (Figure 5.3). The sulphur isotopic ratio for anhydrite in Devonian rocks ranges between 17.1 and 34‰, and when plotted with oxygen isotopic ratio show a distinct signature from that of anhydrite in Triassic rocks (Figure 5.3). There is a natural division or separation of sulphur/oxygen isotopic data that occurs between Triassic and Devonian anhydrite minerals due to the difference in sulphur and oxygen ratios in the seawater at the time of anhydrite formation (i.e., Figure 5.3). This difference is also seen within the data from this study and published data from the WCSB (Figure 5.3), with the Triassic anhydrite (pink, brown, red, black, blue, grey and green circles within green box) being isotopically lighter than Devonian anhydrite (yellow and purple circles in blue box).

The sulphur isotopic ratio between  $H_2S$  is more similar to the sulphur ratios in the Triassic anhydrite than in Devonian rocks; which indicates the Triassic rocks, such as the Charlie Lake Formation, are the

more likely sources of sulphur, and not the Devonian rocks as expected by some operators. The isotopic ratio for sulphur is also too enriched in  $\delta$ 34S to have been generated by BSR. The sulphur ratio is generally much lighter (up to 30‰ less) in BSR-generated H<sub>2</sub>S gas than in thermochemical sulphate reduction processes (Hubbard et al., 2014). The basin modelling indicates the Montney Formation has been buried to a depth of more than 8500 m (this study; Figure 3.16 and Figure 3.17), and is more likely to have developed TSR-generated H<sub>2</sub>S gas as the Montney Formation entered the oil window, while co-generating hydrocarbons and H<sub>2</sub>S gas when the reservoir temperatures were well above 70-80°C. Most bacterial sulphate reduction reactions cease above 60°C (Hubbard et al., 2014).

Sulphur isotopic data from the  $H_2S$  gas in Mississippian- and Devonian-aged reservoirs of Burnt Timber and Crossfield East gas fields, Alberta range between 18 to 25.9‰ (Yang et al. 2001). This is similar to the sulphur isotopic ratio for Devonian anhydrite and indicates that Devonian  $H_2S$  gas is generated by Devonian sulphur sourced from anhydrite. The majority of the sulphur isotopic data from the  $H_2S$  of the Montney producers in northeastern British Columbia shows a signature that is too light to be sourced from the deeper Devonian sour pools. However, data from this study has shown that there are few data points for isotopically lighter Devonian samples (purple circles; Muskeg Formation; Figure 5.3), as well as two isotopically heavier Triassic samples (Halfway and Doig samples; Figure 5.3), which results in a transitional zone between the two data sets (i.e., 18-20‰). Similarly, there is an overlap between  $H_2S$  gas sulphur isotopic data from the Triassic (red dashed box) and the Devonian (Blue dashed box) within the same isotopic range for sulphur at 18-20‰ (Figure 5.3). Sour wells that have  $H_2S$  gas sulphur isotope values in the 18 - 20‰ may represent either 1) the original Devonian or Triassic sulphur (anhydrite) sources that are in the transitional zone; or 2) is a mixture of  $H_2S$  gas sourced from the Triassic and Devonian sour reservoirs. In most cases, this is the exception and not the rule.

Sulphur isotopic ratios for pyrite concentrated samples (n = 3) is inconclusive as the range of 2.9-49.9‰ is greater than the range of sulphur isotopic ratio for H<sub>2</sub>S gas (9-26‰). A continuous supply of dissolved oxygen within frack water or from meteoric groundwater is needed, as the reservoir is under reducing conditions, in order to oxidize pyrite and generate sulphate ions for H<sub>2</sub>S formation. Most frack water provides only a limited supply of oxygen to the formation during hydraulic fracturing operations. This would result in an initial H<sub>2</sub>S spike that would then rapidly decline. Most wells in the Montney Formation that do sour, do not show a rapid decline in H<sub>2</sub>S concentration (i.e., Figure 5, Chalmers et al., 2019). It is also unlikely that oxygenated groundwater would be present at the current reservoir depths of the producing Montney wells in BC. The sulphur ratios for the organic sulphur from kerogen indicate lighter isotopic signatures (-6 to 6‰) compared to the sulphur ratios of the anhydrite and H<sub>2</sub>S gas. The difference between the Montney H<sub>2</sub>S gas sulphur and the kerogen sulphur indicates that the organic sulphur is also not the source of the H<sub>2</sub>S gas (Figure 5.3).

Overall, the cross-plot of sulphur and oxygen isotopes for the anhydrite minerals shows distinct signatures for Triassic and Devonian source anhydrite sulphur (Figure 5.3), and this distinction is also evident in the sulphur isotopic signature of the  $H_2S$  from Triassic and Devonian sour reservoirs. The overlap of Triassic  $H_2S$  sulphur isotopes with Triassic anhydrite sulphur ratio (i.e., 9-20‰) is strong evidence that the sulphur is being sourced from Triassic evaporites (i.e., anhydrite), which is derived from the

isotopically lighter Triassic seawater and not purely from a Devonian evaporite source. For sour Montney wells that have H<sub>2</sub>S sulphur signature below 17‰, it would indicate the H<sub>2</sub>S is being sourced from a Triassic formation and not a Devonian formation. Sour Montney wells that have sulphur signatures in the 17-21‰ range are potentially from a mixture of Triassic and Devonian H<sub>2</sub>S gas or from the lighter isotopically Devonian Muskeg Formation. There is no evidence that sulphur isotopic ratios will fractionate during H<sub>2</sub>S migration which would result in a lighter sulphur isotopic signature. There is no mechanism in place that would cause the sulphur ratio to change during migration in the Montney play area (i.e., BSR, molecular sieve processes). The range of sulphur ratios measured in the H<sub>2</sub>S gas from Montney Formation and Devonian-aged sour wells suggest that the H<sub>2</sub>S gas has not fractionated and represents the sulphur signature of the anhydrite sulphur source.

A H<sub>2</sub>S gas generation model has been developed from the isotopic and SEM-EDX data. SEM and EDX analyses have shown that the anhydrite texture is massive in the Montney Formation. The texture appears to be part of fracture fill cement (secondary texture) and did not form from transportation or evaporative processes (primary textures). As this analysis is performed on drill cuttings, this observation may be due to contamination of drill cuttings from the Charlie Lake Formation above; however, the texture seen in the anhydrite in the Montney Formation (secondary texture) is not the same as the anhydrite in the Charlie Lake Formation (primary, evaporite textures). The anhydrite that is found within the Montney Formation is being sourced from another formation through solution and redeposition as a cement from a sulphate-rich solution prior to hydrocarbon generation. Hydrogen sulphide gas then is generated locally at the anhydrite-cemented fractures, as it reacts with the hydrocarbons being generated in the Montney Formation. This would explain the localised souring of horizontal wells adjacent to sweet horizontal wells on the same multi-well pad and fits the H<sub>2</sub>S generation Model 2 in Figure 5.5. The sulphur and oxygen isotopic data suggest the anhydrite in the Montney Formation is from a Triassic source and most likely from the Charlie Lake Formation, or potentially from the Doig Formation, which contains anhydrite within the phosphatic nodules. The isotopic signature of the H<sub>2</sub>S gas that is produced from the Montney Formation is also of similar ratio to the Triassic anhydrite, and it appears the Triassic anhydrite is the source of the sulphur and generation of H<sub>2</sub>S gas. Only sour Montney producing wells that contain sulphur isotopic ratios above 17‰ for H<sub>2</sub>S may have been derived from a mixture of isotopically heavier H<sub>2</sub>S gas from Devonian rocks with the isotopically lighter Triassic H<sub>2</sub>S gas.

Three geological models are created to explain H<sub>2</sub>S formation in the Montney play in northeastern British Columbia (Figure 5.5). Model 1 represents an in-situ conversion which would be the conversion of anhydrite that is derived from the Montney Formation (i.e., syn-depositional anhydrite). This model is plausible as the Montney Formation does contain small amounts of anhydrite (< 5%); however, the H<sub>2</sub>S distribution would be more evenly distributed across multi-well pads, and we would not observe localised changes between sweet and sour lateral wells on the same pad as the syn-depositional anhydrite would be more laterally continuous. Model 2 is structurally controlled through faults and fractures; with anhydrite or sulphate ions derived from sulphate minerals within the Charlie Lake Formation migrating into the Montney Formation through local fracture/fault systems via circulating groundwater flow during early burial (i.e., prior to hydrocarbon charging and overpressure). The H<sub>2</sub>S gas would form as hydrocarbons are generated within the Montney Formation and encounter the sulphate ions. A similar model has been shown for migration of sulphate ions from the Charlie Lake and into the Halfway Formation (Sharma, 1969), and between the Charlie Lake and Montney formations within the Fort St. John Graben structures (Desrocher et al., 2001). Model 3 is a mixing of sulphur ions from Triassic and Devonian sources, and structural controls would need to include a deeper connection with Devonian sources. This results in a heavier sulphur isotopic signature in the H<sub>2</sub>S compared to Model 2. Liseroudi et al. (2020) shows evidence that dissolved sulphate ions have migrated from the Devonian into the Montney Formation within Alberta and deposited as anhydrite in fractures and vugs, but similar evidence is not observed in this study for the Montney Formation in British Columbia.

The basin model maps that depict the locations most likely to have generated TSR H<sub>2</sub>S gas (Figure 3.27 to Figure 3.34) indicate that most of the H<sub>2</sub>S generation has occurred to the west of the current souring wells (Figure 3.35 to Figure 3.38). As the H<sub>2</sub>S gas formation models presented in this report indicate, structural features have acted as conduits for sulphate minerals or dissolved sulphate ions migrated into the Montney Formation. This is the best explanation that some wells on a multi-well pad can be sweet or sour. Therefore, a model of H<sub>2</sub>S generation in deeper Montney Formation to the west with subsequent migration to the current locations of souring wells to the east, does not fit with the observation of discrete sweet and sour production on one multi-well pad. The maps that show the areas of British Columbia which are more likely to have TSR-generated H<sub>2</sub>S are based on the entry and exit ages of the Montney Formation at a depth that would generate TSR H<sub>2</sub>S and do not represent an actual H<sub>2</sub>S generation map. The sulphate distribution needs to be included in the modelling as the sulphate is controlled by structural lineaments, faults, and fractures that connect with the overlying Triassic sulphate ions/minerals and has been buried to adequate depths/temperatures (i.e., 100-120°C) will the producing well in the Montney Formation sour.

#### 5.6. Summary

The sulphur source for sour Montney wells were investigated using chemical and physical separation techniques, SEM-EDX, XRD and isotopic analyses. The results indicate that the Montney Formation does contain small quantities of anhydrite minerals, which appear to have been formed post-depositionally as a massive anhydrite cement. Sulphur isotopic analyses suggests that the most likely source of sulphur is from the Triassic rocks, in particular, the Charlie Lake Formation due to, 1) its high concentration of anhydrite (i.e., 18-42%); 2) its close proximity; and 3) the evidence that dissolved sulphate ions have circulated in the groundwater in fractures and transported anhydrite into the Halfway Formation (Sharma, 1969) and into the Montney Formation (Desrocher et al., 2001). The sulphur isotopic signature of anhydrite in the Triassic rocks is in a similar range as the sulphur isotope signature of the H<sub>2</sub>S gas in the Montney Formation. The sulphur isotopic signature is heavier in both the Devonian anhydrite and Devonian H<sub>2</sub>S gas and they do not isotopically match the sulphur from the H<sub>2</sub>S in the Montney Formation. There are several sour Montney wells with slightly heavier sulphur signatures in the H<sub>2</sub>S gas and this could be due to the mixing of the H<sub>2</sub>S generated in both the Triassic and Devonian sources.

Operators should map structural features and sour pools both above and below the Montney Formation with special attention to the Charlie Lake Formation above, as this is the likely source of sulphate ions prior to hydrocarbon generation. Operators are also encouraged to continue to sample  $H_2S$  gas and measure the sulphur isotopic ratios to increase the isotopic database and highlight changes in local and regional trends.

# 6. Distribution of Sulphate and Other Major Ions in Montney Completion, Produced and Formation Waters: Implications for the In-Situ Formation of Hydrogen Sulphide and Origins of the Connate Water

## 6.1. Abstract

The distribution of sulphate and other major ions in Montney and Doig formations flowback and produced waters provide insights into the origin and distribution of hydrogen sulphide in produced gas and nature of the connate water. At a regional scale, the salinity (TDS/L) of Montney produced water is generally lowest on the northwest and the southern edges along the deformation front, mostly mirroring the regional structure on the Montney Formation.

Southwest, away from the subcrop edge, the connate water salinity varies and there is no single parameter that accounts for the variation. It is probable that the regional salinity patterns that would be anticipated to mimic burial history have been overprinted in part by differential gas migration, which led to variable dehydration of the reservoir, in many areas to below irreducible water saturation. Most areas of high salinity include a mixture of wells that are enriched in bromine (Br) relative to what would be anticipated by seawater evaporation, suggesting mixing of brines with lower salinity water or fresh water. Produced waters depleted in Br reflect a mixture of evaporated seawater that contacted halite, or waters that contacted halite and are thus interpreted to have been impacted from migrating evaporitic brines from or underlying evaporites. Areas of low Br and chlorine (Cl) concentrations less than seawater were flushed by freshwater. For most produced water, the calcium (Ca) content is higher and the magnesium (Mg) content lower than predicted by the seawater evaporation trajectory, reflecting dolomitisation leading to the consumption of Mg and liberation of Ca from dissolution of calcite.

Regional analyses of flowback waters from completed wells show an increase in major ion concentrations over the flowback period. There is variability in the ion concentrations between wells, reflecting complex interactions between injected and connate fluids and fluid-rock interactions. Using Cl,  $\delta^{18}$ O, and  $\delta^{2}$ H as conservative tracers reveals that the proportion of formation water in the flowback water of different wells over the flowback period is variable. During early flowback, the contribution from formation water ranges between 10% and 35%, while for the final flowback water samples, the formation water proportion is generally between 40% and 60%. Since there is a significant contribution from formation water, the actual volume of the injected hydraulic fracturing fluid recovered during the flowback period for most wells is < 10% of the injected fluid.

Sulphate (SO<sub>4</sub>) concentrations in the flowback fluid are higher than the values predicted by mixing of completion fluid and connate water, due to oxidation of pyrite or  $H_2S$  as a result of the injection of oxic hydraulic fracturing fluid. Decreasing SO<sub>4</sub> concentrations seen in the flowback water from some wells is related to SO<sub>4</sub> reduction by bacteria.

The impact of fluid-rock interactions of produced fluids was investigated through the use of agingleach experiments carried out at reservoir temperature, using surface area to volume ratios anticipated during completion. The salinities of leachate varied with the make-up fluid and tested lithology. Most leachates are slightly saturated with carbonates (calcite, dolomite, and aragonite) and saturation decreases with declining temperature. Barite, quartz, chalcedony, iron oxides and hydroxides are saturated at reservoir temperature and the degree of saturation increases with declining temperature. The leachates are slightly undersaturated with the evaporite minerals anhydrite and gypsum. Where manganese (Mn) is in solution, the Mn minerals are saturated. Halite is undersaturated at reservoir temperature and increases to near saturated with declining temperature. The dissolved sulphate in all the leachates is excessive due to oxidation of pyrite. There is no evidence that sulphur bearing additives in the completion fluid contribute to the sulphate, and it would not be expected to do so at the comparatively low temperatures of the reservoirs. Any H<sub>2</sub>S produced by microbial sulphate reduction (MSR) facilitated by the completion fluid would be comparatively short-lived, with the sulphate source being eventually exhausted through reduction by MSR. MSR would be further curtailed with time due to the progressive return of the reservoir to connate water salinities and reservoir temperature, both of which are at the upper limits of MSR viability.

The sulphate content of most produced Montney waters generally ranges from 50 mg/L to about 300 mg/L, although many exceptions occur. The variation in sulphate concentration in produced water and the coeval production of H<sub>2</sub>S and CO<sub>2</sub> gas are complex, and in many wells inexplicable. For some wells, there are trends of increasing or decreasing H<sub>2</sub>S and CO<sub>2</sub> gas production with time, while in other well there are no consistent trends. The relative abundance of CO<sub>2</sub> compared to methane (CH<sub>4</sub>) varies considerably, with an approximately equal number of wells having higher CO<sub>2</sub> than CH<sub>4</sub> and the remainder having less. The longer-term trends or lack thereof in H<sub>2</sub>S, CO<sub>2</sub> and SO<sub>4</sub> concentrations in the wells do not lead to a simple causative interpretation. The increase in H<sub>2</sub>S with time of production may reflect the greater adsorption affinity of H<sub>2</sub>S, such that H<sub>2</sub>S is enriched in the produced gas at lower pressures later in the reservoir life, whereas the decrease in H<sub>2</sub>S with production may reflect the decline in produced water volumes through time and hence a decrease in H<sub>2</sub>S solution gas.

#### 6.2. Introduction

Hydrogen sulphide (H<sub>2</sub>S) at concentrations ranging from 18% to a few parts per million occur in produced fluids from the Triassic Montney and Doig formations. Although high concentrations of H<sub>2</sub>S are localized geographically, low concentrations of H<sub>2</sub>S present in minor to trace amounts to nuisance levels occur throughout northeastern British Columba and adjacent areas of Alberta. The precursor and a requirement for H<sub>2</sub>S formation is reactive sulphate which, when dissolved, may be subsequently reduced to sulphide by microbial sulphate reduction (MSR) or thermal sulphate reduction (TSR) processes. In the presence of a reductant, there are potentially multiple sources for the sulphate, and hence the H<sub>2</sub>S in the Montney and Doig formations. There is isotopic evidence presented in earlier sections of this report, that in some areas of high H<sub>2</sub>S concentration, the H<sub>2</sub>S may have been sourced elsewhere; this may have occurred either directly, as a migrated gas, or indirectly from sulphate rich waters that migrated from over

or underlying sulphate-rich formations, with H<sub>2</sub>S subsequently forming in-situ by MSR or TSR. It is also suggested, based on mass balance calculations (see earlier sections), that some H<sub>2</sub>S was generated in-situ from reduction of sulphate from the original connate seawater, or sulphate from sulphur-bearing organics or inorganics. Additionally, drilling, completion and production practices may promote the formation of H<sub>2</sub>S fluids that would otherwise be sweet. In this paper the sulphate content and other major ions of flowback waters following hydraulic fracturing and produced waters are described and interpreted, and implications are drawn with respect to their origin and concentration of reservoired and produced H<sub>2</sub>S.

Previous studies (e.g. Machel, 2001; Xia and Ellis, 2016; 7, Marriott et al., 2016) of the sulphate content of produced fluids and basinal brines have shown that the sulphate content may reflect a complex combination of a number of processes including: 1) original sea water composition at time of sedimentation; 2) dissolution of evaporites; 3) fluid-rock interaction during diagenesis; 4) mixing of connate water, meteoric water or migrating basinal brines from other formations; and 5) organic sulphur from kerogen, bitumen or other sulphur-bearing hydrocarbons. In this study we attempt to unravel the sulphate sources through a combination of volumetric and chemical analyses of flowback and produced water and regional mapping and interpretation of fluids.

### 6.3. Methods

This study is based largely on data collected, analysed, and interpreted for the study with the support of industry partners. Some data we utilise is public data submitted by oil and gas companies to the British Columbia Oil and Gas Commission (BCOGC) or the Alberta Energy Regulator in Alberta (AER). The regional distribution of fluid analyses used in the study is almost entirely derived from the public data and was accessed either directly from this source or through use of geoLOGIC's Geoscout program, a third-party aggregator and provider. Detailed descriptions of the methods employed are described in Owen (2017)

#### 6.3.1. Fluids

To understand the potential for H<sub>2</sub>S originating from mixing of drilling and/or completion fluids with connate water, we have analysed a suite of completion fluids, flowback waters and produced water from approximately thirty wells across the Montney/Doig producing area (Figure 6.1). These fluids were specifically collected for analyses of the flowback water chemistry. The details of the sampling and analytical program used in this study are described by Owens (2017), and hence are only summarised here. Hydraulic fracturing fluids, as the base fluid with additives and flowback liquids, were collected at each site in 500 mL or 1 L containers. A separate sample used in each of the hydraulic fracturing stages was collected (14 to 26 samples per well) where possible. The sampling density during the flowback period varied in frequency during the flowback period from an initial 2 to 3 samples per day for the first week to 1 sample per day for the remainder of the flowback period. The variable frequency was used in order to capture the higher variability in chemistry earlier in the flowback period when the flow rate is higher. Samples were stored at 4°C prior to analysis and were heated in 120 mL acid-washed Teflon<sup>®</sup> containers

at reservoir temperature (65-80°C) for a 24-hour period prior to filtering through 0.45 μm filters. The samples were subsequently analysed for pH, conductivity, and total alkalinity, anions, and dissolved metals. The hydraulic fracturing fluid samples were also filtered and sub-divided but were not heated. For dissolved metal analyses, the preserved samples were acid-digested to remove organics prior to analysis. The digested samples were analyzed for the major cations by inductively coupled plasma-optical emission spectrometry (ICP-OES) with a Varian 725-ES ICP-OES using indium (In) as the internal standard. The ICP-OES analysis included Na, K, Ca, Mg, and Sr ions. TDS was calculated by summing the ion concentrations.

A series of geochemical models were developed and run using PHREEQC (Parkhurst and Appelo, 2013) to determine the saturation index of the principal sulphate minerals in the connate water, completion fluid and their mixtures (Table 6.1). The models use the Pitzer database due to the high ionic strength of the liquids. The modelled results were compared to the measured flowback water results in order to determine which geochemical processes are impacting the flowback water chemistry. The mineralogy to support the geochemical model was obtained through a combination of publicly available X-Ray Diffraction (XRD) results and additional samples collected in support of this study. The additional samples were analyzed by XRD following the modified smear mount method (Munson et al., 2016) and the results were interpreted using the Rietveld method (Rietveld, 1967, 1969).



Figure 6.1-Samples for oxygen and hydrogen isotope analyses used for the mixing models, were prepared from a sub-sample of unheated, filtered fluid, and mixing it with activated charcoal for a minimum of 48 hours to remove organic compounds through adsorption, as the organics may interfere with the isotopic measurements. The sample was filtered a second time to remove the activated charcoal. The stable oxygen and hydrogen isotopic analyses were completed using an LGR<sup>®</sup> DLT-100 with an LC-PAL liquid autosampler. High salinity samples were diluted with deionized water prior to the analysis in order to prevent the salts present in the sample from precipitating and plugging the instrument tubing.

#### 6.3.2. Produced water

For our study, the 'produced water' is considered to be the water that is collected after the well has been tied into the mid-stream and is producing oil or gas. The chemistry of the produced water is used to approximate the formation water chemistry for the study wells with the recognition that the impact of the injected fluid on the 'produced water' chemistry may extend well into the productive life of a well. The isotopic values for the formation water for all sites were estimated based on the analysis of the produced water samples collected as part of the present study, as isotope values are not reported in the publicly available geochemical results used for the major ion chemistry.

Table 6.1 - Summary of the four PHREEQC mixing models used for the analysis. The model results were compared to the measured concentrations and the calculated proportions of formation water to provide an understanding of the geochemical processes that are impacting the flowback water major ion concentrations (modified from Owen, 2017; Owen et al., 2020)

Model I – Mixing Only	Model II – Model I plus Secondary Mineral Precipitation	Model III – Model II plus Ion Exchange	Model IV – Model III plus Carbonate Dissolution
<ul> <li>Input parameters:         <ul> <li>Hydraulic fracturing fluid chemistry (25°C)</li> <li>Formation water chemistry estimated from produced water chemistry (75°C)</li> </ul> </li> <li>The MIX function in PHREEQC was used</li> <li>Model was set to mix the fluids together by increasing the proportion of formation water from 0% to 100% in 5% increments</li> </ul>	<ul> <li>Secondary minerals were added to the model using the EQUILIBRIUM_ PHASES function</li> <li>These minerals can precipitate if they are oversaturated in the fluid mixture but cannot dissolve</li> <li>The minerals will precipitate to equilibrium</li> <li>The potential secondary minerals include:         <ul> <li>Calcite, Aragonite</li> <li>Dolomite, Huntite, Magnesite</li> <li>Anhydrite, Gypsum</li> <li>Celestite</li> </ul> </li> </ul>	<ul> <li>Ion exchange was added to the model using the EXCHANGE function</li> <li>The exchange sites are set to equilibrate with the formation water chemistry</li> <li>Since the exchange sites are set to be in equilibrium with one of the solutions in the mixing model, the exchangeable ions do not need to be defined</li> <li>The amount of the exchangeable ions was set to 0.5 mole per kg of water</li> </ul>	<ul> <li>Potential dissolution of calcite and dolomite was included in the model using the EQUILIBRIUM_PHASES function</li> <li>Calcite and dolomite were able to precipitate or dissolve depending on the saturation indices</li> <li>The maximum amount available to dissolve was set to 1 mole per kg of water</li> </ul>

Model I is a mixing model between the injected hydraulic fracturing fluid and the formation water. The proportion of formation water is increased in 5% increments, and as no other geochemical processes are considered in the initial model, the resulting ion concentrations show a linear increase. Model II adds possible secondary mineral precipitation and allows the mixed fluid to reach equilibrium (i.e., if a secondary mineral is oversaturated in the fluid, it is allowed to precipitate until the saturation index (SI) is equal to 0). This model represents the maximum amount of precipitation. Model III adds ion exchange to the model based on the exchange sites being in equilibrium with the formation water. Setting the exchange sites to be in equilibrium with the formation water determines which ions are on the

exchange sites, so they do not need to be entered into the model manually. The amount of exchangeable ions was estimated at 0.5 mole per kilogram based on an average density (2.65 g/cm<sup>3</sup>) and the median cation exchange capacity (CEC) for 15 representative Montney Formation samples that were analyzed for CEC. The 15 samples were selected for varying clay content. Model IV adds carbonate dissolution to the model. Based on the ions considered at the level of detail in the model and the mineralogy of the formation, only the carbonate minerals are both abundant in the Montney Formation and comprised solely of the major ions included in the model. The inclusion of quartz, feldspar, and clay would require the addition of silicon (Si) and aluminum (Al) (Al for feldspar and clay only) to the model; furthermore, due to the stability of these minerals, they would not be expected to dissolve significantly during hydraulic fracturing. Up to 1% (by wt.) of calcite and 1.8% (by wt.) of dolomite are permitted to dissolve if the fluid is undersaturated in these minerals, which is only a fraction of the amount of calcite and dolomite that are available in the Montney Formation. These percentages were selected to represent a small amount of dissolution and are equivalent to 1 mole per litre of water for each of the minerals.

#### 6.3.3. Aging/Leachate/Connate Water/Speciation

In order to determine the potential contribution of rock leachate or precipitation to the sulphate content of the flowback water a series of representative core samples were subjected to leaching.

The analytical program for this study is summarized in Figure 6.2. Samples were tested under conditions simulating hydraulic fracturing in reaction vessel experiments with completion liquids prepared from freshwater, pit water (recycled flowback water), and distilled water. The measured fluid chemistries provide metrics to the model and then predict the interaction of the reservoir rock leachate and connate water with the fracturing fluid. These experiments also provide data that can be used to anticipate the composition of the reservoir connate water and flowback fluid, as well as the tendency for scaling or corrosion of tubulars and damage to the reservoir matrix or fracture systems by precipitates.

The leaching/aging and extraction experiments were designed to approximate, as closely as possible, the surface area to fluid ratio, temperature, and time of exposure of the fracturing fluid to the reservoir during completions. The experiments were conducted in reactor/aging vessels at reservoir temperatures that ranged between 65° and 85°C, and for the estimated time until flowback. Representative samples were crushed to a particle size of an equivalent surface area that was calculated to correspond to the surface area of rock in the reservoir exposed to the fracturing fluid. The size of particles was chosen to be large enough that each face can be considered an independent surface for the purpose of the leaching experiments. The volume of frac fluid per surface area used in the experiments was then calculated by utilising the predicted or measured stimulated reservoir volume per frac stage and the volume of frac fluid pumped per stage. Based on these calculations, on a mass basis, the ratio of rock/fluid utilized in the reactor vessels was typical about 1/1.36. The pH, conductivity, dissolved oxygen, and alkalinity of the leachate from each vessel was determined immediately following the experiment, prior to and following filtering of solids. Sub-samples were then prepared for anion and cation/metal analyses. The anion samples were preserved at 4 °C prior to analysis by ion spectroscopy. The

cations/metals were filtered and then preserved by reducing the pH to less than 2 via titration with ultrapure 0.6 M nitric acid (HNO<sub>3</sub>). The cations/metals were analyzed using a certified laboratory by ion chromatography and inductively coupled plasma mass spectrometry.



Figure 6.2 - Analytical program for core and fluids. Only elements in black text in green boxes are described in this report.

# 6.4. Results

#### 6.4.1. Montney Formation Connate, Flowback and Produced Water Chemistry

The Montney Formation flowback waters collected in the study and reported elsewhere by operators have elevated concentrations of the major ions with TDS up to approximately 290,000 mg/L (Figure 6.3; Table 6.2). These values are similar to what has previously been reported for flowback waters from other formations where hydraulic fracturing is occurring (e.g., Marcellus Shale – Barbot et al., 2013; Haluszczak et al., 2013; Ziemkiewicz and He, 2015). Together, Cl and Na ions account for 75 to 95% (median: 92%) of the TDS in the sampled Montney Formation flowback water. The other ions that are elevated in the flowback water are Ca, K, Mg, Sr, and, in some wells, SO<sub>4</sub> (Table 6.3). The concentrations of the major ions, and therefore TDS, increase over the flowback period, since all of the study wells used injected fluids with major ion concentrations that were lower relative to those in formation water (Figure 6.4, Table 6.2). The geochemistry data is reported in detail by Owen (2017) and much of the data reported here is extracted from Owen et al. (2020). Notably, the SO<sub>4</sub> concentrations do not show a continuous

increase and are often constant over the flowback period during which the fluids were sampled. The pH remains neutral for the majority of the flowback water samples (median: 7.2) and most samples have moderate total alkalinity (median: 184 mg  $CaCO_3/L$ ), although both the pH and the total alkalinity show a decreasing trend over the flowback period. Organic compounds were not analyzed in the flowback water from the study wells.



Figure 6.3 - Total Dissolved Solids (mg/L) of produced or producing Montney wells from Alberta and British Columbia. For wells with multiple analyses the values are averaged.

There is variability in the flowback water chemistry between the different wells (Table 6.2 andTable 6.3, Figure 6.4). The TDS in the initial flowback water samples from the study wells range from 3,610 mg/L (well D-4) to 123,000 mg/L (well C-7) while TDS of the final samples range from 23,800 mg/L (well E-2) to 228,000 mg/L (well B-1). In general, the TDS and major ions are higher in the initial flowback water from the upper Montney Formation wells, relative to the initial flowback water from both the lower and middle Montney Formation wells. In the late flowback period water, the major ion concentrations reach similar levels in the samples from the upper and lower Montney Formation wells, whereas the major ion concentrations in the middle Montney Formation flowback water from the different Montney Formation members. The wells completed on the same site and within the same member of the Montney Formation have similar flowback water chemistries (e.g., well D-3 and well D-4; well E-1 and well E-2), although there are exceptions (e.g., well I-1 and well I-2). Comparisons between the flowback water chemistry produced from the different members of the formation, or even between wells completed in the same member, are

complicated as the chemistry is impacted by variables related to well completion; these variables include the hydraulic fracturing fluid chemistry, the number of stages, and shut-in time, in addition to the properties of the formation, the response of the well to hydraulic fracturing, and the length of the flowback period (Owen, 2017; Owen and Bustin, in preparation). Longer shut-in periods, in particular, were found to correlate with higher TDS and major ion concentrations in the flowback water. The effect of shut-in period length contributes to the variability between wells, obscuring relationships with the member of the formation where the well was completed.

The rate of increase in TDS and the major ion concentrations during the flowback period can vary between different wells (Figure 6.4). For some wells, the flowback water major ion concentrations do not reach a stable plateau concentration by the end of the sampled flowback period, as has been observed in the flowback water from other formations (e.g., Marcellus Shale – Blauch et al., 2009; Haluszczak et al., 2013; Horn River Basin – Zolfaghari et al., 2015). The increase in ion concentrations over the full length of the flowback period for some wells has been attributed to the development of a more extensive fracture network, as a result of access to a greater volume of formation water (Bearinger, 2013; Ghanbari et al., 2013; Zolfaghari et al., 2015a). However, the major ion concentrations must eventually reach a plateau, as the formation water acts as an endmember in the system, or potentially decline, if water of condensation comprises a significant component of the flowback.

Mixing between the injected hydraulic fracturing fluid and the formation water is mainly responsible for the increasing TDS over the flowback period. The approximately linear relationship between the major ion concentrations provides support for mixing as a dominant influence since a linear relationship suggests mixing between higher concentration and lower concentration fluid sources (Figure 6.5). Although the Montney Formation generally has low water saturation, the high surface area accessed by the created fracture network and any natural fractures in the formation, increases the area of contact and thus increases the access to the formation water. Mixing between the formation water and the hydraulic fracturing fluid would occur in the fracture space. Additional access to formation water may be from countercurrent imbibition. Countercurrent imbibition is an important consideration in hydraulically fractured wells, as it can increase oil production (e.g., Dehghanpour et al., 2013; Rokhforouz and Amiri, 2017). When the hydraulic fracturing fluid is injected into the formation, a large portion of the fluid is imbibed into the formation (Engelder et al., 2014). Imbibition experiments have shown that shale samples placed in deionized water result in an increase in conductivity of the water over the length of the experiment (e.g., Zolfaghari et al., 2016). The increase in conductivity could be inferred to be a consequence of the movement of formation water, in addition to oil and/or gas, out of the rock through countercurrent imbibition. Physical mixing would occur between the formation water and the remaining hydraulic fracturing fluid in the fractures. Other potential sources of the high TDS are diffusion of the ions in the formation into the injected fluid, and osmosis, where water would move into the formation and the ions in the remaining fluid in the fractures would become more concentrated (BCOGC, 2015; Zolfaghari et al., 2016; Wang et al., 2016; 2017). Based on our data, the influence of diffusion and/or osmosis cannot be separated from the influence of mixing with formation water accessed in the fracture apertures and through countercurrent imbibition.

Based on oxygen and hydrogen isotopic values and Cl- content of the make-up, produced and connate waters, we developed mixing models to determine the relative contribution of formation water and injected water to the flowback fluids. We have summarised and detailed the methods and results in Owen et al. (2020). The increasing major ion concentrations in the flowback water over the flowback period indicates that mixing between the relatively low TDS hydraulic fracturing fluid and the high TDS formation water is the dominant geochemical process that is influencing the flowback water chemistry. In addition to physical mixing between the injected fluid and formation water accessed in the fracture network and through countercurrent imbibition, other potential contributors to high TDS are ion diffusion (Balashov et al., 2015; Zolfaghari et al., 2016; Wang et al., 2016, 2017) and/or osmosis (Wang et al., 2016, 2017). With the current data, it was not possible to differentiate between these processes, so that they may all contribute to the increasing TDS.

Through the use of Cl,  $\delta^{18}$ O, and  $\delta^{2}$ H as conservative tracers, the proportion of formation water contributing to flowback water was calculated for each of the samples analysed in the study wells. There was variability in the proportion of formation water in the flowback water at different wells over the flowback period (Table 6.4). For the initial flowback water samples, the contribution from formation water generally was in the range of 10%-35%, while for the final flowback water samples the formation water proportion was generally 40%-60%. Since there is a significant contribution from formation water, the actual volume of the injected hydraulic fracturing fluid recovered during the flowback period, is much less than the volume of total fluid recovered. For the study wells, the calculated volume of hydraulic fracturing fluid recovered based on the mixing proportions is typically < 10% of the injected fluid (Owen et al., 2020).

Table 6.2 - Summary of pH, conductivity, total alkalinity, TDS, and major ion concentrations in the flowback waters collected in the study. Data for wells at the same site and completed within the same member of the Montney Formation are grouped. For the TDS and the major ions, lower values for all wells are from earlier in the flowback period, while higher values are from later in the flowback period.

Montney For		up	per			lower				
membe	er		-				_	_		
Sito		A (0	В (Э	D	Н	D	E	F	G	1
Site		(ð wells)	(Z wells)	(Z wells)	(1 well)	(Z wells)	(4 wells)	(Z wells)	(1 well)	(Z wells)
Parameter	n	22	30	19	18	22	26	12	8	28
	min	7.5	6.3	2.3	6.1	6.6	6	3.4	6.8	6.4
На	median	7.8	7	6.9	6.3	7.2	7.4	6.3	7.3	7.1
r.	max	8.1	7.9	9.2	8.1	9.5	7.8	6.7	7.6	7.7
Conductivity	min	60.8	47.6	50.4	33.8	7.12	22.1	29.1	27.9	11.1
(mS/cm)	median	102	123	86.4	113	36.1	35.7	37.5	64.8	56.1
	max	131	190	107	135	74.6	51.8	50.4	95.4	130
Total Alkalinity	min	115	71	<10	67	135	222	<10	205	172
(mg CaCO <sub>3</sub> /L)	median	195	119	104	80	236	337	51	228	232
	max	405	188	685	128	475	395	91	260	403
TDS	min	41,358	30,135	31,522	20,713	3,609	11,105	18,655	13,972	4,587
(mg/L)	median	61,220	89,949	62,520	83,807	21,631	18,672	24,009	38,963	31,998
	max	92,731	228,259	80,944	112,226	56,800	32,864	34,139	65,052	90,178
Cl	min	25,722	18,541	19,303	12,308	1,893	6,671	10,295	8,186	2,260
(mg/L)	median	43,437	55,235	38,355	49,006	12,510	12,251	14,455	24,790	17,678
	max	65,777	164,018	50,963	66,998	34,565	21,611	21,495	41,783	51,038
Na	min	8,264	9,162	9,960	6,451	1,344	2,787	6,849	3,895	1,991
(mg/L)	median	12,759	25,609	18,489	28,509	7,884	5,256	9,066	10,999	12,112
	max	17,818	51,027	23,974	37,637	18,872	9,119	10,575	18,244	33,782
Ca	min	1,616	1,789	1,169	629	13	350	560	174	110
(mg/L)	median	3,059	5,950	2,874	2,798	628	641	702	845	1,032
	max	5,389	11,705	4,058	3,677	2,112	1,126	795	2,229	4,081
К	min	553	284	466	414	49	187	166	186	105
(mg/L)	median	796	1,035	860	1,534	257	295	196	410	558
	max	1,239	1,920	1,171	1,806	466	474	251	650	1,296
Mg	min	296	154	171	102	9	62	93	74	32
(mg/L)	median	547	619	418	650	79	107	117	273	166
	max	941	1,369	611	808	223	220	136	586	524
Sr	min	298	60	123	30	4	38	33	29	13
(mg/L)	median	630	404	264	141	55	72	44	73	206
	max	1,219	924	358	195	268	161	69	101	1,011
SO <sub>4</sub>	min	51	<0.1	134	575	98	90	379	1308	0.7
(mg/L)	median	91	59	189	899	126	113	560	1370	19
	max	234	174	645	1084	189	202	824	1407	48

Table 6.3 - Summary of the hydraulic fracturing fluid and formation water chemistry. The formation water chemistry is based on the median values for the produced water samples collected in the present study (sites A, B, and I) and produced waters from nearby wells with publicly available results (sites D-H).

Site	Well	рН	Total Alkalinity	TDS	Cl	Na	Са	Mg	к	Sr	SO4
Hydr	aulic I	Fracti	uring Fluid								
	1	6.8	108	15,285	10,276	3,212	1,004	162	181	161	8.5
	2	6.5	96	16,802	10,423	3,873	1,428	227	226	245	25
	3	7.3	76	239	71	69	42	22	21	<10	18
Δ	4	6.7	86	25,297	18,108	4,555	1,566	256	255	309	15
А	5	6.7	94	28,072	19,850	5,365	1,791	274	273	332	18
	6	6.7	89	16,824	11,365	3,486	1,052	205	224	217	15
	7	7.2	81	3,386	966	1,733	420	59	63	59	20
	8	6.7	110	25,382	17,495	5,046	1,724	261	280	295	4
D	1	7.5	157	22,018	6,276	11,973	2,828	299	379	160	45
D	2	7.3	134	23,459	6,432	12,980	3,067	284	417	175	41
	1	7.3	64	549	160	208	46	10	11	1	78
<b>D</b>	2	7.1	87	1,284	639	398	58	12	46	2	98
U	3	7.2	66	711	289	209	50	10	10	1	104
	4	7.1	258	4,717	2,044	1,605	142	29	241	6	273
	1	6.5	171	11,246	6,414	3,659	608	96	187	59	129
E	2	6.6	107	5,052	3,150	1,237	322	53	96	28	95
L	3	6.4	152	6,059	3,842	1,546	323	53	89	16	111
	4	6.8	161	8,464	4,740	2,788	453	79	150	47	112
F	1, 2	7	83	12,218	7,448	3,948	372	60	105	25	165
G	1	7.2	150	5,604	1,841	3,047	305	64	137	40	74
Н	1	4.9	3	786	5.1	573	42	16	11	<1	28
	1	7.7	242	1,849	1,204	66	74	16	8	<1	<0.1
I	2	7.7	258	1,863	760	67	77	16	8	<1	<0.1
Form	nation	Wat	er								
А		7.1	201	125,443	90,395	25,191	7,638	1,073	1,365	1,297	82
В		5.1	84	181,321	128,802	32,591	14,835	1,469	1,982	1,037	155
D-F		6.9	238	97,354	60,215	29,050	5,375	778	1,575	869	73
G		6.8	166	67,172	47,585 <sup>ª</sup>	18,850	3,897	600	578	119	1,320
Н		6.2	116	129,744	77,735	34,800	5,635	1,100	2,010	115	489
Ι		5.9	63	91,254	89,168	54,000	10,000	1,140	2,040	1,620	<0.1



Figure 6.4 - Flowback water TDS for the study sites plotted as a function of the cumulative volume of flowback collected (Owen, 2017). a) Site A wells – upper Montney Formation; b) Site B wells – upper Montney Formation; c) Site D wells – upper (well D-1 and well D-2) and middle (well D-3 and well D-4) Montney Formation; d) Site E and Site F wells – middle Montney Formation; e) Site G and Site H wells – middle (well G-1) and upper (well H-1) Montney Formation; f) Site I wells – lower Montney Formation.



Figure 6.5 - Relationship between major ions in the Montney Formation flowback water. a) Na-Cl plot; b) Ca-Mg plot. The linear relationship between the major ions suggests mixing between two endmembers – the injected hydraulic fracturing fluid with relatively low TDS and the high TDS formation water. The three samples with elevated Cl concentrations at site B are from well B-1 at the end of the flowback period, following a 24-day shut-in period. The flowback water results are grouped by site, although the site D wells are divided into the upper (u) and middle (m) Montney Formation wells.  $\blacktriangle$  - upper Montney Formation wells;  $\blacklozenge$  - middle Montney Formation wells;  $\blacksquare$  - lower Montney Formation wells. Modified from Owen et al. (2020).

Table 6.4 - Summary of proportions of formation water contributing to the flowback water for the conservative tracers used in the study. The minimum value is early in the flowback period, while the maximum value is late in the flowback period. A –  $\delta^{18}$ O values excluded as the values were interpreted to be contaminated by organics that were not removed by the activated charcoal treatment. B – isotopic values are potentially contaminated, as the mixing ratios calculated using the isotopes do not agree with those calculated using the CI concentrations.

		]	Percenta	ge of For	mation v	vater (%)	)
Site	Well	Based	on $\delta^2 \mathbf{H}$	Based	on δ <sup>18</sup> O	Based	l on Cl
		Min	Max	Min	Max	Min	Max
	1	79	85	92	107	54	58
	2	31	44	11	44	25	57
	3	29	37	26	42	42	48
	4	28	33	34	44	27	38
A	5	46	53	69 77		41	51
	6	56	79	57 104		59	69
	7	29	39	53 61		28	37
	8	43	60	52	69	31	43
Ъ	1	1	47			18	129
В	2	3	67	i	а		63
	1	24	69	29	121	32	85
	2	20	29	19	54	45	81
	3	16	31	17	36	5	34
	4	0	29	0	38	0	56
	1	2	24	6	27	3	28
Б	2	16	31	31	69	7	24
E	3	6	39	28	46	16	26
	4	1	8	8	11	3	22
Th	1	32	43	12	50	13	19
F	2	31	49	17	72	5	27
G	1	2	58	14	64	14	87
Н	1	8	33	8	51	16	86
т	1	8	31	7	32	1	33
	2	14	59	16	43	5	57

#### 6.4.2. Sulphate

In contrast to Cl and the major cation concentrations, the measured sulphate ( $SO_4$ ) concentrations in the Montney Formation flowback water do not show a consistent increasing trend over the flowback period for most wells, indicating that geochemical processes other than mixing are operative (Figure 6.6). The measured  $SO_4$  concentrations are generally higher than the concentrations of connate water. The
elevated SO<sub>4</sub> concentrations may be due to oxidation of pyrite (Wilke et al., 2015; Harrison et al., 2017), the oxidation of H<sub>2</sub>S, or dissolution of anhydrite, all of which may be the product of completion of the wells with injection of oxic hydraulic fracturing fluid into the anoxic formation. Laboratory experiments described in the next section of this paper document pyrite oxidation during leachate experiments carried out on time scales of hydraulic fracturing and flowback with completion fluid and reservoir rocks. Pyrite is present in the Montney Formation at an average abundance of approximately 2% by weight, based on the XRD results compiled for samples from the areas near the study wells. Oxidation of H<sub>2</sub>S gas and formation of sulphate is likely to occur in some areas of Montney production (Kirste et al., 1997; Desrocher et al., 2004), but most flowback fluids analysed in this study had no measurable H<sub>2</sub>S. Flowback water at site A and site F locations do, however, contain detectable  $H_2S$ . Samples from site A were collected prior to treatment for  $H_2S$ . The SO<sub>4</sub> concentrations in the site A flowback waters are relatively stable over the flowback period and range from 51 to 234 mg/L for the different wells. The SO<sub>4</sub> concentrations are greater than the SO<sub>4</sub> concentrations in the hydraulic fracturing fluids (median: 18 mg/L), and often greater than the estimated value for formation water at site A (82 mg/L). The site F samples were collected following  $H_2S$  treatment with sodium hypochlorite (NaOCI) to remove  $H_2S$ . Both site F wells show increasing  $SO_4$ concentrations over the flowback period up to 824 mg/L, which is likely related to the production of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) during treatment with NaOCI. The presence of the acid is supported by the decreasing pH in the flowback waters from these wells (pH < 4 in late flowback water samples).

The impact of anhydrite dissolution on the sulphate content of the flowback water in this study is minimal. Anhydrite is absent or rarely reported in public data from core analysis from the wells in the study area, and our XRD, thin section and SEM analyses of core samples show no to little anhydrite or barite present and little to no evidence of an earlier dissolved anhydrite phase. Our results are in contrast to the study of Liseroudi et al. (2020), who describe an early and later pervasive phase of barite and anhydrite in select Montney cores. The difference in our results may simply be that the Liseroudi et al. (2020) study focused on anhydrite-bearing core and areas of high H<sub>2</sub>S gas, whereas this study is more regional in extent.



Figure 6.6 – Sulphate concentrations in the injected hydraulic fracturing (HF) fluid, the flowback water, and the formation water for each of the sites. For sites with multiple wells, a median value is presented for the HF fluid and the minimum, median, and maximum values for flowback water are calculated for the combined dataset.

The SO<sub>4</sub> concentrations in the flowback waters from site I are lower than almost all other flowback water samples collected as part of the study (< 50 mg/L) and decrease over the flowback period (Figure 6.7). The relatively elevated SO<sub>4</sub> concentrations in the early flowback waters are not related to SO<sub>4</sub> concentrations in the injected hydraulic fracturing fluid, which remain below the detection limit (< 0.1 mg/L) but may be due to pyrite oxidation (Wilke et al., 2015; Harrison et al., 2017). Bacterial SO<sub>4</sub> reduction likely contributes to the decreasing SO<sub>4</sub> concentrations with time in the flowback water from the site I wells. The injection of the relatively fresh hydraulic fracturing fluid, containing organic additives, reduces the salinity in the formation making a more favorable environment for sulphate reducing bacteria (Engle and Rowan, 2014). The reduction of SO<sub>4</sub> could in turn increase the solubility of barite, which would result in higher barium (Ba) concentrations in areas where SO<sub>4</sub>-reducing bacteria are more active. The highest Ba concentrations among the study wells were measured in the late flowback samples from well I-1 (215 mg/L) and well I-2 (467 mg/L), supporting this possibility.



Figure 6.7 - Top plot shows Ba and SO<sub>4</sub> concentrations for well I-1 and I-2. Ba concentrations are initially low in the flowback water from both wells. As Ba concentrations increase, the SO<sub>4</sub> concentrations decrease. Bottom plot shows saturation indices<sup>1</sup> (SI) for barite for well I-1 and well I-2. The flowback water is initially close to equilibrium with barite. The increasing SI is due to increasing Ba from formation water, while the decreasing SI supports barite precipitation. Both barite dissolution and mixing with high-Ba formation water increases the Ba concentrations, whereas bacterial SO<sub>4</sub> reduction and barite precipitation contribute to the removal of SO<sub>4</sub> from the water.

The mineral celestite (SrSO<sub>4</sub>) is slightly oversaturated (0 < SI < 1) in the flowback water in several of the studied wells, including the well G-1 samples and some samples from the site A wells. The geochemical model predicts celestite precipitation in the later flowback water samples from well G-1 when the model reaches equilibrium, which should correspond to a decrease in both Sr and SO<sub>4</sub> concentrations. However, the SO<sub>4</sub> concentrations at well G-1 remain relatively constant (range: 1308 to 1407 mg/L) over the flowback period. The lack of a decrease in concentrations in the flowback water results indicates that equilibrium has not been reached in the flowback water and celestite precipitation is not occurring.

<sup>&</sup>lt;sup>1</sup> The saturation index is the log10 ratio of ion activity product to the chemical activity of dissolved ions. SI =  $log(IAP/K_{sp})$ . The SI is a measure of the tendency of minerals to precipitate (values > than 0), to be at equilibrium (equal to 0) or undergo dissolution (values < than 0). SI was calculated using PHREEQC, version 3.2.0 (Parkhurst and Appelo, 2013) using the Pitzer database due to the high ionic strength of the formation and flowback waters.

## 6.4.3. Insights from Barium Concentration

Within the sampled flowback waters, the Ba concentrations range from below the detection limit (< 1 mg/L) up to 467 mg/L (Owen, 2017). There is generally an increase in Ba in flowback water over the flowback period for each of the study wells with considerable variability between different sites (Figure 6.8). The shut-in time has some effect on the Ba concentrations, with a longer shut-in period correlating to a higher Ba concentration in the initial flowback water samples ( $R^2 = 0.37$ ). The length of the shut-in period for the study wells would influence the chemistry by controlling the amount of time for mixing and geochemical reactions prior to the initiation of flowback from the well. Barium concentrations across the study area decrease from the northwestern region of the study area, near sites A and I, to the southeastern region near site H. The site C wells in the central region of the study area are an exception to the trend, with higher Ba concentrations (12 to 311 mg/L), relative to wells at nearby sites, which have concentrations that remain < 10 mg/L. The higher Ba concentrations in flowback water from site C are likely related, at least in part, to the length of the shut-in period for these wells. Regional variability in Ba concentrations in flowback water has previously been observed in samples from the Marcellus Shale in Pennsylvania, although in the Marcellus Formation flowback water the Ba concentrations are often in excess of 1,000 mg/L after one week of flowback (Chapman et al., 2012; Barbot et al., 2013), which is considerably higher than those measured in our study on the Montney Formation.



Figure 6.8 - Barium (Ba) concentrations over the flowback period plotted as cumulative flowback volume for the indicated wells. The Ba concentrations increase over the flowback period for the majority of wells. The upper Montney member wells include the site A wells, the site B wells, wells C-1 through C-5, well D-1, well D-2, and well H-1; the middle Montney member wells include well C-6, well C-7, well D-3, well D-4, the site E and site F wells, and well G-1; the lower Montney member wells include the site I wells. Note the variability in the scales.

The Ba concentrations in both the formation water and the flowback water may be impacted by different geochemical processes in different regions. Overall, Ba concentrations in the study wells are negatively correlated with SO<sub>4</sub> concentrations (Figure 6.8). A negative correlation has also been observed in previous studies with Marcellus Shale flowback water and was explained by the occurrence of bacterial SO<sub>4</sub> reduction. The injection of hydraulic fracturing fluid into the formation would have created a more favorable, lower temperature and salinity environment for the bacteria, accelerating bacterial SO<sub>4</sub> reduction as a result (e.g., Engle and Rowan, 2014). The presence and abundance of SO<sub>4</sub> reducing bacteria in different regions would vary the amount of SO<sub>4</sub> reduction occurring in the formation. If the bacteria are present, the onset of  $SO_4$  reduction is rapid (Machel, 2001). The removal of  $SO_4$  would increase the barite solubility in the formation, thereby increasing the Ba concentrations. Barite dissolution has previously been suggested as a source of Ba in flowback water, which if it is the case, Ba concentrations in flowback water would be positively correlated to the amount of barite in the formation (Renock et al., 2016; Zolfaghari et al., 2016). Barite is not found in the Montney Formation at a high enough percentage to be detected by XRD analysis; however, small (< 0.5 cm) barite crystals occur in core examined by SEM from the region near site A. Additional factors contributing to higher barite solubility in the formation in comparison to the solubility in freshwater at surface, include: the high ionic strength of the water involved in the water-rock interactions during hydraulic fracturing combined with the reducing conditions in the formation (Renock et al., 2016); the elevated temperatures and pressures in the formation (Blount, 1977); and the presence of organic matter (He et al., 2014), which may also act to inhibit barite precipitation (Marcon et al., 2017).



Figure 6.9 - The relationship between Ba and SO<sub>4</sub> concentrations for the sampled wells. Results for individual wells are grouped by site. These parameters are negatively correlated, which is related to SO<sub>4</sub> reduction and barite solubility. Note the logarithmic scale is used due to the large variability in concentrations between wells.  $\blacktriangle$  - upper Montney member wells;  $\bullet$  – upper and middle Montney member;  $\blacklozenge$  - middle Montney member wells;  $\blacksquare$  - lower Montney member wells.

Overall, the results do not support barite dissolution as a dominant geochemical process impacting the Ba or SO<sub>4</sub> concentrations, given that the Ba and SO<sub>4</sub> concentrations in flowback water do not increase together as would be expected if only barite dissolution was occurring. The SI for barite in the flowback water is close to equilibrium or slightly over/under-saturated for site A, site B, and site D, with SI values generally remaining between -0.4 and 0.4 (Owen, 2017). The flowback water from the wells at sites A (Figure 6.7) and D typically have increasing Ba concentrations and stable SO<sub>4</sub> concentrations over time. The increase in Ba may be primarily due to mixing with formation water inasmuch as the SI values do not show an increasing trend, which would indicate barite dissolution. Site B is notable in that it has relatively stable (well B-1) or decreasing (well B-2) Ba concentrations over the flowback period, differing from the increasing Ba concentrations that are observed in the flowback water from the majority of the other wells. The flowback water from the site B wells also show constant or decreasing SO<sub>4</sub> concentrations and negative SI values for barite. Well B-1 has barite SI values that generally remain between -0.4 and -0.1 indicating that the flowback water from this well is close to equilibrium with barite. The decreasing Ba and SO<sub>4</sub> concentrations at well B-2, along with the decreasing barite SI values from -0.1 to -1.0, support barite precipitation in this well.

The site C wells have high Ba in flowback water, reaching concentrations > 20 mg/L by the middle of the flowback period, and low (< 30 mg/L) SO<sub>4</sub> concentrations. As these wells were shut-in for 21 to 30 days prior to beginning flowback, bacterial SO<sub>4</sub> reduction along with barite dissolution may have taken place in the reservoir during the shut-in time. These two processes in combination explain the low SO<sub>4</sub> and high Ba in the flowback water from these wells. Mixing with formation water also likely contributes to the Ba concentrations. The SI for barite in several of these wells is negative (site C, wells 1 through 5) and often below -1. If SO<sub>4</sub> reduction was occurring at a faster rate than barite dissolution, the flowback water could still remain undersaturated with respect to barite. Flowback water from well C-6 and well C-7 is oversaturated in barite, although the SI is stable over time, which may indicate that SO<sub>4</sub> reduction is occurring at a slower rate for these wells.

Flowback water from well E-1, well E-2, and well E-4 have barite SI values that are slightly oversaturated early in the flowback period (SI = 0.6.0.7) and remain positive but show a decreasing trend towards equilibrium. The decreasing SI indicates barite precipitation. The decreasing SO<sub>4</sub> concentrations in the flowback water from these wells may be due to Ba precipitation rather than SO<sub>4</sub> reduction, while the increasing Ba concentrations may be due to mixing with formation water with higher Ba concentrations, as opposed to Ba dissolution. Well E-3 has barite SI values that increase over the flowback period from 0.2 to 0.4 and shows a more rapid increase in Ba concentrations relative to the other site E well. The increasing SI, along with the increase in Ba and SO<sub>4</sub> concentrations support barite dissolution in this well. Sulphate reduction may be occurring but at a slower rate relative to SO<sub>4</sub> production by barite dissolution.

The site F wells have increasing SO<sub>4</sub> and decreasing Ba over the flowback period. The barite SI for both wells decreases over the flowback period from slightly oversaturated (SI = 0.3 to 0.5) to either equilibrium (-0.04; well F-2) or undersaturated (-0.4; well F-1). The decreasing trend for SI indicates barite precipitation and is supported by the decreasing Ba concentrations over the flowback period. The site F flowback waters show increasing SO<sub>4</sub> concentrations; however, this is likely a result of the chemical

reaction that occurs due to the addition of NaOCl to treat  $H_2S$  in the flowback water at surface. Sulphate concentrations would continue to increase, as it is continually produced by the oxidation of the  $H_2S$  present in the flowback water at this site.

The site G and site H wells have high SO<sub>4</sub> (> 600 mg/L) and among the lowest Ba in the study, with Ba concentrations that remain below 1.5 mg/L and often below the detection limit (< 1 mg/L). The elevated SO<sub>4</sub> is likely related to pyrite oxidation which has been suggested as a source of SO<sub>4</sub> in both formation water (Dresel, 1985) and in flowback water, as pyrite oxidation may increase during the hydraulic fracturing process due to the injection of oxic hydraulic fracturing fluid into the formation (Wilke et al., 2015; Harrison et al., 2017). There is no indication that SO<sub>4</sub> reduction is a dominant process in these wells, as the SO<sub>4</sub> concentrations remain high and relatively stable. The stable SO<sub>4</sub> concentrations may indicate that SO<sub>4</sub> reducing bacteria are not present or are inactive in the site G and site H wells. The decreasing SI of barite over the flowback period at well G-1 (SI = 0.8 to 0.1) and well H-1 (SI = 0.6 to 0.2) indicates that the flowback water is moving towards equilibrium, as any barite introduced through mixing with formation water would precipitate with the excess SO<sub>4</sub>.

The flowback water from the two site I wells attain among the highest Ba concentrations of the wells in our study, with maximum values of 215 mg/L and 467 mg/L for well I-1 and well I-2, respectively. The initial Ba concentrations in the flowback water from these wells, however, are low (< 10 mg/L), and the highest SO<sub>4</sub> concentrations are measured during this period of flowback (Figure 6.7). The elevated SO<sub>4</sub> may be due to pyrite oxidation caused by the injection of the hydraulic fracturing fluid (Wilke et al., 2015; Harrison et al., 2017). In the early flowback water, the SI for barite is near equilibrium (-0.1 < SI < 0.1). Later in the flowback period for both wells, the SO<sub>4</sub> concentrations decrease, which may be related to barite precipitation and SO<sub>4</sub> reduction. The barite SI initially increases due to the increase in Ba from formation water (up to 0.6 and 0.8, for well I-1 and well I-2, respectively) then decreases (to 0.2 and -0.4, for well I-1 and well I-2, respectively), showing that the system is moving back towards equilibrium (Figure 6.7). The decreasing SI values suggest barite precipitation; however, the continually increasing Ba concentrations do not support precipitation, and may indicate that the source of the high Ba in these wells is from mixing with formation water with high Ba concentrations. The variable behavior of Ba and SO<sub>4</sub> concentrations in the study wells shows that these ions are influenced by both barite precipitation and dissolution, as well as SO<sub>4</sub> reduction and mixing with formation water, depending on the well and duration of flowback.

## 6.4.4. Sulphate from Fluid – Rock Interactions

The SO<sub>4</sub> concentrations of flowback waters for many wells are higher than anticipated by simple mixing models of connate water and completion fluid (i.e., fluid-fluid interactions) and cannot be accounted for by dissolution of sulphate minerals. Further, the mixing models described earlier cannot capture or predict reactions that may have taken place in the reservoir, particularly those related to dynamic redox conditions or those related to bacterial activity.

In order to determine the contribution of the solid reservoir matrix to the produced fluid (i.e., fluidrock interactions), a comprehensive set of experiments and analyses were undertaken on representative core samples from the Montney and Doig formation reservoirs in the study area. The experiments were designed to determine the chemistry of the connate water of the reservoir rock, and leachate generated from completion fluid-reservoir rock interaction. Connate water present in the rock at the time of testing, is mixed with the drilling fluid during drilling, and completion fluid during fracing, and at the same time, liable minerals or compounds may react with the fluids. Although the rock at reservoir conditions is in, or near equilibrium with the connate water, the rock is not in equilibrium with the drilling and completion fluids, which not only have a different chemistry, but are at a lower temperature and may introduce microbes including sulphate-reducing bacteria as well as organic nutrients. Additionally, during burial, the connate water may become supersaturated with respect to certain mineral species (i.e., salts), which may precipitate. These relatively soluble minerals are labile to dissolution by the undersaturated drilling or completion fluids. Hence, the leachate will not be a simple mixture of completion fluid and connate water but may also include the products of dissolution or precipitation of minerals from the rock, which were previously in equilibrium with the connate water. The leachate chemistry is thus a product of the combination of connate water, completion fluid, and reaction products due to fluid-rock interactions.

## 6.4.5. Water/Leachate/Aging/Extraction Experiments

The aging and leachate/extraction experiments were carried out using a variety of completion fluids and associated additives, including cross-linked gels, viscoelastic fluids, surfactants and slickwater in a roller-oven at reservoir temperature. Additionally, in order to create a baseline for leachate production, for some tests leachates comprised of a synthetic brine with a total dissolved solids of 140 000 mg/L were used, while distilled water was employed for other samples. The completion fluids used for the tests were the same as the ones applied during completing the corresponding well from which the core samples were collected. The completion fluids were prepared from a base of freshwater or produced water provided by well operators and additives provided by completion companies. Experiments were also carried out in Montney-produced oil for comparison of fines liberation, but no chemical analyses of this fluid were undertaken, and hence the results are not discussed here. The connate water chemistry was estimated based on mass balance.

In this section the results from four Montney wells and one Doig well are presented. The locations of the wells are shown in Figure 6.1, if not otherwise noted. The saturation index and activities were calculated for the raw fluids, leachate (aged fluid) and connate water, and modeled with decreasing temperature using PHREEQC. In the PHREEQC modelling, the saturated phases were not allowed to precipitate: the logic being that flowback waters would be produced quickly enough that saturated phases would not precipitate at the saturations determined by the modelling. The results of the modelling reported here are only for those minerals that are near, at, or oversaturated and which react at rates that have the potential to impact the fluids of this study. Although the kinetics of the reactions are not specifically considered here, important phases such as precipitation of barite and some carbonates and

iron oxides/hydroxides occur rapid enough to impact the fluid chemistry in the timeframe of fracing and flowback.

#### 6.4.5.1. Well 1A

The chemical analyses of the leachate from Well 1A are summarised in Table 6.5 and the saturation indices of the leachate for freshwater and produced water-based slickwater calculated from reservoir to surface temperature are show in Figure 6.9.

The leachate closely follows a mixing of model of the connate/produced water and completion fluid with the more saline pit water (37,200 mg/L) resulting in a more saline leachate ( $\approx$ 111,000 TDS/L) than the freshwater-based slickwater. The sulphate composition of the leachate exceeds the concentration of a simple mixing of the connate water and completion fluid, indicating sulphate is being produced during the aging experiments.

The freshwater leachate is saturated at all temperatures with the carbonate minerals (mainly calcite, dolomite, and aragonite), and the degree of saturation declines with declining temperature. The sulphate barite is saturated at all temperatures and the degree of saturation increases with declining temperature. The iron oxides/hydroxides are highly oversaturated at all temperatures and as discussed later, the available iron is probably sourced from the oxidation of pyrite. Quartz and chalcedony are undersaturated at high temperature and become slightly oversaturated with declining temperature.

Table 6.5 - Measured chemistry of raw fluids and leachate following 7 days at 72 °C. EC.= conductivity. TDS= total dissolved solids, DO- dissolved oxygen. All compositional data is in mg/L. All

Sample	DO	field ph	Alkalinity (as CaCO3)	HCO3	Br	CI	EC	F	Hardness (as CaCO3)	TDS (Calc)
Slickwater - fresh base	7.2	7.6	287	350	0.65	381.5	3165	6.835	997	2138
Distilled Water	8.0	7.5	180	215	0.60	198.0	2210	1.1	0579	1510
Slickwater - produced base	7.8	6.0	105.3	128	190.5	68000.0	106750	20	15800	111250
Base Water	8.4	8.5	103	120		2.4	313	0.099	145	174
Pit Water M	8.3	5.9	48.9	59.7		73400	141000		15300	117000
Distilled Water	8.7	7.1			0.12	48	162		3.4	60
	SO4	Sb	As	Ва	В	Cd	Ca	Cr	Со	Mg
Slickwater - fresh base	889	0.0145	0.0055	0.172	1.21	0.00056	311.8	0.1649	0.0096	53
Distilled Water	729	0.0042			1.2	0.00075	0149	0	0.0053	51
Slickwater - produced base	1039	0.0009		112	0.67	0.00052	2650.5		0.0034	375
Base Water	56			0.101		7.9E-05	66.6		0.00104	18
Pit Water M				810	69		5060			649
Distilled Water				0.0125	0.12		1.11			00
	Mn	Мо	Ni	K	Se	Si	Na	Sr	TI	U
Slickwater - fresh base	0.792	1.088	0.418	49	0.0090	11.2	275	5	0.0011	0.00121
Distilled Water	0.130	2.303	0.711	52	0.0008	14.1	226	3		0.00012
Slickwater - produced base	3.262	2.038	3.433	442	0.0021	9.1	18479	647		0.00009
Base Water	0.0115	0.00434	0.0196		0.00132	2	3.1	0.43		0.00109
Pit Water M				780			37200	1350		
Distilled Water				0.99			9.1	0.0036		

compositional data is in mg/L.



Well A1 Slickwater-Fresh Water Base



Satuartion Index

-0.2

-0.4 -0.6

-0.8

-1

🔺 Halite

Λ

20 📕

•

٠

40

Temperature <sup>o</sup>C

60

80

Aragonite

Calcite

🔺 Dolomite

Δ

-1.48

-1.5

-1.52

Δ

Temperature <sup>o</sup>C

#### 6.4.5.2. Well H1

The chemical analyses of the leachate from Well H1 are summarised in Table 6.6 and the saturation indices of the leachate for fresh water and produced water-based linked gel, calculated from reservoir to surface temperature, are show in Figure 6.10. The produced water used as make-up water in this well is highly saline (210 000 TDS/L), although the SO<sub>4</sub> content is similar to that of freshwater. There is some Al in the leachate resulting in a number of aluminum silicates being variably saturated, including the feldspars and clays. All of the aluminum silicates increase in saturation with declining temperature, from being slightly undersaturated at reservoir temperature with freshwater-based completion fluid, to over saturated with produced water-based completion fluid. For both fluids, barite, iron oxides/hydroxides, alunite and quartz/chalcedony have similar saturation trajectories as the aluminum silicates, which increase in saturation with declining temperatured at reservoir temperature, from undersaturated to slightly oversaturated at all temperature. Anhydrite and gypsum are slightly undersaturated in the two completion fluids at all temperatures. The carbonate minerals in the fresh water-based linear gel completion fluid are slightly oversaturated at reservoir temperature with declining temperature.

Sample	DO	field ph	Alkalinity (as CaCO3)	НСО3	CI	EC uS/cm	F	Hardness (as CaCO3)	Ion Balance	lab pH	TDS (Calculated)	SO4	Al	
Linear Gel - fresh base	6.255	6.6685	132.5	162	312.5	3568	3.02	1268	109	7.8	2665	1379	0.04	
Linear Gel - produced base	4.5575	6.2425	1.25	1.25	152750	191750	9.75	34050	88	4.9	239000	472.5	15.78	
Fabricated 140 g/L brine	6.9225	7.3225	145	176.75	96475	155250	5	947	84	7.5	151250	420	1.00	
Distilled Water	6.465	7.3675	150.65	183.75	284.75	2863	1.7925	683	92	7.9	1880	913	0.00	
Fresh Water	8.82	7.77	60.7	74	85.6	1180		155	99	7.6	681	331	0.18	
Produced Water	7.21	7.1	126	154	139000	193000		28600	80	6.7	210000	442	2.20	
Distilled Water	8.67	7.14			48.4	162		3	36	6.9	59.8			
Sample	Sb	As	Ba	Bi	В	Cd	Ca	Cr	Со	Cu	Fe	Pb	Li	Mg
Linear Gel - fresh base	0.001	0.026	0.097		1.220	0.000	360	0.214	0.002	0.082	6.173	0.002	0.3	89
Linear Gel - produced base	0.038	6.535	4.728	0.007	88.250	8.102	10650	7.649	7.703	7.691	54.075	2.884	33.3	1950
Fabricated 140 g/L brine	0.019	0.007	1.725	0.001	3.150	0.004	259	0.293	0.007	0.054	0.450		0.4	57
Distilled Water	0.001	0.002	0.077		1.263	0.000	171	0.001	0.003	0.005			0.3	88
Fresh Water	0.002	0.004	1.120		0.290	0.000	40	0.006		0.024		0.003		13
Produced Water			6.390		82.000		8840	0.120					24.3	1590
Distilled Water							0		1.110					
Sample	Mn	Мо	Ni	К	Se	Si	Ag	Na	Sr	Th	Sn	Ti	U	Zn
Linear Gel - fresh base	0.54	0.63	0.39	63.85	0.00	22.23	0.00	376	6	0.00		0.00	0.00	0.04
Linear Gel - produced base	21.93	0.29	9.92	3380.00	6.54	3.95	0.10	69950	491	5.36	0.01	0.14	8.48	11.78
Fabricated 140 g/L brine	0.79	3.70	1.10	5275.00	0.08	7.58	0.00	48925	11	0.00	0.00	0.02	0.00	
Distilled Water	0.27	0.98	0.75	115.43	0.00	16.85		242	4				0.00	0.02
Fresh Water		0.00	0.01	13.90	0.00	2.78		160	0			0.02	0.00	0.36
Produced Water	7.30			2820.00				57500	550	0.04				
Distilled Water		0.16				0.99				9.10	0.00			

Table 6.6 - Well H1. Measured chemistry of raw fluids and leachate following 7 days at 78 °C. EC.= conductivity. TDS= total dissolved solids, DO- dissolved oxygen. All compositional data is in mg/L.



Temperature <sup>o</sup>C

#### Well H Linear Gel Fresh Water Base



Well H Linear Gel Produced Water Base

Figure 6.11 - Well H1 Saturation indices are shown only for minerals that are oversaturated or near saturation for the indicated leachate.

#### 6.4.5.3. Well H2

The chemical analyses of the leachate from Well H2 are summarised in Table 6.7 and the saturation indices from reservoir to surface temperature are show in Figure 6.10. All fluids are freshwater based. The total TDS in the leachates varies from 3800 to 4700 TDS/L, with slickwater having the lowest values and

the cross-linked gel having the highest values. The slickwater fluid has also lower sulphate content (1500 and 1700 mg/L). The slickwater and viscoelastic surfactant sample is saturated with respect to barite and carbonates at all temperatures. Quartz and chalcedony are undersaturated at reservoir temperature and become saturated at lower temperatures. Talc and sepiolite are both saturated, with talc decreasing in saturation with declining temperature, whereas talc does the reverse. The sulphates are undersaturated.

In the cross-linked gel leachate, the carbonates are saturated at all temperatures. Quartz and chalcedony are undersaturated at reservoir temperature and become saturated at lower temperatures. Talc is saturated at reservoir temperature, whereas kaolinite and K-mica are undersaturated at reservoir temperature and become saturated at lower temperatures. The iron oxides and hydroxides are saturated. Anhydrite and gypsum are slightly undersaturated.

Table 6.7 - Well H2. Measured chemistry of leachate following 7 days at 76 °C. EC.= conductivity. TDS= total dissolved solids, DO- dissolved oxygen. All compositional data is in mg/L.

Sample	DO	field ph	Alkalinity	HCO3	Cl	EC uS/cm	F	Hardness	Ion Balance	TDS (Calculated)	SO4	Al
Slickwator	0	9.2	256	312	514	4740	19	1847	130	3808	1500	0.004
Slickwater	°	5.2	250	512	514	4740	1.5	1047	150	5000	1200	0.004
X-linked gel	10	8.9	284	346	1063	6200	1.1	2202	120	4638	1956	0.036
Viscoelastic surfactant	9	9.5	212	259	889	6223	1.9	2013	152	4473	1847	0.007
Sample	Sb	As	Ва	В	Cd	Ca	Cr	Со	Cu	Fe	Pb	Li
Slickwater	0.003	0.005	0.159	1.545	0.0007	365	0.003	0.005	0.039	3.380		0.259
X-linked gel	0.003	0.007	0.170	1.545	0.0006	451	0.137	0.028	0.200	47.250	0.006	0.262
Viscoelastic surfactant	0.001	0.002	0.079	1.4225	0.0004	392		0.012	0.010	0.000		0.245
Sample	Mg	Mn	Мо	Ni	К	Se	Si	Na	Sr	Th	U	Zn
Slickwater	227	0.59	1.85	0.7995	68	0.002775	16	540	2.23		0.000295	0.0085
X-linked gel	261	1.01	1.35	2.68825	79	0.0019	19	648	2.61	0.00047	0.0005575	0.11875
Viscoelastic surfactant	251	0.52	1.25	0.87025	89	0.001525	12	873	2.48		0.0001925	



## Well H2- Slickwater - Freshwater Base



Well H2 X-linked Gel Freshwater Base



Well H2 Viscoelastic Surfactant - Freshwater Base

Figure 6.12 - Well H2 Saturation indices are shown only for minerals that are oversaturated or near saturation for the indicated leachate

#### 6.4.5.4. Well B

The chemical analyses of the leachate from Well B are summarised in Table 6.8 and the saturation indices at reservoir to surface temperatures are show in Figure 6.10. Analyses were run for three leachates: slickwater with a freshwater, and produced water base, and distilled water. The distilled water and slickwater with a freshwater base yielded similar salinities of about 23,000 TDS/L, whereas the produced water-based slickwater has a salinity of about 65,000 TDS/L. The sulphate content of the three samples ranges from 670 mg/L for the produced water slickwater, to 880 mg/L for the fresh water-based slickwater.

The slickwater with a produced water-base is saturated with barite, as well as Fe and Mn oxides and hydroxides (not plotted). The carbonates are undersaturated at all temperatures and the degree of undersaturation increases with declining temperature. Anhydrite is slightly saturated and becomes undersaturated with declining temperature, whereas gypsum is slightly undersaturated at all temperatures.

The slickwater with a freshwater base has traces of Al and Si in solution and hence feldspars and clay are slightly saturated at lower temperatures. The common carbonates are saturated at all temperatures with the degree of saturation declining with temperature. Quartz and chalcedony are undersaturated at reservoir temperature and become saturated at lower temperatures. Talc is saturated at reservoir temperature, whereas kaolinite and K-mica are undersaturated at reservoir temperature, becoming saturated at lower temperatures. Mn and Fe oxides and hydroxides are saturated at all temperatures. Anhydride and gypsum are slightly undersaturated, whereas jarosite is undersaturated at reservoir temperature with declining temperature.

Sample	DO	field ph	Alkalinity (as	HCO3	Cl	EC uS/cm	F	Hardness	Ion Balance	lab pH	TDS (Calculated)	SO4	Al	
			Cacusj					(as CaCUS)			(Calculateu)			
Slickwater- fresh base	9.5	7.0	228.2	278.5	13821	28030	5.2	2504.3	98	7.8	22515	876	0.01	
Slickwater- produced base	9.8	6.9	178.5	217.5	42066	78760	1.6	5745.0	83	7.6	64633	672	0.00	
Distilled Water	10.0	7.4	197.0	240.25	15473	27333	0.9	2275.8	85	8.0	23773	768	0.00	
Sample	Sb	As	Ва	Bi	В	Cd	Ca	Cr	Со	Cu	Fe	Pb	Li	Mg
Slickwater- fresh base	0.006	0.007	0.7		3.8	0.003	789	0.206	0.065	0.056	0.913	0.001	11.5	130
Slickwater- produced base	0.001	0.001	2.1		9.0	0.018	1853	0.358	0.176	0.088	2.355	0.000	34.5	272
Distilled Water	0.003	0.000	0.6		3.9	0.026	706	0.000	0.051	0.022	0.000	0.000	11.7	125
Sample	Mn	Мо	Ni	К	Se	Si	Ag	Na	Sr	Th	Ti	U	Zn	
Slickwater- fresh base	1.63	4.46	0.82	240	0.01	7.68		6506	123	0.0033	0.0063	0.006	0.02	
Slickwater- produced base	4.06	2.84	3.15	599	0.01	8.38		19059	349	0.0252	0.0010	0.002	0.10	
Distilled Water	1.41	4.12	1.89	229	0.01	14.13		6346	111	0.0081	0.0028	0.000	0.01	

Table 6.8 - Well B. Measured chemistry of leachate following 7 days at 76 $^\circ$	C. EC.= conductivity.
TDS = total dissolved solids, DO = dissolved oxygen. All compositional data	a is in mg/L.



## Well B Slickwater Produced Water Base



Well B Slickwater Freshwater Base

Figure 6.13 - Well B Saturation indices are shown only for minerals that are oversaturated or near saturation for the indicated leachate

#### 6.4.5.5. Well I - Doig

The chemical analyses of the Doig Formation leachate from Well I are summarised in Table 6.9, and the saturation indices at reservoir to surface temperatures are shown in Figure 6.10. Analyses were run for three leachates: slickwater with a freshwater-, and produced water base, and distilled water. The

distilled water and slickwater salinities are low, ranging from 1130 to 1710 TDS/L. The sulphate content of the three samples ranges from 1020 mg/L for the distilled, to 1200 and 1250 mg/L for the freshwater-based slickwaters.

The slickwater leachates are both saturated with barite at all temperatures, and the degree of saturation increases with declining temperature. The carbonates (aragonite, dolomite, calcite) are saturated at all temperatures, and show little or no trend in saturation with declining temperature. The aluminum silicates (not plotted) and quartz and chalcedony are undersaturated at reservoir temperature and become saturated with decreasing temperature. Gypsum and anhydrite are slightly undersaturated at all temperatures.

Leachate	Alkalinity (as CaCO3)	HCO3	рН	Cl	EC uS/cm	F	Hardness (as CaCO3)	TDS (measured)	SO4	
Slickwater A Fresh Base	403	492	7.8	356.5	3585	9.1	1745	2640	1200	
Slickwater B Fresh Base	282	344	7.9	268.5	3235	1.2	1485	2370	1250	
Distilled Water	189	231	7.8	82.8	2080	1.2	1130	1710	1020	
Leachate	Al	Sb	As	Ва	В	Ca	Cr	Со	Cu	Fe
Slickwater A Fresh Base	0.0161	0.00292	0.010645	0.103	0.546	544	0.591	0.074	0.046	
Slickwater B Fresh Base	0.0058	0.0016	0.000355	0.086	0.520	420	0.085	0.021	0.032	3.13
Distilled Water	0.0047	0.00283	0.00042	0.057	0.812	277	0.001	0.012	0.005	0.347
Leachate	Pb	Li	Mg	Mn	Mo	Ni	К	Se	Si	Ag
Slickwater A Fresh Base	0.002055	0.202	94	0.30	1.94	3.105	14	0.00584	12.645	0.000042
Slickwater B Fresh Base	0.000305	0.193	106	0.16	1.70	0.802	19	0.00709	13.755	0.000061
Distilled Water		0.144	107	0.01	3.04	1.62	25	0.00982	13.1	0.000073
Leachate	Na	Sr	Th	Sn	Ti	U	V	Zn		
Slickwater A Fresh Base	182	2.8	0.006895	0.000645	0.0069	0.009645	0.00125	0.04255		
Slickwater B Fresh Base	138	2.3	0.013409		0.0009	0.004981		0.0319		
Distilled Water	83	1.5	0.00659		0.00209	0.0071	0.0011	0.0408		

Table 6.9 - Well I Doig Measured chemistry of leachate following 7 days at 75 °C. EC.= conductivity. TDS= total dissolved solids, DO= dissolved oxygen. All compositional data is in mg/L



Well Doig A Slickwater A Freshwater Base







## 6.4.6. Contribution of Oxidation of Pyrite to Sulphate Concentration in Flowback Water

The sulphate content of all the leachates from fluid-rock interaction from the aging tests of the Montney and Doig formations are much higher than predicted for the connate or completion fluid chemistries. The sulphate content of the flowback waters from wells is, for the most part, higher than predicted by our geochemical models of mixing and reactions between completion fluids and show a varied trend with flowback time. Since the Montney Formation includes traces to a few percent of fine-grained and/or framboidal pyrite, and since both the drilling and completion fluids contain dissolved oxygen, it is likely that at least some of the SO<sub>4</sub> was generated from oxidation of pyrite in real time during drilling, completion and flowback. The elevated SO<sub>4</sub> concentrations in other pyrite-bearing reservoirs had also been attributed to the oxidation of pyrite or H<sub>2</sub>S due to the injection of the hydraulic fracturing fluid by Wilke et al. (2015) and Harrison et al. (2017). It has further been postulated by Engle and Rowan (2014), that the sulphate can be subsequently reduced by sulphate-reducing bacteria, forming H<sub>2</sub>S, or precipitate as barite, which has been argued in this study for the I wells.

The mineralogy of the sample suite is relatively insoluble or has low solubility in the test fluid systems, with the exception of pyrite; however, there are significant clays which are susceptible to ion exchange with the completion fluid. Trace abundances of other minerals or amorphous deposits, not seen by XRD may also be present, but below the detection limit of techniques used in this study. In the samples tested here pyrite, with a high surface area, is present in all samples and all the fluid systems include dissolved oxygen.

In order to access the potential for formation of SO<sub>4</sub> from oxidation of pyrite under the conditions of completions and flowback, a sample of pyrite was aged using the sample particle size and the same sample to fluid (distilled water) ratio used during aging of the rock samples. The sample was aged at the same temperature and time as the reservoir rock, and the leachate was subject to the same handling and chemical analyses. The results of the chemical analyses are provided in Table 6.10. The ion balance of the analyses is very poor (0.5), due to the unusual chemistry (that was repeatable) created by the oxidation of the pyrite. Accepting the data at face value suggests there in an excess of iron over sulphur based on the stoichiometry of pyrite. Nevertheless, the results unequivocally show that introduction of oxygen through drilling or completion fluids will lead to oxidation of pyrite present in the reservoir rock, which will result in significant production of sulphate at the time scale of completion and flowback. The following reactions are anticipated:

$$\begin{aligned} & \operatorname{FeS}_2 + 3.5 \ O_2 + H_2 O \Longrightarrow \operatorname{Fe}^{+2} + 2 \ \operatorname{SO}_4^{-2} + 2 \ \operatorname{H}^4 \\ & \operatorname{Fe}^{+2} + 0.25 \ O_2 + \operatorname{H}^+ \Longrightarrow \operatorname{Fe}^{+3} + 0.5 \ \operatorname{H}_2 O, \\ & \operatorname{Fe}^{+3} + 3 \ \operatorname{H}_2 O \Longrightarrow \operatorname{Fe}(OH)_3 + 3 \ \operatorname{H}^+. \end{aligned}$$

The Fe released by the oxidation of pyrite would at least in part precipitate in the presence of dissolved oxygen as iron hydroxides and/or ferrihydrite in the reservoir, or in tubulars causing scaling. Dissolved Fe is present in the flowback waters from our analysed wells, and there is weak correlation ( $R^2=$  0.16) with SO<sub>4</sub> concentration. Even a poor correlation is suggestive of a relationship, considering there is a high likelihood of the Fe readily forming oxides and hydroxides in the presence of dissolved oxygen. Inasmuch as there is a possibility of the introduction of sulphate-reducing bacteria into the reservoir via the completion fluid and, in many wells a food source for the bacteria also provided (i.e., polyacrylamide or guar), it is reasonable to predict that the souring during the early production of a well would occur in the presence of SO<sub>4</sub>. It is likely, however, that bacterial SO<sub>4</sub> reduction would be short-lived due to the finite supply of SO<sub>4</sub> and the presence of reactive Fe in solution. Additionally, although the reservoir would be initially cooled by the completion fluid, the reservoir temperature would eventually re-equilibrate to temperatures generally in excess of 70°C and hence would be near the upper temperature boundary for a viable population of sulphate-reducing microbes.

DO	field ph	Alkalinity (as CaCO3)	HCO3	CO3	CI	EC	F	
2.94	0.9	<5.0	<5.0	<5.0	<50	75000	<50	
Hardness (as CaCO3)	ОН	Ion Balance	Nitrate and Nitrite (as N)	Nitrate (as N)	Nitrite (as N)	lab pH	TDS (Calculated)	
215	<5.0	0.5	<27	<25	<10	1.01	45700	
SO4	Al	Sb	As	Ва	Ве	Bi	В	
45600	6.54	0.0041	2.7	00.1	<0.010	0.0077	<0.20	
Mn	Hg	Mo	Ni	К	Se	Si	Ag	
5.9	<0.00025	0.275	3.71	<100	<0.0020	18	0.00206	
Cd	Ca	Cr	Со	Cu	Fe	Pb	Li	Mg
0.00713	86	32.000	0.0298	0.096	18600	0.320	<0.10	<20
Na	Sr	TI	Sn	Ti	U	V	Zn	Zr
<200	0.366	<0.0010	0.0055	0.319	0.158	0.154	1.51	1.23

Table 6.10 - Chemical analyses of pyrite aged at 72 °C for 7 days.

## 6.4.7. Contribution of Sulphate from Completion or Drilling Fluid Additives

The potential for formation of  $SO_4$  and subsequently  $H_2S$  through thermal reduction has been discussed by Pizadeh et al. (2014) and others. Drilling and/or completion fluid additives can provide the reductants (organics) and  $SO_4$  for the thermal sulphate reduction. Some completion fluid additives such as sodium dodecyl sulphate is susceptible to TSR. The studies by Pizadeh et al. (2014), Pasaheh and Marriott et al. (2016) amongst others, indicate that temperature on the order of 100 °C or higher are required for TSR of common sulphur-bearing additives, which is higher than most (all?) producing

Montney reservoirs. The Montney reservoir temperature is also too low for aquathermolysis reaction with sulphur-bearing kerogen.

The completion fluids tested in this study carried out at reservoir temperatures (less than 80 °C) included all completion additives used for the corresponding wells (surfactant, biocides, scale inhibitors etc.) and no evidence was found for TSR in the leachates.

# 6.4.8. Comparison of Sulphate Concentration in Flowback and Produced Water and Subsequent H<sub>2</sub>S and CO<sub>2</sub> in Produced Gas

Wells for which flowback analyses were performed in this study, were subsequently tied into the midstream facilities and produced. Since initiating production, the produced fluids have been sampled and analysed at least once, and for many wells multiple times. In this section, the results of the analyses are presented in an attempt to document how SO<sub>4</sub> composition has changed through time and what is its relationship, if any, with subsequent H<sub>2</sub>S and CO<sub>2</sub> production.

In Figure 6.15, the variation in dissolved sulphate composition and mole fraction H<sub>2</sub>S and CO<sub>2</sub> in the produced gas are shown through time. The SO<sub>4</sub>content of produced waters generally ranges from 50 mg/L to a maximum of about 300 mg/L. Most waters, sampled several years after the wells have been put on production, have sulphate contents of about 60 mg/L. This contrasts with formation waters in the overlying Charlie Lake and underlying Belloy formations, that typically have SO<sub>4</sub> concentrations of about 1000 mg/L, and the overlying Halfway and underlying Debolt formations' waters, where SO<sub>4</sub> commonly exceed 3000 mg/L. Some Halfway waters yield SO<sub>4</sub> values in excess of 15 000 mg/L. Wells in the flowback study for the most part produce no measurable or trace amounts of H<sub>2</sub>S.

In wells for which water analyses are available at least a year after start of production, the SO<sub>4</sub> content is generally higher (red dot on the charts in Figure 6.15) than during the flowback period; the exceptions include wells where the SO<sub>4</sub> content is significantly less and where there is no difference from the flowback values. In wells where there is a distinct upward trend in SO<sub>4</sub> concentration during flowback (i.e., well E. 7-8-13W6; F. 4-31-77-12-72W6, F. 16.30-14W6), this trend is manifested early in the flowback period (after less than about 1000 m<sup>3</sup> of liquid produced). Such results suggest active SO<sub>4</sub> production was occurring during the flowback period, and it is likely the SO<sub>4</sub> was derived from pyrite oxidation or anhydrite dissolution through introduction of unsaturated and oxygenated completion fluids. Where SO<sub>4</sub> content declines through flowback (A. 8-54-D/94-H-4; A-B32-D/94-H-4; B. 8-10-81-18W6; C. 10-35-78-18W6; F. 16.30-77-12W6; I C-89-G/96-B-09) even though salinity is increasing, there is an indication that the source of SO<sub>4</sub> is being depleted. The decline in SO<sub>4</sub> with time may be due to a combination of factors, including that the introduced oxygen is consumed and/or undersaturated anhydrite is fully leached. It is unlikely the SO<sub>4</sub> decline is due to MSR or TSR, inasmuch as there is no corresponding trend in H<sub>2</sub>S, and most Montney reservoir temperatures and salinities are too high to be conducive to MSR and the temperatures too low for TSR.

In the wells in Figure 6.15, there is no correlation between the concentration of sulphate in the produced water and either the mole fraction of  $H_2S$  or  $CO_2$ . During the flowback time there are no gas analyses reported for these wells. None of the wells show trends in  $H_2S$  and  $CO_2$  during the production period. Most of the wells have been on production for a comparatively short time and the concentration of  $H_2S$  and  $CO_2$  is low, and hence the produced  $H_2S$  and  $CO_2$  is likely solution gas. Any partitioning of the gas due to adsorption affinity would not be expected to be manifested until low pressures are reached, and hence much later into the production life of the wells.

















Ε.





Figure 6.15 - Variation in SO<sub>4</sub> in flowback water (left plot) with cumulative flowback. Red dot is the produced water SO<sub>4</sub> after a minimum of one year of production. Right plot is CO<sub>2</sub> and H<sub>2</sub>S mole fraction of produced gas vs time of sample collection. H<sub>2</sub>S values that plot on the x-axis are where analyses were made but the result at or below detection limit. The letter corresponds to the well location in Figure 6.1.
The flowback wells described above, all have a comparatively low concentration of H<sub>2</sub>S. In order to explore the relationship between dissolved SO<sub>4</sub> and H<sub>2</sub>S production in high(er) H<sub>2</sub>S wells, a series of wells of varying H<sub>2</sub>S production across the basin were surveyed, for which there are analyses for H<sub>2</sub>S and CO<sub>2</sub> gas and dissolved SO<sub>4</sub>. For some wells there are trends in H<sub>2</sub>S and CO<sub>2</sub> production with time, while in others no consistent trend exists. There are many fewer water analyses then gas analyses, so it is not possible to directly compare trends, but as a generality there is no simple correlation between SO<sub>4</sub> and H<sub>2</sub>S and CO<sub>2</sub> concentrations in samples collected at the same time. Of the sixteen wells shown in Figure 6.16, four exhibit trends of increasing H<sub>2</sub>S concentration through time (8-17-74, 8-11-58, 12-24-75, 16-27-86), one well shows a weak trend of declining H<sub>2</sub>S with time (8-4-77), and the remaining wells show no trend. In well 6-34-74-7W6, CO<sub>2</sub> increases with production time and in well 12-24-75-8W6, CO<sub>2</sub> decreases with time of production, whereas other wells display no trend. The relative abundance of CO<sub>2</sub> compared to CH<sub>4</sub> varies considerably in the dataset with about an equal number of wells having higher CO<sub>2</sub> than CH<sub>4</sub>, and the remainder having less. In any given well, CO<sub>2</sub> either remains consistently higher or consistently lower than H<sub>2</sub>S throughout the time of production, with the rare exceptional sample.

The longer-term trends or lack of trends in  $H_2S$ ,  $CO_2$  and  $SO_4$  concentrations in the wells in Figure 6.16 does not lead to a simple causative interpretation. The increase in  $H_2S$  with time of production may reflect the greater adsorption affinity of  $H_2S$  than other gases, such that  $H_2S$  is enriched in the produced gas at lower pressures later in the reservoir life (discussed more fully in Chapter 7). In contrast, the decrease in  $H_2S$  with production may reflect the decline in produced water volumes through time, and hence a decrease in  $H_2S$  solution gas. Since  $H_2S$  is much more soluble in water/brines than  $CH_4$  or  $CO_2$ , if  $H_2S$  is in the reservoir at suitable partial pressures (as per Henry's Law), there will be a comparatively higher percentage of  $H_2S$  in solution gas, and hence a higher fraction of  $H_2S$  will be associated with higher water cuts.







Figure 6.16 - Variation in mole fraction  $H_2S$  and  $CO_2$  and dissolved  $SO_4$  with date of sampling for wells of low through high  $H_2S$  concentration.

## 6.4.9. Regional Distribution of Sulphate and other Major Ions - Implications

There have been numerous studies of fluids in the Western Canadian Sedimentary Basin. Of particular importance to our study is the paper by Kirste et al. (1997) on the regional chemistry of Triassic formation water/brines and gases and their origin, and the papers on the regional Alberta Basin by Conolly et al. (1990), on the evolution of formation waters, and Hutcheon (1999) on the regional distribution and origin of hydrocarbons. Additionally, there have been numerous more recent smaller scale studies that contribute to understanding the complexities of fluid distributions, particularly in producing formations, including the Doig and Montney formations.

Since the regional study of Kirste et al. (1997) twenty-five years ago, literally thousands of new wells have been drilled, almost all of which include fluid analyses. In the following section, we map and interpret the regional formation water composition of the Montney Formation in search of insights in understanding the controls on the distribution of SO<sub>4</sub> and other major ions and their potential relationship

with H<sub>2</sub>S occurrence. Our data set is the public data available through AER and OGC. As recognised by Kirste et al (1997), there are a number of potential sources of errors in the public data, including contamination of samples and data entry, sampling, and reporting mistakes. We error checked and filtered the data, eliminating the sample from the data set where any entries were in error. Many wells have multiple analyses collected with time. The data for these wells was averaged after screening for extraneous values. In total, the dataset for the Montney Formation is made up of 5250 wells, although for some plots fewer wells are used due to more limited data analyses — for example, only 2570 wells have useable bromine analyses. It is not possible to differentiate the water fluid chemistry by zone in the Montney Formation. Since essentially all wells are fraced, without knowledge of the drainage volume (stimulated reservoir volume), and particularly fracture height, the source of fluids cannot be isolated. Since we know, based on our flowback study described earlier, that the connate water in the Montney Formation varies stratigraphically and aerially, prudence is required in interpreting the aggregated data.

In the maps and charts presented in this section we compare dissolved ion concentrations to that anticipated from seawater that is progressively evaporated until minerals such as halite, calcite and gypsum begin to precipitate. These plots provide interpretive value as popularized by Rittenhouse (1967) and Carpenter, (1978), and used for example, by Franks (2016) in his excellent study of the Tubular Bay field in the Gulf of Mexico. The seawater evaporation trajectory for fluids is determined using the most conserved elements<sup>2</sup> in seawater, which are Br and Cl (Figure 6.17). These two ions are particularly useful since they are major ions and are included in most routine oil field water analyses. Cross-plotting the log base 10 of ions present in connate water and comparing them the seawater evaporation trajectory (SET) provides a useful interpretative tool since ions that deviates from the SET must be affected by other processes than evaporation. Using the evaporative curve (SET) for modern seawater required an assumption that the major ions (or their ratio) in seawater during Montney deposition in the Early Triassic is similar to that of modern seawater.

Based on isotopic analyses, Alego et al. (2015) and others have shown that since the end of the Permian, total SO<sub>4</sub> in seawater has been generally similar to modern seawater, apart from during about two million-year intervals of widespread ocean anoxia. There are numerous studies of other ions in paleoseawater, based mainly on fluid inclusions and isotopic analyses (e.g. Zeebe et al., 2019), that explore the nuances of ion concentrations, which is beyond the scope and relevance to this study. During seawater evaporation, the Br/Cl ratio will remain constant to the point of halite saturation after which Cl will remain constant (as halite precipitates), since neither Br nor Cl participate in reactions at lower seawater concentrations. In modern seawater, calcite begins to precipitate at a concentration of about 1.65 times that of normal seawater, and gypsum precipitates at approximately 3.5 times. At even higher concentrations of seawater, a myriad of Mg and KCl and SO<sub>4</sub> minerals precipitate. Mixtures of seawater, and seawater evaporated to the point of halite precipitation, result in Br/Cl ratios that follow the sea-level evaporation trajectory (SET; Figure 6.17). Mixing of seawater, and water evaporated past the point of halite precipitation, form mixing lines to the right of the SET, and with increasing seawater the mixing lines to the right of the SET, and with increasing seawater the mixing lines to the right of the SET, and with increasing seawater the mixing lines to the right of the SET, and with increasing seawater the mixing lines to the right of the SET, and with increasing seawater the mixing lines to the right of the SET, and with increasing seawater the mixing lines to the right of the SET, and with increasing seawater the mixing lines to the right of the SET.

<sup>&</sup>lt;sup>2</sup> lons not impacted by precipitation nor diagenesis

right of SET, and a mixing line would parallel the seawater curve (from point A on Figure 6.18). On the other hand, dissolution of halite with fluids on the SET, results in excess Cl and will plot above the SET<sup>3</sup> (Figure 6.19). Of interest to this study is that porewater impacted by brine formed from the dissolution of evaporite deposits (and hence excess Cl) plot above the sea water evaporation curve (i.e., Frank, 2016).



Figure 6.17 - Trends in concentration of ions in seawater compared to bromine in response to evaporation and precipitation of evaporite minerals. Modified from Carpenter (1978). The Cl/Br SET line is normally plotted since neither Cl nor Br participate in precipitate reactions prior to halite being saturated, nor are impacted by usual diagenesis.

<sup>&</sup>lt;sup>3</sup> The small amount of Br that may substitute for Cl in NaCl and thus can be incorporated in the water on halite dissolution or recrystallisation (Franks, 2016) is not consequential



Figure 6.18 - Log Cl vs Log Br showing the impact of mixing NaCl saturated brines (i.e., at Point A) with freshwater. Additional freshwater results in the mixing line trajectory with a 1:1 slope towards point B. The addition of seawater to NaCl at point A results in the trajectory shown by the curved lines that converge at seawater (i.e., 100% seawater). The numbered horizontal lines show the percentage of sea water in the brine-seawater mixture (modified from Carpenter, 1978).



Figure 6.19 - Log Cl vs Log Br showing the results of adding halite to a brine on the seawater trajectory. The isopleths are the amount of Cl added via the halite dissolution (modified by Carpenter, 1978).

#### 6.4.10. Structural Relationship

To provide a framework for the regional fluid analyses, the regional tectonic and structural elements that impact the Triassic succession in northeastern British Columbia and adjacent parts of Alberta are shown in Figure 6.20. In Figure 6.21, the H<sub>2</sub>S concentration in produced Montney gas is plotted. Throughout the map area, isolated areas of high H<sub>2</sub>S production occur. On a regional scale, the highest H<sub>2</sub>S production occurs south of a listric fault that trends east-west south of Dawson Creek and turns southwest paralleling the H<sub>2</sub>S high centred around Grande Prairie. There are no major structural features on Figure 6.20 associated with the southern boundary of the H<sub>2</sub>S high, although it is coincident with the Swan Hills Margin. Examination of proprietary 3D seismic does suggest a genetic relationship between the H<sub>2</sub>S and faults, suggesting the faults facilitated migration into the Montney reservoir of either H<sub>2</sub>S gas or SO<sub>4</sub> rich waters from the overlying Charlie Lake Formation, that would later be subjected to TSR.



# **Montney and Doig Structural Elements**

Figure 6.20 - Regional tectonic and structural features and Doig and Montney subcrop distribution. Modified from compilation by Silva (2021)



# **Total Montney H2S**

Figure 6.21 - Regional variation of concentration of H<sub>2</sub>S in Montney produced gas

#### 6.4.11. Produced Water Salinity

The salinity (TDS/L) of Montney produced water generally is lowest on the northwest edge and the southern edge of the Montney subcrop area, mostly mirroring the structure on the Montney (Figure 6.22). Southwest, away from the subcrop edge, the connate water salinity varies, and there is no single interpretation that accounts for the large-scale trends. It is probable the regional salinity patterns that would be anticipated to mimic burial history have been overprinted in part by differential gas migration, which led to variable dehydration of the reservoir, in many areas to below irreducible water saturation. Water of condensation from producing gas wells is assumed not to impact the dataset, since wells producing very low water cuts are not routinely sampled, but the validity of this assumption is unknown.

#### 6.4.11.1. Implications of Regional Cl/Br Ratios

In Figure 6.23, the Cl/Br ratio for produced Montney water are plotted together with the seawater evaporation trajectory (SET) and the line that separates saturated from undersaturated halite, which is the natural limit of Cl saturation. Brines that plot above the curve (zone 1, Figure 6.24) have Cl higher than anticipated by evaporation of seawater, and hence are comprised of fluids that dissolved halite or fluids that were mixed with a brine that contacted halite, and subsequently migrated into the reservoir. Thus, zone 1 liquids were impacted likely from migration of brines from over or underlying evaporites. Connoly et al. (1990) suggests the enriched Br (plot to the right of SET, zone 2) in some Alberta basin shales are the result of Br desorption from organic-rich Jurassic shales. This is not considered to be the case in the Montney Formation, which does not include organic rich shales, but is stratigraphically proximal to evaporites. The cluster of samples that have the highest Br concentration appears (albeit with some imagination) to form a mixing trend line with a slope of 1:1 that parallels the SET. It is thus suggestive of freshwater mixing (see zone 2, Figure 6.23). The scattering of samples with Cl values less than seawater (zone 3, Figure 6.23) taken at face value would require significant freshwater dilution following contact with halite, or alternatively mixed with water of condensation as result of gas production. The Cl/Br ratio of samples in the Alberta basin plotted by Connolly et al. (1990) all plot to right of the SET which they interpret to indicate that no studied fluids were impacted by dissolution of halite. Kirste et al. (1997) did not consider the ratios of Cl/Br in their study.

In Figure 6.24, wells are plotted according to their zone designation in Figure 6.23, to highlight any regional trends that may exist in the genesis of the produced water. Most areas of high salinity include a mixture of wells with fluids enriched in Br (zone 2) and high salinity fluids but depleted in Br (zone 1), and hence impacted from migrating evaporitic brines. Zone 3 wells have been severely but variably diluted by freshwater incursion or include water of condensation. The uneven distribution of wells with Br measurements greatly limits the interpretation of the distribution of Cl/Br ratios.



# **Montney Water Total Dissolved Solids**

Figure 6.22 - Total dissolved solids in produced water from Montney Formation.



Figure 6.23 - Chlorine and bromine in produced waters of the Montney Formation. The expected change in Cl/Br with simple seawater evaporation (SET) assuming present-day seawater ratio is shown as a red circle. The halite saturation line (dashed orange line) plotted represents the upper boundary of Cl concentration, since at higher concentrations Cl will precipitate out as halite. Further evaporation continues to enrich the brine in Br while the Cl remains constant.



# Montney Water Br to Cl Relationship and TDS Contours

Figure 6.24 - Distribution of wells that plot in the different zones of Cl/Br ratio identified on Figure 6.23.

#### 6.4.11.2. Sulphate in Solution

Sulphate concentration in produced waters of the Montney Formation is highly variable but almost all values are less than the 2700 ppm (~2.65 g/l) that is present in modern seawater (Figure 6.25). The data in Figure 6.25 through to 6.28 are an amalgamation of production from all producing zones in the Montney. Sulphate is plotted with Cl rather than Br due to fewer Br analyses for the higher salinity fluids.

The sulphate concentration in most Montney brines is less than that in seawater (Figure 6.25). Loss of connate water sulphate has been mainly attributed to the reduction of  $SO_4$  in the presence of organic matter and subsequently formation of sulphide minerals (mainly pyrite) and/or  $H_2S$  gas. Additionally, the precipitation of  $SO_4$  minerals when the point of saturation is reached, will result in loss of  $SO_4$  (i.e., Carpenter, 1978). If all the  $SO_4$  loss was due to  $SO_4$  precipitation (i.e., anhydrite or barite), a predictable trend would exist on a plot of  $SO_4/Br$  or  $SO_4/Cl$ , such as described by Carpenter (1978) for the Black Sea. No such trend is evident in the Montney dataset, indicating that the genesis of the current  $SO_4$  concentration is more complex.

The brines currently at depths deeper than about 2800 m have generally significantly higher dissolved sulphate compared to shallower wells, that have a broader range of values (Figure 6.26). Such an observation does not suggest causation since deeper wells occur to the southwest, which also corresponds to the area of better developed evaporite facies in the overlying Charlie Lake Formation.

Spatially, the highest dissolved sulphate concentrations (Figure 6.27) occur in localized areas aligned more or less parallel to the regional structure on the Montney Formation, which also generally coincides with high SO<sub>4</sub>/Cl ratios (Figure 6.28). There is no correlation with the conserved element Br (not plotted), nor Cl (Figure 6.25), and there is no consistent areal variation apart from the local high levels that are presumably related to the distribution of evaporites in overlaying intervals (Kirste et al., 1997). Our dataset is more extensive than Kirste et al. (1997) had available during their study. With our larger dataset, the correlation of high Triassic SO<sub>4</sub> pore water concentrations and the distribution of anhydrite in the overlying Charlie Lake Formation is less obvious. However, our data does reinforce the Kirste et al. (1997) map showing the high SO<sub>4</sub> concentrations centred around a latitude of 56° N and a longitude range between -120 to -120° W.



Figure 6.25 - Dissolved SO<sub>4</sub> and Cl in Montney produced water. The red dot is modern seawater (~2680 mg/l) and the dashed red line is a projected SET.



Figure 6.26 - Variation in concentration of dissolved SO<sub>4</sub> with depth.

# **Montney Water SO4**



Figure 6.27 - Concentration of  $SO_4$  in Montney produced water



# Montney Water log10(SO4) to log10(Cl) Ratio

Figure 6.28 - Contours of SO<sub>4</sub>/Cl molar ratio.

#### 6.4.11.3. H<sub>2</sub>S in Solution and H2S in Produced Gas

Hydrogen sulphide was sampled contemporaneously, in solution in produced water and in produced gas in about 500 wells. In Figure 6.29, the relationship between solution gas and free gas is plotted. On a log-log plot there is general trend between H<sub>2</sub>S dissolved in brine and in free gas at concentrations of dissolved gas greater than about 10 mg/L, whereas at lower concentrations there is no apparent correlation. Hydrogen sulphide has a low Henry's Law constant, with the solubility of H<sub>2</sub>S in water at 1 bar is about 4 g/L<sup>4,5</sup> and hence, the measured values indicate the sampled liquids are undersaturated with H<sub>2</sub>S. If H<sub>2</sub>S is present as free gas, if at equilibrium, the associated water will have gas in solution corresponding to the partial pressure of gas as required by Henry's Law. Sampling and handling the liquids would result in substantial outgassing of the samples, so the degree of undersaturation may be a sampling artifact. Because H<sub>2</sub>S is much more soluble in water than  $CH_4$ <sup>5</sup>, if H<sub>2</sub>S is present in the reservoir, higher water cuts would be associated with higher H<sub>2</sub>S concentrations, everything else being equal.



Figure 6.29 - Relationship between H<sub>2</sub>S in solution and H<sub>2</sub>S in produced gas shown on log-log scale.

<sup>&</sup>lt;sup>4</sup> www.engineeringtoolbox.com/gases-solubility-water-d\_1148.html

 $<sup>^{5}</sup>$  at 1 bar and 60°C solubility of H2S 1.5 g/L, CH4 0.0013 g/L, CO2 0.6 g/L

#### 6.4.11.4. Other Major Ions in Montney Produced Water

The concentration of Ca, Mg, K and Na relative to Cl is plotted in Figure 6.30 and Figure 6.31. For most produced water, the Ca content is higher, and the Mg content is lower than predicted by the SET. Sodium and K follow the SET up to the halite precipitation line, after which K continues to increase in concentration. The most likely explanation for the higher Ca concentration and lower Mg, is due to dolomitisation of calcite via:

$$2CaCO_3 + Mg^{2+} => CaMg (CO_3)_2 + Ca^{2+}$$

Some of the Ca generated by dolomitisation may contribute to the low  $SO_4$  content through precipitation of anhydrite via:

$$Ca_{2} + SO_{4}^{2} => CaSO_{4}$$

Dolomite, at least some of which is authigenic based on fabric, is widely distributed in the Montney Formation. Anhydrite occurs locally but is not pervasive.

Carpenter (1978) suggests the variation in K and Na from that predicted by the SET may reflect the precipitation of illite and feldspar, both of which are a common minor phase in the Montney Formation.



# Ca and Cl in Montney Produced Water

Figure 6.30 - Variation in Ca/Cl and K/Cl ratios with respect to the seawater evaporation trajectory (red line) of the ions. The red dot is the ion pair composition in modern seawater.



Figure 6.31 - Variation in Na/Cl and Mg/Cl ratios with respect to the seawater evaporation trajectory (red line) of the ions. The red dot is the ion pair composition in modern seawater.

## 6.5. Discussion and Conclusions

Sulphate and other major ions in Montney flowback and produced waters have been investigated for insights into controls on the distribution of  $H_2S$  in produced gas.

Major ion chemistry of the Montney Formation flowback water from thirty wells across the producing Montney area provides insight into the geochemical processes in the reservoir. The major ion concentrations, and TDS, increase over the flowback period, while the SO<sub>4</sub> concentrations are generally variable. There is variability in the ion concentrations between wells. However, wells completed at the same site and within the same member of the Montney Formation generally show similarity in flowback water chemistry relative to those completed at different sites, which is the result of wells on the same site having comparable completions and reservoir properties. The increasing major ion concentrations in the flowback water over the flowback period indicate mixing between the relatively low TDS hydraulic fracturing fluid and the high TDS formation water as the dominant geochemical process influencing the flowback water chemistry. Additionally, countercurrent imbibition, ion diffusion and/or osmosis and fluidrock interaction may contribute to the flowback water chemistry. The use of Cl,  $\delta^{18}$ O, and  $\delta^{2}$ H as conservative tracers demonstrates that the proportion of formation water in the flowback water is variable in different wells over the flowback period. Ion exchange causes the concentrations of the divalent ions to be lower over the course of the flowback period. For the initial flowback water samples, the contribution from formation water is generally between 10% and 35%, while for the final flowback water samples, the formation water proportion was generally 40% to 60%. Since there is a significant contribution from formation water, the actual volume of the injected hydraulic fracturing fluid recovered during the flowback period is much less than the volume of total fluid recovered (Owen et al., 2020). For the studied wells, the volume of hydraulic fracturing fluid recovered based on the mixing proportions is typically < 10% of the injected fluid. Sulphate concentrations in the flowback fluid are higher than the values predicted by the mixing model. The elevated SO<sub>4</sub> concentrations are the result of oxidation of pyrite or  $H_2S$  due to the injection of oxic hydraulic fracturing fluid. Decreasing SO<sub>4</sub> concentrations seen in the flowback water from some wells is likely related to SO<sub>4</sub> reduction by bacteria.

The impact of fluid-rock interactions of produced fluids was investigated through use of aging-leach experiments carried out on samples from four Montney wells and one Doig well. The experiments were carried out at reservoir temperature, using surface area to volume ratios anticipated during completion, and for the duration of soaking and flowback of the test wells. The test fluids were slickwater, cross-linked gels, linear gel and viscoelastic fluids prepared with either freshwater or recycled frac fluid. The saturation indices of raw fluids and leachates were calculated at reservoir temperatures through surface temperatures of 10°C. The salinities of leachate varied with the make-up fluid and tested lithology. Most leachates are slightly saturated with carbonates (calcite, dolomite, and aragonite), and saturation decreases with declining temperature. Barite, quartz, chalcedony, and iron oxides and hydroxides are saturated at reservoir temperature, and the degree of saturation increases with declining temperature, and the degree of saturation increases with declining temperature. The leachates for all samples are slightly undersaturated. Halite is undersaturated at reservoir temperature and gypsum. Where Mn is in solution, the Mn minerals are saturated. Halite is undersaturated at reservoir temperature and increases to near saturation with declining temperature.

that, depending on the ratio of frac fluid to connate water, the flowback fluid will vary from being undersaturated to highly oversaturated with respect to a number of important scaling minerals, such as salts, barite, carbonates and Fe and Mn oxides. The dissolved SO<sub>4</sub> in all the leachates is high due to oxidation of pyrite. Aging experiments with pyrite clearly show that the fine-grained pyrite, which is pervasive in the Montney and Doig formations at low concentrations, readily oxidise in completion fluids in a matter of days contributing to SO<sub>4</sub> and Fe in solution. There is no evidence of the sulphur-bearing frac additives contributing to the SO<sub>4</sub>, and they would not be expected to do so at the reservoir temperature of the Montney Formation. The SO<sub>4</sub> generated by the oxygen-bearing completion fluid, combined with introduced sulphate-reducing microbes and a ready food source through organic frac additives, would contribute to early formation of H<sub>2</sub>S. The completion fluid would also decrease the connate water salinity and temporarily reduce the reservoir temperature, both of which are more favorable for MSR. Production of H<sub>2</sub>S by MSR facilitated by the completion fluid would be comparatively short-lived, with the sulphate source being eventually exhausted through reduction by MSR. The increase in salinity of the produced liquids and increasing reservoir temperature with time following completion would also limit MSR.

The relationship between SO<sub>4</sub> concentration in produced water and the coeval production of  $H_2S$  and CO<sub>2</sub> gas is complex in the Montney Formation. The sulphate content of produced waters generally ranges from 50 mg/L to a maximum of about 300 mg/L. Wells for which water analyses are available greater than a year after start of production have generally higher SO<sub>4</sub> concentrations than during flowback period. In wells where there is a distinct upward trend in SO<sub>4</sub> concentration during flowback, this trend is manifested mainly early in the flowback period, suggesting that active SO<sub>4</sub> production was occurring during the flowback period and likely, that the SO<sub>4</sub> was made available via pyrite oxidation or anhydrite dissolution through introduction of unsaturated and oxygenated completion fluids. The reason(s) SO<sub>4</sub> content declines through the flowback period in some wells, even though salinity is increasing, may be due to a combination of factors including that the introduced oxygen is consumed, and/or undersaturated anhydrite is fully leached. It is unlikely the SO<sub>4</sub> decline is due to MSR, inasmuch as there is no corresponding trend in H<sub>2</sub>S, and most Montney reservoir temperatures and salinities are too high to be conducive to MSR.

For some wells, there are trends of increasing or decreasing  $H_2S$  and  $CO_2$  gas production with time, and in others there are no consistent trends. The relative abundance of  $CO_2$  compared to  $CH_4$  varies considerably in the dataset, with about an equal number of wells having higher  $CO_2$  than  $H_2S$ , and the remainder having less. The longer-term trends, or lack of trends in  $H_2S$ ,  $CO_2$  and  $SO_4$  concentrations in the wells does not lead to a simple causative interpretation. The increase in  $H_2S$  with time of production may reflect the greater adsorption affinity of  $H_2S$ , such that  $H_2S$  is enriched in the produced gas at lower pressures later in the reservoir life, whereas the decrease in  $H_2S$  with production may reflect the decline in produced water volumes through time, and hence a decrease in  $H_2S$  solution gas.

At the basin scale, the salinity (TDS/L) of Montney produced water generally is lowest on the northwest and southern edge of the Montney Formation subcrop. To the southwest, away from the subcrop edge, the connate water salinity varies and there is no single interpretation that accounts for the large-scale trends. It is probable that the regional salinity patterns that would be anticipated to mimic

burial history have been overprinted, in part by differential gas migration, which led to variable dehydration of the reservoir, in many areas to below irreducible water saturation. Most areas of high salinity include a mixture of wells that are enriched in Br, suggesting mixing of brines with lower salinity water or freshwater. Produced waters depleted in Br reflect a mixture of evaporated seawater in contact with halite or waters that contacted halite and are thus interpreted to have been impacted from migrating evaporitic brines. Areas of low Br and Cl, less than that of seawater, were severely impacted by freshwater incursion, and the analysed samples included water of condensation from producing gas. For most produced waters, the Ca content is higher than predicted by the seawater evaporation trajectory, and the Mg content is lower, likely reflecting dolomitisation leading to the consumption of Mg and liberation of Ca from dissolution of calcite.

# 7. Comparative Hydrogen Sulphide, Carbon Dioxide and Methane Adsorption Affinity: Implication for Acid Gas Production from the Montney and Doig Formations

## 7.1. Abstract

The methane (CH<sub>4</sub>) and CO<sub>2</sub> adsorption capacity of a suite of mudstone samples from the Montney and Doig formations, and H<sub>2</sub>S adsorption capacity of kerogen of equal maturity to the mudstones, have been investigated to anticipate partitioning of gases during reservoir production. The adsorption capacity of all gases by the mudstones s is a function of their total organic carbon (TOC) content and nature of the organic carbon, including maturity. The mineral matrix contributes immeasurably small amounts to the adsorption capacity, as a result of the low surface area to volume ratio of most minerals, and wateroccupying adsorption sites on high surface area clays. The adsorption capacity/affinity of the kerogen to H<sub>2</sub>S is five to six times that of CH<sub>4</sub> and three times that of CO<sub>2</sub> at virgin reservoir pressures and temperature. The adsorbed gas capacity of a typical Montney/Doig mudstone with 3% TOC and 5% porosity comprises about 20% of the total reservoir storage capacity at a fluid pressure of 35 MPa. Until the reservoir pressure decreases to about 6 MPa for CH<sub>4</sub>, and much lower for H<sub>2</sub>S and CO<sub>2</sub>, no significant adsorbed gas is produced due to the low or zero slope of the isotherm at higher pressures.

Most and potentially all Montney and Doig reservoirs are undersaturated in H<sub>2</sub>S due to its low abundance and the high adsorption capacity of the kerogen. Due to much higher adsorption capacity and affinity for H<sub>2</sub>S than CH<sub>4</sub> and CO<sub>2</sub>, it will not be produced in significant quantities until low pressures (few MPa) are reached, after which H<sub>2</sub>S would be anticipated to progressively increase in abundance in the produced gas. Because the producing reservoir will have high pressure gradients, the desorbing H<sub>2</sub>S may not show a simple increase with reservoir compression anticipated from simple mixed gas model such as the Langmuir model.

## 7.2. Introduction

The abundance of H<sub>2</sub>S and CO<sub>2</sub> in produced gas from the Montney and Doig formations is highly variable spatially, stratigraphically and with production time. Early term transient variations in the mole fraction of H<sub>2</sub>S in produced gas following drilling and completion of some wells has been shown to be the result of the in-situ creation of SO<sub>4</sub> by oxidation of ubiquitous pyrite and/or dissolution of anhydrite by the introduction of oxygenated and undersaturated fluids during drilling and fracing. The produced SO<sub>4</sub> combined with organics introduced in the completion fluid (e.g., guar gum, polyacrylamide, and other additives; Ran et al., 2014, Nixon et al., 2017) and favorable temperatures due to introduction of cooling fluids with microbes, facilitates microbial sulphate reduction in real time, producing H<sub>2</sub>S. Inasmuch as the introduced organics (Nixon et al., 2017) and oxygen are limited, it would be anticipated that their

exhaustion and/or return to higher ambient temperatures would inhibit microbial sulphate reduction (MSR) and thus result in cessation of  $H_2S$  produced by MSR. However, many Montney and Doig formation wells have low concentrations of  $H_2S$  in produced gas, which persists for years; thus, the variability in concentration and timing with respect to completion and production, indicate other factors also play a role in determining produced  $H_2S$ . These factors include but are not limited to: 1) ongoing reduction of SO<sub>4</sub> in connate waters by indigenous microbes utilising inherent organics in the reservoir, where the reservoir temperature is low enough; 2) high dissolved  $H_2S$  levels that inhibit sulphate reducing bacteria (Reis et al., 1992) may be alleviated in some(?) instances by producing the well and reducing the partial pressure of  $H_2S$ , thereby facilitating ongoing production of  $H_2S$  by MSR; 3) the higher inherent solubility and lower diffusion rate of  $H_2S$  in water compared to CH<sub>4</sub> or CO<sub>2</sub>; and 4) the much higher adsorption affinity of  $H_2S$  than CO<sub>2</sub> or CH<sub>4</sub>. In this paper we investigate the potential impacts of adsorption affinity on the relative production of  $H_2S$  while acknowledging other factors may be of equal or of contributing importance.

Previous studies have determined the relative adsorption affinities of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>S on kerogen (Bustin, 2000; Cui et al., 2007), zeolites (Maghjsoudi et al., 2013), and activated carbons (e.g., Habeeb et al., 2016). Our earlier laboratory and theoretical studies have established that the selective adsorption affinity of H<sub>2</sub>S on organic or mineral matter may lead to retention of H<sub>2</sub>S until late in the productive life of a reservoir when pressures are substantially reduced (Bustin, 2000; Laxminarayana et al. 2004). The importance of adsorption affinity on production of mixed gases from coal is well documented (Bustin, 2002). The CO<sub>2</sub> with a stronger adsorption affinity than CH<sub>4</sub> is selectively retained over CH<sub>4</sub> in the adsorbed state, such that CO<sub>2</sub> content commonly increases during the productive life of coal seam wells. Similar partitioning of produced gas is anticipated to be even more prominent for H<sub>2</sub>S due to its multifold stronger adsorption affinity for kerogen than CO<sub>2</sub> (Bustin, 2002; Cui et al., 2007). Selective H<sub>2</sub>S adsorption has been considered a potential contributor to H<sub>2</sub>S gas partitioning in the Eagle Ford shale by Xia and Ellis (2016) although not demonstrated.

In order to evaluate the potential impact of varying adsorption affinities, solubilities, and diffusion rates of H<sub>2</sub>S production in the Montney and Doig formations, a series of adsorption experiments coupled with numerical analyses were undertaken. In this paper we present our results, quantify and compare the adsorption affinity of gases as determined by adsorption isotherms, and model the comparative partitioning of the gases and their abundance with pressure decline during production using a mixed gas Langmuir model. The experiments provide metrics required for full reservoir predicative modelling.

## 7.3. Methods

The adsorption affinity of the tested gases was determined using a high-pressure Boyle's Law apparatus on particles with a medium size of 0.7 mm. The Langmuir pressure ( $P_L$ ) and volume ( $V_L$ ) were derived from a series of isothermal adsorption experiments (steps). The principle for the adsorption experiments is Boyle's Law coupled with mass balance. In these analyses, a known volume of an experimental gas is injected into a sample cell for which the sample volume and mass and void volume

are known. As gas in the sample cell is adsorbed, there is a corresponding decrease in pressure that is proportional to the volume adsorbed. The gas pressure in the sample cell is computer-monitored until equilibrium pressure is reached. The volume adsorbed is calculated as the difference between the gas injected and the gas in the void volume in the sample cell. Corrections are made to account for the change in void volume of the sample cell since the adsorbate occupies space. Gas of known mass is repeatedly injected at progressively higher pressures into the equilibrated sample cell and the cumulatively adsorbed gas (Vg) at a newly equilibrated pressure (P) can be determined. Repeating the process at progressively higher pressures, a series of adsorbed gas volumes (Vg) at different pressures (P) is obtained, and then curve-fitted, yielding an equation for the isotherm. In this study, 6 to 12 pressure steps were undertaken utilising a fully automated adsorption apparatus.

In this study we fit the data to the Langmuir equation, which has as variables the Langmuir pressure (P<sub>L</sub>) and volume (V<sub>L</sub>) for the gas. Although other isotherm models exist, for geological materials at reservoir pressure and temperatures where a monolayer of adsorbent is anticipated, the Langmuir isotherm is most commonly used and normally provides an excellent data fit as found in this study. The Langmuir model is based on a theory that assumes that a state of dynamic equilibrium is established between the adsorbate vapor and the adsorbent surface, and that adsorption is restricted to a single monolayer (Gregg and Sing, 1982). The adsorbent surface is considered as a regular array of energetically homogeneous adsorption sites upon which an adsorbed monolayer is assumed to form. The rate of condensation is assumed to be equal to the rate of evaporation from the adsorbed monolayer at a given relative pressure and constant temperature. The Langmuir equation with these assumptions takes the following form:

$$V(P) = \frac{V_{LP}}{P_{L+P}}$$

P = gas pressure

V(P) = predicated amount of gas adsorbed at P

V<sub>L</sub> = Langmuir volume parameter

P<sub>L</sub> = Langmuir pressure parameter

where P is the equilibrium pressure, V is the volume of gas adsorbed at equilibrium pressure, P,  $V_m$  is the volume of adsorbate occupying a monolayer. A plot of P/V versus relative pressure should yield a straight line whose inverse of the slope will yield  $V_m$  from which the surface area may be obtained.

For this study, a series of isotherms were measured for the Montney and Doig formations at reservoir pressures and temperatures. In mudstones (and other materials) the adsorption capacity depends on the availability of the sites for adsorption for the gas being tested. In mudstones and kerogen, water molecules may occupy sites and/or block access of gas to surface area in extremely fine pores

irrespective of whether the rock is water-wet or not. A vacuum-dried sample of mudstone or coal will thus have a markedly higher adsorption capacity to gas than samples that have water saturation. Traditionally the adsorption capacity of subsurface samples is measured at equilibrium moisture content since the tested samples are, in part, water saturated in-situ in the reservoir. Our study samples were brought to equilibrium moisture following the Australia Standard for equilibrium moisture analyses (AS 2434.3-1984). Since many Montney Formation and likely Doig Formation mudstones were dehydrated by migrating gas and are thus variably below irreducible water saturation, a definitive moisture content for analyses is unknown. In mudstones, even those rich in high surface-area clays, the adsorption capacity is dominated by the kerogen fraction since the internal surface area of kerogen is high and most clays have variably bound-water. For all isotherm plots the adsorbed gas (Y-axis) is reported in volume of gas per gram of rock. In this study a disproportionate number of organic rich mudstones were analysed and hence the proportion of samples with a particular adsorption capacity should not be extrapolated to determine the formation adsorption capacity.

At early stages of exploration of the Montney Formation as an unconventional reservoir (2000-2010), samples from cored wells were desorbed following standard coalbed methane desorption techniques. The captured gas was regarded as gas that was in the adsorbed state in the reservoir (Bustin and Clarkson, 1998). It is now generally recognised that the gas captured at the wellsite in sealed canisters of competent mudstone core is gas that is variably reservoir adsorbed, free gas and solution gas. Public data from four field-desorbed wells are presented in this study to complement the adsorption isotherms. To our knowledge, there are no wellsite desorbed Montney or Doig wells that contain significant H<sub>2</sub>S, likely due to safety issues.

## 7.4. Results

## 7.4.1. Desorption Data/Adsorption Capacity

The desorbed gas content of the Montney, Doig and Halfway formations from four wells is shown in Figure 7.1. These data show a general correlation between desorbed gas and the TOC content. Such results are anticipated since almost all the adsorption capacity of the rock is on the high surface area of the organic fraction and most adsorption sites on high surface area minerals (i.e., clays) are hydrophilic and occupied by water.

Adsorption capacity measured by adsorption at >20 MPa pressure to  $CH_4$  for approximately twenty wells with varying TOC contents are shown in Figure 7.2. At a pressure of 20 MPa the  $CH_4$  isotherm is approximately flat and hence at this pressure is taken as maximum storage capacity for the mudstones. The experimental temperature for the suite of samples plotted is between the 60°C and 95°C. None of these desorbed wells had measurable  $H_2S$ . The scatter in the adsorption and desorption data is undoubtably due to the variation in type of organic matter, which is not captured in the data, as well as unavoidable testing errors and resolution of the instrumentation.

For most wells, the cannister desorption gas content significantly exceeds the gas capacity of the

samples for adsorption, indicating that during canister desorption, free and solution gas are also captured. For example, a TOC of 2% correlated with a maximum adsorption capacity about 0.5 cc (Figure 7.2), whereas the canister-desorbed gas for samples with 2% TOC corresponds to about 1 cc/g. The amount of free gas and solution gas captured during 'desorption' is not however great enough to mask the anticipated correlation between organic carbon content and adsorption capacity. Further, if the reservoir is entirely or partly self-sourced, higher TOC would be anticipated to result in greater free and solution gas, thus strengthening the TOC to gas content correlation.



Figure 7.1 - Example of the strong correlation between TOC and measured desorbed gas content. Total canister-desorbed gas (data from 4 wells) and measured total carbon content (TOC) from the same sample.



Figure 7.2 - Adsorption capacity of methane at >20 MPa vs TOC. The green ellipse captures the region where most data plot. The general trend exists since the most important variable in adsorption capacity is the abundance of kerogen (TOC), and the Montney/Doig kerogen is of the same general type and maturity (Tmax > 430), as well as similar reservoir temperature range of 55 to 95°C.

#### 7.4.2. Methane Adsorption Capacity

#### 7.4.2.1. Doig Formation

Methane adsorption isotherms were measured on a series of Doig mudstones of varying TOC content. Methane adsorption capacity varies between 0.19 and 1.64 cm<sup>3</sup>/g (6.32 and 55.8 ft<sup>3</sup>/ton) at the mean reservoir pressure of 16.2 MPa (2,350 psi) and 67 °C for a suite of samples ranging from 0.27 to 6.48 wt.% of TOC (Figure 7.3). The adsorption data fits well the Langmuir model, with R<sup>2</sup> values ranging from 0.87 to 0.99. Langmuir volumes range from 0.19 to 2.04 cm<sup>3</sup>/g (6.4 to 69.3 ft<sup>3</sup>/ton) and Langmuir pressures range from 1.9 to 12.6 MPa (275 to 1,834 psi), with a median value of 4.1 MPa (590 psi). A strong positive correlation (R<sup>2</sup> = 0.78) exists between Langmuir volume and TOC. The mineralogy of the sample suite based on XRD analyses (Silva, 2021) is dominated by quartz, feldspar, and carbonate. The clay minerals comprise less than 20% by weight of the rock. There is no correlation between adsorption and mineralogy including the abundance of illite, the dominate clay mineral.



Figure 7.3 - Cross-plot of cumulative methane adsorbed versus equilibrium pressure from methane adsorption isotherm experiments at 67 °C with samples of different values of TOC, and Langmuir fit (top). Distribution histogram of calculated Langmuir pressures showing the median value (bottom left), and crossplot of calculated Langmuir volume against TOC, linear fit equation, and marker color by fit quality (bottom right). Modified from Silva (2021). AA- 100/04-09-084-22W6; Al-c-073-J 094-A-12; AM-01-10-082-23W6; CD- c-082-F 094-H-0; MH- a-063-A/93-P-09; SS- 15-34-80-18W6; TG- 9-33-79-21W6.

#### 7.4.2.2. Montney Formation

Methane adsorption isotherms from wells across the basin are provided in Figure 7.4 to Figure 7.10. Methane and  $CO_2$  isotherms for two samples are provided in Figure 7.9 and Figure 7.11. Overall, as anticipated, the adsorption isotherms track the TOC content, although there is scatter in the data likely reflecting that significant measured TOC is related to bitumen rather than kerogen and due to the variation in kerogen composition. Theoretically and in practice, the adsorption capacity decreases with increasing temperature and increases with increasing maturity (Bustin and Clarkson, 1998). In the data suite of this study abundance of organic matter is the primary control on adsorption capacity and masks other controls.

For two samples, one in Horse Range and one in the Tupper strike areas, methane and  $CO_2$  isotherms were collected, in addition to an ethane ( $C_2H_6$ ) isotherm in Horse Range (Figure 7.12 and Figure 7.13). Carbon dioxide has a stronger adsorption affinity than  $CH_4$  and the storage capacity of  $CO_2$  at the same thermal maturity and gas pressures is about twice that of  $CH_4$ ; this is similar to that found in our previous studies with kerogen-rich samples. The  $C_2H_6$  capacity is intermediate between that of  $CO_2$  and  $CH_4$ . The relative affinity, and hence adsorption capacity of  $CO_2$  over  $CH_4$ , decreases with increasing thermal maturity and with decreasing moisture content (Laxminarayana and Bustin, 2003).

#### 7.4.3. Hydrogen Sulphide Adsorption

Hydrogen sulphide adsorption analyses measured on kerogen-rich samples with maturities equivalent to the gas condensate-volatile oil generative level (~Tmax 470 °C) and oil window (~Tmax 450 °C) are provided in Figure 7.14 and Figure 7.15. At these levels of maturities, the affinity and adsorption capacity of H<sub>2</sub>S is about five times that of CH<sub>4</sub> and twice that of CO<sub>2</sub>. At reservoir temperatures typical of the Montney, H<sub>2</sub>S is a liquid at pressures on the order of 5 MPa, although the experimental data is from much lower partial pressures.

## 7.4.4. Adsorption Affinity Contribution to Gas Portioning During Production

In order to model the portioning of CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>S due to adsorption affinity, a series of type isotherms and corresponding Langmuir parameters were created based on the measured isotherms (Figure 7.4 to Figure 7.12) and recalculated based on TOC content for TOC contents varying from 1% to 7%. The extrapolations are based on the assumption that only the organic fraction contributes to the adsorbed gas capacity. For the Montney Formation CH<sub>4</sub> and CO<sub>2</sub> isotherms, the variation within a dataset at any given maturity level, is as great as the variation with maturity; hence, only a single maturity level was investigated based on data from the C-86-I/94-B-1 well for CH<sub>4</sub> (Figure 7.5) and Tupper for CO<sub>2</sub> (Figure 7.10). There is a significant difference in adsorption for H<sub>2</sub>S for the two maturities tested, so they were both considered in the model (Figure 7.11 and Figure 7.12).



Figure 7.4 - Montney isotherms with TOC contents that range between 2 and 6% by weight from wells C-18-H/94-H-5(3.58% TOC), 15-34-80-18W6 (3.95%,2.3% TOC), C-85-I/94-B-1 (6% TOC), 10-82-23W6 (3.55%), and B-51-E/94-A-16 (2.0% TOC).



Figure 7.5 - Type I isotherms for Montney Formation with varying TOC contents that range between 2 and 6% by weight. Samples are from wells C-85-I well.



Figure 7.6 - Type I isotherms for Montney Formation with varying TOC contents that range between 1 and 2.5% by weight. Samples are from Groundbirch wells.



Figure 7.7 - Type I isotherms for Montney Formation with varying TOC contents of about 2.5% are from the Sunset strike area.



Figure 7.8 - Montney adsorption isotherms from the Alberta Montney Formation as reported by the AGS (2012). The data are internally inconsistent for unknown reasons but are reported here for completeness.


Figure 7.9 - Montney methane and carbon dioxide isotherms from the Horse Range strike area.



Figure 7.10 - Montney methane and carbon dioxide isotherms from the Tupper strike area.



Figure 7.11 - Kerogen hydrogen sulphide isotherms measured (dots) and extrapolated curves for Tmax of 450 °C.



Figure 7.12 - Kerogen hydrogen sulphide isotherms measured (dots) and extrapolated curves for Tmax of 470°C.

The type isotherms with data interpolated for varying TOC content are shown in Figure 7.13 for  $CH_4$ , Figure 7.14 for  $CO_2$ , and Figure 7.11 and Figure 7.12 for  $H_2S$ . The Langmuir parameters used in the models are summarised in Table 7.1.

The proportion of sorbed gas to total gas (sorbed + free + solution) storage capacity will vary with the amount, type and maturity of organic matter and gas composition (for sorption), whereas the free gas will vary with porosity and liquid saturation. Pressure and temperature impacts both the adsorbed gas and free gas capacity but not equally. At high pressures the adsorption isotherms flatten and the slope approaches zero, as the adsorbed monolayer becomes occupied, such that incremental pressures above the plateau of the isotherm do not contribute to the gas in place, whereas, depending on the gas composition, increasing pressure will continually increase the gas content to the critical pressure (Figure 7.15). Due to the flatness of the isotherm, gas held in the adsorbed state will not begin to desorb until the reservoir pressure decreases to about 15 MPa in the example of Figure 7.15. Although gas will be in solution in equilibrium with the adsorbed gas, solution gas is a minor component of the total gas. Also, if the sorption isotherms are measured at in-situ water saturation, then the solution gas is captured in the isotherm. Due to the much higher adsorption affinity and capacity of H<sub>2</sub>S compared to CO<sub>2</sub> or CH<sub>4</sub>, the H<sub>2</sub>S gas will be preferentially sorbed and hence the ratio of sorbed to free gas in the produced gas will impact the fraction of H<sub>2</sub>S in the produced gas. The ratio of sorbed gas to total gas in the produced gas is a function of the sorption capacity, which is mainly determined by TOC and free gas; the latter being dependent on effective porosity. Figure 7.16 and Figure 7.17 show how the ratio of adsorbed gas to free gas changes with pressure, porosity and TOC based on the sorption isotherms. These figures show that lower porosity, higher TOC, and lower pressure result in a higher sorbed/free gas ratio. The 'average' Montney/Doig reservoir with about 5% porosity and 2-3% TOC can be anticipated to have about 20% of it's total gas storage capacity in the sorbed state at virgin reservoir pressure. The proportion of gas in the sorbed state will increase during production as free gas is produced preferentially to adsorbed gas. Later production when reservoir pressure is low, the proportion of adsorbed gas in the produced gas stream will progressively increase following the shape of the isotherm. For mudstones with higher TOC and/or lower porosity, the fractional volume of adsorbed gas will be proportionately higher. All these summations are made on the assumption that H<sub>2</sub>S is or was generated or migrated into the reservoir and is available for sorption. Although this paper is concerned with sorption affinity, it needs to be noted that due to the much higher solubility of H<sub>2</sub>S in water than CO<sub>2</sub> ( $\approx$  2x) or CH<sub>4</sub> ( $\approx$  10000x), everything else being equal (which it never is), higher water cuts with solution gas would result in a measurably higher proportion of  $H_2S$  in solution, again assuming there is a source of  $H_2S$ .

To investigate the potential partitioning of gases due to selective sorption affinity, the production of gas was modeled with declining reservoir pressure for sorption in the TOC cases of 7% and 3% as well as a 5% effective porosity available for gas. The model requires the initial reservoir gas composition as an input parameter. For both models, the gas composition by mole fraction used is 2.9% H<sub>2</sub>S, 1.5% CO<sub>2</sub> with 95.6% for CH<sub>4</sub> (Figure 7.18 and Figure 7.19). The onset of H<sub>2</sub>S and CO<sub>2</sub> production is impacted by the isotherms but also the low amounts of gas present (low partial pressure) resulting in the organic matter being markedly undersaturated with respect to these gases. Although the two models demonstrate the same behavior, the 7% model with higher amounts of adsorbed gas capacity begins producing sorbed CH<sub>4</sub>

at higher pressures (note difference in x-axis in Figure 7.18 and Figure 7.19). Figure 7.18-A and Figure 7.19-A show the absolute produced gas with reduced pressure; Figure 7.18-B and Figure 7.19-B show the fractional percentage of total produced gas of each gas with reduced pressure. Figure 7.18-C and 7.18B show the relative abundance of the gas by composition of the sorbed component of the produced gas. The sorbed gas only becomes a significant part of the produced gas at pressures less than a few MPa for the TOC 3% model conditions, but even at a few parts per million H<sub>2</sub>S must be remediated. At 7% TOC, the higher sorbed content results in earlier desorption of sorbed gas. The onset of desorption of the sorbed gas begins at the critical saturation pressure; the pressure where the in-situ gas concentration plots on the relevant isotherm. Hence, if the concentration of H<sub>2</sub>S is higher, then the onset of desorption would be at a higher partial pressure.

CH4	Langmuir Vol (cc/g)	Langmuir Pressure MPa	
1% TOC	0.58	5.74	
3% TOC	1.68	5.73	
5% TOC	2.56	5.80	
7% TOC	3.45	6.02	
CO2	Langmuir Vol (cc/g)	Langmuir Pressure MPa	
1% TOC	1.00	6.48	
2.5% TOC	2.49	6.48	
3% TOC	2.99	6.48	
5% TOC	4.98	6.48	
7% TOC	6.97	6.48	
H2S (Tmax 470ºC)	Langmuir Vol (cc/g)	Langmuir Pressure MPa	
1% TOC	0.94	0.24	
3% TOC	2.87	0.24	
5% TOC	4.71	0.24	
7% TOC	6.59	0.24	
H2S (Tmax 450ºC)	Langmuir Vol (cc/g)	Langmuir Pressure MPa	
1% TOC	0.75	0.39	
3% TOC	2.24	0.39	
5% TOC	3.73	0.39	
7% TOC	5.23	0.39	

Table 7.1 - Langmuir parameters derived from type curve and curves interpolated to other TOC values based on type curves.



Figure 7.13 - Type methane isotherm based on well C-55-I interpolated to TOC weight values of 1, 3, 5 and 7% by weight.



Figure 7.14 - Type carbon dioxide isotherm based on the Tupper well interpolated to TOC values of 1, 3, 5 and 7% by weight.



Figure 7.15 - Gas capacity of methane in the Montney with increasing pressure. The porosity of 5% and TOC of 3% is used for the free gas and sorption metrics discussed in the text. At pressures of about 15 MPa, additional pressure does not contribute further to the sorbed gas storage capacity.



Figure 7.16 - Variation in ratio of sorbed to total gas capacity with pressure for samples of varying effective porosity to gas, and varying adsorption capacity as proxied by TOC content.



Figure 7.17 - Variation in ratio of sorbed to total gas capacity with pressure for samples of TOC of 1%, 3% and 5% by weight and the indicated effective porosity to gas.



Figure 7.18 - Modeled desorption and production of CH4, CO2, and H2S assuming 5% porosity and using isotherms based on TOC of 3% by weight. Desorption is shown from a starting pressure of 6 MPa, which is the critical desorption pressure for the isotherms. Initial gas ratios are 2.9%  $H_2S$ , 1.5%  $CO_2$ , 95.6%  $CH_4$ .



Figure 7.19 - Modeled desorption and production of  $CH_4$ ,  $CO_2$ ,  $H_2S$  assuming 5% porosity and based on isotherms for TOC of 7% by weight. Desorption is shown from a starting pressure of 6 MPa, which is the critical desorption pressure for the isotherms. Initial gas ratios are 2.9% for  $H_2S$ , 1.5% for  $CO_2$  and 95.6% for  $CH_4$ .

# 7.5. Summary and Conclusions

Adsorption isotherms of Montney and Doig reservoir rocks show the overwhelming dependence of sorption capacity on the amount of organic carbon content present within the reservoir. These results, similar to those found in studies of other mudstones, demonstrate that mineral matter plays no measurable role in determining sorption capacity; which is mainly due to the low surface area to volume of most minerals compared to TOC content and due to water occupying adsorption sites on high surface area clays (Bustin and Bustin, 2016). The sorbed gas on a typical Montney/Doig mudstone with 2 to 3% TOC and 5% porosity comprises about 20% of the storage capacity at a reservoir fluid pressure of about 35 MPa. Until the reservoir pressure decreases to about 6 MPa for CH<sub>4</sub>, and much lower for H<sub>2</sub>S and CO<sub>2</sub>, no significant sorbed gas is produced due to the flatness of the isotherm at higher pressures and low partial pressures of H<sub>2</sub>S and CO<sub>2</sub>. The organic fraction is markedly undersaturated in H<sub>2</sub>S, which is present in minor (although important) concentrations, and hence is not produced until much lower pressures.

Due to the much higher sorption capacity and affinity of H<sub>2</sub>S than those of CH<sub>4</sub> (and CO<sub>2</sub>), it will not be produced in quantity until the well reaches the critical desorption pressure which is dependent on the shape of the isotherm and amount of gas present (i.e., a few MPa reservoir pressure); after this pressure is reached, the proportion of H<sub>2</sub>S would be anticipated to progressively increase in the produced gas. Although our simple models are instructive in understanding the role of adsorption and desorption on the produced gas composition, our models in practice do not capture the pressure complexity of a producing reservoir. During reservoir production, the reservoir pressure gradient that is created results in zones, for example near the well bore or adjacent fracture faces, where pressure will be markedly less than that of the reservoir rock matrix further from the pressure sink. Hence some areas of the reservoir will have reached the critical desorption pressure while others will have not, resulting in a produced gas composition that is potentially variable, complex, and not simply predicted.

# 8. Production of Hydrogen Sulphide from the Montney Formation: Insights from Reservoir Modelling

# 8.1. Abstract

The impact of varying gas contents and initial concentrations of H<sub>2</sub>S on the producibility of H<sub>2</sub>S and CH<sub>4</sub> was investigated through a series of 3D reservoir models based on a Montney shale gas reservoir. The models consider the confounding impacts of gas storage (solution, free and sorbed) that are dynamic with production, and the impact of different gas diffusivities.

Models show that  $H_2S$  in solution and in the free state is produced from the onset of production; however, production is dominated by  $CH_4$ , which is preferential in the free state. Later in production, with lower reservoir pressures, the  $H_2S$ , which has a higher sorption capacity and affinity than  $CH_4$ , comprises a greater proportion of the produced gas.

Reservoirs with higher TOC (and hence Langmuir volume) and lower H<sub>2</sub>S concentrations predict higher volumes of produced CH<sub>4</sub>; and models with higher TOC and higher H<sub>2</sub>S concentrations predict higher volumes of produced H<sub>2</sub>S. Variations in TOC have a greater impact on the CH<sub>4</sub> production than variations in H<sub>2</sub>S concentrations, variations in H<sub>2</sub>S concentrations have a greater impact on the H<sub>2</sub>S production. The impact of varying TOC on the CH<sub>4</sub> production increases with decreasing H<sub>2</sub>S concentrations; however, no trend was apparent on the H<sub>2</sub>S production, with the middle H<sub>2</sub>S concentration showing a greater impact than higher and lower H<sub>2</sub>S concentrations. The variations in the total gas production predicted for the different models is thus very complex.

Reliably modelling  $H_2S$  production requires careful measurements of a number of important metrics, including the sorption affinity of the gas.

## 8.2. Introduction

Hydrogen sulphide (H<sub>2</sub>S) at concentrations ranging from 18% to a few parts per million occur in produced fluids from the Triassic Montney and Doig formations (Figure 8.1). Although high concentrations of H<sub>2</sub>S are localized geographically, low concentrations of H<sub>2</sub>S, present in minor to trace amounts to nuisance levels, occur throughout northeastern British Columba and adjacent areas of Alberta. The occurrence of H<sub>2</sub>S in produced gas, even in trace amounts, impacts the economics of drilling, production, treatment, and marketing of gas and associated liquids. The occurrence of H<sub>2</sub>S in produced fluids is also one of the most important environmental hazards and hence risks to development. A main challenge operators face with respect to H<sub>2</sub>S is predicting how much H<sub>2</sub>S will be produced and how will the fraction of H<sub>2</sub>S vary with time. In some wells, during production, H<sub>2</sub>S increases in concentration through time (souring), in other wells H<sub>2</sub>S decreases with time (sweeting) and in still other wells the concentration varies in a seemingly inexplicable manner. The inability to accurately predict H<sub>2</sub>S production makes planning and implementing mitigating measures, including design of midstream facilities to accommodate H<sub>2</sub>S, difficult and consequently economic evaluations onerous.



**Total Montney H2S** 

Figure 8.1 - Regional distribution of hydrogen sulphide production from the Montney Formation.

Hydrogen sulphide, and the normally associated CO<sub>2</sub>, have properties significantly different from hydrocarbon gases that impact production. These include different PVT behavior, sorption affinities, solubilities in water and brines, and diffusivities. The impact of these variables on H<sub>2</sub>S production in a reservoir containing variables amounts of H<sub>2</sub>S cannot be simply predicated due to their incongruent and confounding behavior during the productive life of the reservoir.

In order to better understand and hence predict the production of  $H_2S$  from Montney gas wells we have built a reservoir model using parameters from a much-simplified Montney-like reservoir using known metrics for  $H_2S$  and associated gases and sorption affinities from Section 7 of this report (Bustin et al. in preparation). Our investigation is simplified in that we purposely do not explore the myriad number of variables that impact field production. Rather, we designed our model to predict varying production of  $H_2S$  with a prolonged production history and pressure depletion in order to capture the impact of the much higher sorption affinity and solubility of  $H_2S$  compared to hydrocarbon gases.

## 8.3. Model Parameters

The producibility of the  $H_2S$  in the Montney Formation was investigated through a series of 3D reservoir models. The commercial CMG's GEM advanced general equation-of-state compositional simulator was employed for the modelling. The production from a 1 km long lateral in the centre of a 195 m thick reservoir within a 1550×2000 m model was simulated for a 100-year history in order to image the role of desorbing gases at very low reservoir pressures. The model geometry and its discretization are shown in Figure 8.2.

The model parameters were chosen as the P50 values used for the static modelling (refer to Chapter 3 for mass balance calculations). Additional parameters, not necessary for the static models, were constrained based on average expected values for the Montney based on producing wells. To focus on the impact of variabilities in H<sub>2</sub>S, all parameters were held constant between the series of models except the TOC, and thus the Langmuir parameters (derived in Chapter 7), and a range for initial gas concentrations (Table 8.1). A series of six models were simulated and compared with Langmuir parameters for the CH<sub>4</sub> and H<sub>2</sub>S calculated for a TOC of 1% and 7% and with initial H<sub>2</sub>S concentrations of 1%, 5%, and 15%. The ranges of TOC and H<sub>2</sub>S concentrations chosen for the modelling are provided in Table 8.1. The initial mass of H<sub>2</sub>S and CH<sub>4</sub> and the original gas and water in place in the six models, as calculated by GEM, are provided in Table 8.2.

## 8.4. Results and Interpretation

The cumulative gas production and gas production rates predicted for all models are plotted in Figure 8.3 (note that the gold curve for model 1-1 in Figure 8.3-A is hidden by the cyan curve for model 5-1). The model with the lowest H<sub>2</sub>S concentration and higher TOC (i.e., 1% H<sub>2</sub>S and 7% TOC; model 1\_7) predicts the highest peak gas (CH<sub>4</sub> plus H<sub>2</sub>S) production rate, with a rate of 1.139e7 m<sup>3</sup>/day after 90 days of production (blue curve in Figure 8.3-B). The lowest peak gas production rate, 1.067e7 m<sup>3</sup>/day after 80 days of production, is predicted from the model with the medium H<sub>2</sub>S concentration and the lower TOC

(i.e., 5% H<sub>2</sub>S and 1% TOC; model 5\_1, cyan curve in Figure 8.3-B). The highest and lowest peak gas production rates differ by a factor of 1.07. At the end of the 100-year production history, the highest gas production rate is 14,952 m<sup>3</sup>/day, a factor of twenty greater than the lowest gas production rate of 758 m<sup>3</sup>/day. The highest gas production rate at the end of the production history is predicted from the model with the highest H<sub>2</sub>S concentration and higher TOC (i.e. 15% H<sub>2</sub>S and 7% TOC; model 15\_7, lime curve in Figure 8.3-B), while the lowest gas production rate is predicted from the model with the lowest H<sub>2</sub>S concentration and the lower TOC (i.e. 1% H<sub>2</sub>S and 1% TOC; model 1\_1, gold curve in Figure 8.3-B).



Figure 8.2 - (a) 3D and (b) cross-sectional view of the model geometry used in this study.

The gas production rate from model 15\_7 becomes greater than model 5\_7 after ~6100 days of production and model 1\_7 after ~10,900 days of production. While the cumulative gas production from model 15\_7 remains lower than models 5\_7 and 1\_7, at the end of the 100-year simulations, the produced gas from model 15\_7 is only 0.7% higher than model 5\_7. The gas production rate from model 5\_7 also becomes greater than for model 1\_7; however, not until ~23,500 days of production and thus the cumulative production from model 5\_7 remains lower than model 1\_7.

Parameter		Value
Temperature, T	°C	72
Pressure	MPa	20
Water Saturation, Sw	%	30
Density, ρ	g/cc	2.66
Matrix perm, km	mD	1×10-5
Matrix porosity, φm	%	5
Eff fracture spacing, a	m	0.5
Fracture perm, kmax	mD	5
H2S concentration	%	1, 5, 15
CH4 Langmuir volume, VL	cc/g	0.58, 3.45
CH4 Langmuir pressure, pL	MPa	5.74, 6.02
H2S Langmuir volume, VL	cc/g	0.75, 5.23
H2S Langmuir pressure, pL	MPa	0.39

Table 8.1 - The input parameters used during the modelling. The first Langmuir pressure is for 1% TOC and the second corresponds to 7% TOC.

Model		OGIP	OWIP	СН4	H2S
H₂S	тос				
1%	7%	9.50e9	1.04e7	2.44e9	2.51e9
5%	7%	1.17e10	1.04e7	1.44e9	7.71e9
15%	7%	1.36e10	1.04e7	6.57e8	1.18e10
1%	1%	5.03e9	1.04e7	4.17e8	3.47e8
5%	1%	5.36e9	1.04e7	2.49e8	1.08e9
15%	1%	5.79e9	1.04e7	1.15e8	1.67e9

Table 8.2 - Original gas (OGIP) and water in place (OWIP) ( $m^3$ ) and original mass of CH<sub>4</sub> and H<sub>2</sub>S (kg) absorbed in the model.

The impact of varying H<sub>2</sub>S concentrations is smaller on the models with 1% TOC than 7% TOC due to the higher proportion of H<sub>2</sub>S in the sorbed gas with 7% TOC. While the variability in the models with high and low TOC are of similar magnitude near the end of the simulations, the models with higher TOC show higher variability earlier in the simulations. The peak and final gas production rates from model 15\_1 (15% H<sub>2</sub>S, 1% TOC) are higher than the gas production from the other two models with 1% TOC and lower H<sub>2</sub>S concentrations (i.e., models 5\_1 and 1\_1). Following the peak production rates, the gas production from the model with lowest H<sub>2</sub>S concentrations (model 1\_1) declines at a slightly slower rate, resulting in higher gas production rates than model 15\_1 between ~800 days and ~2700 days of production. The gas production rates predicted from model 1\_1 are lower than for model 5\_1 after ~4850 days of production. The similar gas production rates for models 1\_1 and 5\_1 also result in identical cumulative gas production histories (note the gold curve for model 1\_1 is under the cyan curve for model 5\_1 in Figure 8.3-A).



Figure 8.3 - (A) Cumulative gas production versus time in years and (B) gas production rates versus time in days predicted for the 6 models. Note that the gold curve for model  $1_1$  in plot (A) is hidden by the cyan curve for model  $5_1$ .

To summarize, the results show higher gas productions for models with higher TOC, as anticipated; however, the impact of the H<sub>2</sub>S concentrations are more complex due to its higher sorption capacity and hence the strong correlation with TOC. For models with a 7% TOC, lower H<sub>2</sub>S concentrations result in higher cumulative gas production. However, the production rates for the model with higher H<sub>2</sub>S concentrations eventually exceed the rates for the models with lower concentrations. Thus, the cumulative gas production from models with high H<sub>2</sub>S concentrations would eventually result in higher cumulative gas production. The impact of varying H<sub>2</sub>S concentrations on the produced gas is much smaller for lower TOC. Whereas for 7% TOC, the highest cumulative gas production is from the model with the lowest H<sub>2</sub>S concentration; and for 1% TOC, the highest cumulative gas production is from the model with

the highest  $H_2S$  concentration. The models with 5% and 1%  $H_2S$  concentration predict nearly identical cumulative gas production; however, the gas production rate for the model 5\_1 is higher than for the model 1\_1 and the cumulative gas production for the model 5\_1 would eventually exceed that for 1\_1. Therefore, higher or lower  $H_2S$  concentrations can result in higher gas production depending on TOC and the production history.

The relative variations in gas production rates observed between the six models results from the relative contribution of CH<sub>4</sub> versus H<sub>2</sub>S production. The gas production rate from model 5 7 presented in Figure 8.3 is also shown in Figure 8.4 along with the  $CH_4$  and  $H_2S$  production rates for comparison. Additionally, the distribution of pressure and mole fraction of  $H_2S$  after fifty years of production, at the depth of the well, showing the areal extent of the reservoir accessed during production, are presented in Figure 8.5. As a consequence of the high solubility of  $H_2S$ , the  $H_2S$  in solution is produced from the onset of production with a similar trend in production rates as  $CH_4$ , but with a slightly smaller rate of increase. The production rate of H<sub>2</sub>S after one day is a factor of 19.2 lower than the production rate of CH<sub>4</sub> and is a factor of 19.5 lower after eighty days of production when the CH<sub>4</sub> production reaches its peak. The initial production rates are lower for H<sub>2</sub>S than CH<sub>4</sub> since the H<sub>2</sub>S is selectively retained and not as readily available for production. The peak production rate for H<sub>2</sub>S occurs forty days later than the peak production rate for CH<sub>4</sub>, after which the CH<sub>4</sub> production rate declines at a much faster rate than the H<sub>2</sub>S production rate. After ~9000 days of production, the production rate of  $H_2S$  is higher than CH<sub>4</sub>. As a result, the CH<sub>4</sub> production rate closely follows the total gas production rate until ~1000 days of production, then the total gas production rate is a combination of the  $H_2S$  and  $CH_4$ . The variability in the decline in  $H_2S$  and  $CH_4$ production rates predicted for the models with different TOC and H<sub>2</sub>S concentrations, thus results in complex relative variations in total gas production rates, as observed in Figure 8.3.



Figure 8.4 - Gas production rate, CH<sub>4</sub> production rate, and H<sub>2</sub>S production rate predicted for model 5\_7.



Figure 8.5 - Map view of the layer containing the wellbore showing (left) the pressure distribution and (right) the mole fraction of  $H_2S$  in the reservoir after 50 years of production.

The cross-over between CH<sub>4</sub> and H<sub>2</sub>S gas production can alternatively be visualised in Figure 8.6-A, which shows the fraction of the produced gas composed of CH<sub>4</sub> versus H<sub>2</sub>S for the two models with 5% H<sub>2</sub>S concentration, at a block located adjacent to the centre perforation. At this location in the model, the fraction of H<sub>2</sub>S in the produced gas becomes greater than the fraction of CH<sub>4</sub> after ~12,000 days of production. The cross-over between CH<sub>4</sub> and H<sub>2</sub>S occurs earlier in the production history for the model with the lower TOC, but the same H<sub>2</sub>S concentration (model 5\_1). The fraction of H<sub>2</sub>S is higher than the fraction of CH<sub>4</sub> after ~9000 days of production for model 5\_1. The cross-over between CH<sub>4</sub> and H<sub>2</sub>S occurs earlier in time for the model with higher TOC when the highest H<sub>2</sub>S concentrations are simulated (Figure 8.6-B). The fraction of H<sub>2</sub>S is higher than the fraction of CH<sub>4</sub> after ~2200 days of production for model 15\_7 and ~3100 days of production for model 15\_1. In contrast, to the models with higher H<sub>2</sub>S concentrations, the fraction of CH<sub>4</sub> remains higher than the fraction of H<sub>2</sub>S through the production history for the two models with a H<sub>2</sub>S concentration of 1%. The ratio of H<sub>2</sub>S to CH<sub>4</sub> is higher for the model 15\_1, model 5\_1, model 5\_7, model 1\_1, and is lowest for model 1\_7.

The resulting  $H_2S$  production rates for the six models are shown in Figure 8.7-A and the  $CH_4$  production rates are shown in Figure 8.7-B. As anticipated, the  $H_2S$  production rates are higher for the models with higher TOC and for the models with higher  $H_2S$  concentrations. The  $H_2S$  production rate is a factor of 5.1 higher for the models with higher TOC for  $H_2S$  concentrations of 15% and 1% at the end of the 100-year production history (model 15\_7 compared to model 15\_1, and model 1\_7 compared to model 1\_1) and a factor of four higher for model 5\_7 than model 5\_1. The model with highest  $H_2S$  concentration and higher TOC (model 15\_7) predicts a factor of 3.3 higher  $H_2S$  production rate at the end

of the simulation than the model with the same TOC, but a H<sub>2</sub>S concentration of 5% (model 5\_7) and a factor of 5.0 higher H<sub>2</sub>S production rate than the model with the same TOC but a H<sub>2</sub>S concentration of 1% (model 1\_7). For the models with the lower TOC, the model with 15% H<sub>2</sub>S predicts a factor of 2.5 higher H<sub>2</sub>S production rate than the model with 5% H<sub>2</sub>S and a factor of 6.4 higher H<sub>2</sub>S production rate than the model with 5% H<sub>2</sub>S and a factor of 6.4 higher H<sub>2</sub>S production rate than the model with 1% H<sub>2</sub>S. Variations in the H<sub>2</sub>S concentration thus has a greater influence on the producibility of H<sub>2</sub>S for mudstones with lower TOC (i.e., greater variability in produced H<sub>2</sub>S with H<sub>2</sub>S concentration for 1% TOC than 7% TOC). The highest H<sub>2</sub>S production rate at the end of the simulations, predicted for model 15\_7, is ~32,400 m<sup>3</sup>/day a factor of 83 higher than the lowest H<sub>2</sub>S production rate, a value of 393 m<sup>3</sup>/day predicted for model 1\_1.



Figure 8.6 - Gas mole fraction of  $CH_4$  and  $H_2S$  for models with TOC of 1% and 7% with  $H_2S$  concentrations of (a) 5%, (b) 15%, and (c) 1%, showing the cross-overs between  $CH_4$  and  $H_2S$ .



Figure 8.7 - Production rate of (a)  $H_2S$  and (b)  $CH_4$  for the six models.

The predicted variability in  $CH_4$  production rates is much lower than the variability in  $H_2S$  production rates. As anticipated, at the end of the simulation, the highest  $CH_4$  production rate (5674 m<sup>3</sup>/day) is predicted for the model with the lowest  $H_2S$  concentration and the higher TOC (model 1\_7) and the lowest  $CH_4$  production rate (297 m<sup>3</sup>/day) is predicted for the model with the highest  $H_2S$  and the lower TOC (model 15\_1). Similar to the  $H_2S$  production rates, the influence of  $H_2S$  concentration on the  $CH_4$  production rates is greater for the 1% TOC models; model 1\_7 is a factor of 3.6 higher than model 15\_7 and model 1\_1 is a factor of 7.1 higher than model 15\_1. The influence of TOC on the  $CH_4$  production rates, however, increases for decreasing  $H_2S$  concentrations, in contrast to  $H_2S$  production rates which had a smaller difference between models 5\_1 and 5\_7, while the differences were higher for both the lower and higher  $H_2S$  concentrations. The  $CH_4$  production rate for model 1\_7 is a factor of 1.1 higher than for model 1\_1, model 5\_7 is a factor of 1.2 higher than for model 5\_1, and model 15\_7 is a factor of 2.3 higher than for model 15\_1.

The cumulatively produced  $H_2S$  and  $CH_4$  for the six models are plotted in Figure 8.8. As anticipated, the models with higher TOC and lower  $H_2S$  concentrations predict higher volumes of produced  $CH_4$  and models with higher TOC and higher  $H_2S$  concentrations predict higher volumes of produced  $H_2S$ . The impact of varying TOC has a greater impact on the produced  $CH_4$  than varying the  $H_2S$  concentration, as indicated by the three models with higher TOC predicted higher cumulative  $CH_4$  production than the three models with lower TOC. The impact of varying the TOC on the produced  $CH_4$  increases with decreasing  $H_2S$  concentrations and the impact of varying the  $H_2S$  concentrations increases with increasing TOC. Increasing the TOC from 1% to 7% results in a factor of 1.2 more produced  $CH_4$  for a 15%  $H_2S$  concentration, by 1.4 for a 5%  $H_2S$  concentration, and by 1.6 for a 1%  $H_2S$  concentration. Decreasing the  $H_2S$  concentration from 15% to 1% results in a factor of 1.2 more produced  $CH_4$  for a TOC of 1% and 1.6 more produced  $CH_4$  for a TOC of 7%. As such, the model with a low  $H_2S$  concentration and low TOC (model 1\_1) predicts very similar cumulative  $CH_4$  production as the model with a high  $H_2S$  concentration and high TOC (model 15\_7).



Figure 8.8 - Cumulatively produced  $H_2S$  (thicker dashed lines) and  $CH_4$  (thin solid lines) for the six models.

Whereas variations in TOC have a greater impact on the cumulative CH<sub>4</sub> production than variations in H<sub>2</sub>S concentration, the opposite is true for their impact on the cumulative H<sub>2</sub>S production. The models with high TOC, but lower H<sub>2</sub>S concentrations, thus predict less produced H<sub>2</sub>S than models with low TOC but higher H<sub>2</sub>S concentrations. Increasing the H<sub>2</sub>S concentration from 1% to 15% for a TOC of 7% results in a factor of 11.6 more H<sub>2</sub>S and a factor of 12.0 more H<sub>2</sub>S for a TOC of 1%. The impact of varying the H<sub>2</sub>S concentration on the produced H<sub>2</sub>S is thus slightly higher for lower TOC. While the impact of varying the TOC on the produced CH<sub>4</sub> increases with decreasing H<sub>2</sub>S concentrations, a similar trend is not apparent for the produced H<sub>2</sub>S. Increasing the TOC from 1% to 7% for a H<sub>2</sub>S concentration of 1% results in a factor of 2.0 more H<sub>2</sub>S, a factor of 1.8 for a H<sub>2</sub>S concentration of 5%, and a factor of 1.9 for a H<sub>2</sub>S concentration of 15%.

## 8.5. Summary and Conclusions

The impact of varying gas contents and initial concentrations of H<sub>2</sub>S on the producibility of H<sub>2</sub>S and CH<sub>4</sub> was investigated through a series of 3D reservoir models. As a consequence of the high solubility of H<sub>2</sub>S, the H<sub>2</sub>S in solution is produced from the onset of production with a similar trend in production rates as CH<sub>4</sub>, but with values an order of magnitude lower and with a slightly smaller rate of increase. Following the peak production rates however, the CH<sub>4</sub> production rate declines at a much faster rate than the H<sub>2</sub>S production rate due to high H<sub>2</sub>S in the sorbed state that thus supports the H<sub>2</sub>S production later in the production rate of H<sub>2</sub>S eventually exceeds that of CH<sub>4</sub> for models with higher H<sub>2</sub>S concentrations. The cross-over between CH<sub>4</sub> and H<sub>2</sub>S production rates occurs earlier in the production history for higher H<sub>2</sub>S concentrations. For a 5% H<sub>2</sub>S concentration, the cross-over occurs earlier for the lower TOC model. The predicted ratio of H<sub>2</sub>S to CH<sub>4</sub> therefore, is highest for model 15\_7, then model 15\_1, model 5\_1, model 5\_7, model 1\_1, and is lowest for model 1\_7.

As anticipated, the results show that models with higher TOC and lower H<sub>2</sub>S concentrations predict higher volumes of produced CH<sub>4</sub> and models with higher TOC and higher H<sub>2</sub>S concentrations predict higher volumes of produced H<sub>2</sub>S. The predicted variability in CH<sub>4</sub> production rates is much lower than the variability in H<sub>2</sub>S production rates. The results also showed that whereas variations in TOC have a greater impact on the CH<sub>4</sub> production than variations in H<sub>2</sub>S concentrations, variations in H<sub>2</sub>S concentrations have a greater impact on the H<sub>2</sub>S production. The impact of varying the H<sub>2</sub>S concentrations on the CH<sub>4</sub> production is greater for higher TOC, while the impact of varying the H<sub>2</sub>S concentrations on the H<sub>2</sub>S production is greater for lower TOC. The impact of varying the TOC on the CH<sub>4</sub> production increases with decreasing H<sub>2</sub>S concentrations; however, no trend was apparent on the H<sub>2</sub>S production, with the middle H<sub>2</sub>S concentration showing a greater impact than higher and lower H<sub>2</sub>S concentrations. The variations in the total gas production predicted for the different models is thus very complex.

The results of this study show the utility of reservoir modelling in predicting the variability in production of reservoir  $H_2S$ . The complexities in production rates that may exist are difficult to impossible to forecast without reservoir modelling due to the confounding impacts of gas storage mechanisms that

are dynamic with production and the effects of varying diffusivity of the gases. Reliable modelling of  $H_2S$  production requires careful measurements of a number of important metrics including the gas contents, initial concentrations, and the sorption affinity of the gas.

# 9. Variation in Petrophysical Properties of the Montney and Doig Formations: Implications for Production of Hydrocarbon Liquids

## 9.1. Abstract

The regional petrophysical properties of the Early Triassic Montney and Doig formations in Alberta and British Columbia have been investigated as part of a study to determine the controls on the distribution and production of  $H_2S$  and hydrocarbon liquids. Reservoir properties in the Montney and Doig formation are controlled by a complex interplay between depositional environment, diagenesis, and mechanical compaction.

In the Doig Formation, depositional environment had a major influence in determining the largescale distribution of quartz, clay, apatite and to a lesser extent calcite. Due to their relatively coarser grain-size, low clay-content and greater degree of sorting, quartz-rich siltstones and phosphatic grainstones tend to be macroporous to coarse mesoporous and correspond to the highest permeabilities found in the Doig Formation. The primary intergranular porosity of quartz-rich siltstones is enhanced by grain dissolution; secondary porosity created by early grain dissolution in the diagenetic sequence was later occluded by later dolomite cementation. Compaction by grain rearrangement and pressure solution, imposes a dominant control on porosity, with an observable trend of porosity reduction from the shallow northeastern edge of the depositional basin towards the deeper southwest, despite local variations caused by depositional and diagenetic influences discussed above. The compaction influence in porosity reduction is also seen by the negative correlations of porosity to thermal maturity and pore throat sizes. Permeability in the Doig Formation is highly variable, and primarily controlled by pore throat size and porosity, and subordinately by quartz and clay volumes. The relatively coarse quartz-rich siltstones have the highest permeabilities, occasionally in the millidarcy range when enhanced by grain dissolution. Clay and TOC have a detrimental effect on permeability due to their influence in inhibiting advective flow, although the correlation of permeability with clay and TOC contents shows significant scatter. The relationship between carbonate and permeability is obscured by dolomitisation, which is often associated with grain dissolution, and high permeability phosphorites with relatively high calcite content.

Currently some 4,000 Montney wells produce some liquid hydrocarbons. The liquid production at a large scale mirrors the distribution of the current Montney oil window as mapped by the thermal maturity indicators. Most of the hydrocarbons in the Montney Formation are self-sourced or have undergone short distances of migration. However, in some areas the hydrocarbon liquids production does not follow the regional trend with isolated wells producing significant liquids in area of dry gas. Correlating production performance with petrophysical measurements has proven difficult due to varying drilling and completion strategies on a well-to-well basis. To determine in-situ capillary pressures, analyses of wettability of core and produced fluids as well as the interfacial tension of produced fluids were performed, and the results combined with mercury injection capillary pressure (MICP) analyses. A continuous core through the entire Montney interval in the northern Montney shows a decrease in the contact angle (wettability) with depth for fresh water, completion fluid and Montney oil. These decreases in wettability are correlated to the TOC content of the strata. Conventional versus unconventional reservoir facies are readily differentiated by capillary pressure. The upper Montney Formation conventional reservoir at Kahntah has very low entry pressures and required a trap and seal to retain hydrocarbons. The entire Montney Formation is in many areas a laterally continuous unconventional reservoir. The uppermost Montney is the preferred drilling and completion target due to higher porosity and permeability. However, in areas where the upper Montney is a clean tight sandstone, capillary pressures may be too low to self-seal the reservoir and, in the absence of external seal and trap, the reservoir will be wet.

## 9.2. Introduction

Predicting the distribution and producibility of liquid hydrocarbons in the Montney and Doig formations, like with other fine-grained heterogenous units, has proven difficult. Although numerous studies have addressed the complex stratigraphy and lateral variability of these units (Davies et al., 1997; Moslow, 2000) and many studies have intricately documented their pore structure (e.g., Ghanizadeh et al., 2018; Cui and Nassichuk, 2018; Vaisblat et al. 2021), there have been few successful attempts to integrate the data to a scale which would enable prediction of reservoir performance and particular liquids production. Both the Montney and Doig formations have a wide range of reservoir properties that vary laterally and stratigraphically. Both formations were initially and still are exploited as conventional reservoirs, but the majority of production and exploration is focused on unconventional resources requiring horizonal drilling and fracturing. In some areas, the Montney Formation is a hybrid reservoir with coarser-grained, more porous and permeable units requiring a trap and seal to host hydrocarbons, whereas the fine-grained facies are a continuous self-sourced and sealed reservoir.

In this section, we characterize the variability in reservoir properties of the Montney and Doig reservoirs, stratigraphically and aerially, in an attempt to understand the geological controls on fluids distribution and their selective production. In particular, we characterize the variation in capillary pressures and its dependence on pore throat size, as well the varying wettability and interfacial tensions of reservoir fluids (Figure 9.1).

## 9.3. Methods

A total of 135 samples were selected from 470 m of core from thirteen wells in British Columbia and 190 m from seven wells in Alberta, for petrophysical analyses. The wells were chosen based on well logs with the objective of maximising the stratigraphic and spatial coverage of the Doig Formation across the entire subcrop area in northeastern British Columbia and central western Alberta. Samples were chosen to adequately represent the lithofacies identified and capture the vertical variability in petrophysical properties. Approximately 120 plugs parallel to bedding and 80 plugs perpendicular to bedding were cut, measuring 30 mm in diameter and between 24 and 65 mm in length, for permeability measurements.

#### 9.3.1. Mineralogy

Mineralogy was determined on a subsample split, which was crushed to an ultra-fine powder, then prepared as smear mounts and XRD was performed from 3 to 60° using a Co X-ay source. The results of the XRD analyses were quantified using TOPAS®, a commercial Rietveld (1967) analysis program for quantification of mineralogy. In samples in which the minerals have fixed cell dimensions, such as quartz and pyrite, the accuracy of the analysis by Rietveld is about ± 3% relative, by weight. In rocks with disordered minerals, the accuracy of the data is lower, the amount of which varies with the amount of disordered minerals.

The mineralogy and rock fabric were also investigated by thin section petrography and SEM. The SEM was used with an accelerating voltage of 20 keV and a working distance between 10 and 11 mm.

#### 9.3.2. Porosity

The skeletal density was determined on core plugs, whereas the grain density was measured on finely crushed material, such that there are no non-accessible pores. Both skeletal density and grain density were determined by helium pycnometry, according to the American Petroleum Institute (1998) standard. The bulk density of the core plugs was determined by mercury immersion using Archimedes principle. Total accessible porosity was determined from the difference between the skeletal and bulk density. An approximate measure of the bulk and grain density, and porosity of each sample was also obtained from the mercury injection capillary pressure (MICP) analyses (Comisky et al., 2011; Munson, 2015).

## 9.3.3. Wettability, Surface, and Interfacial Tension

The wettability to the samples was measured by the pendent and captive drop method, and the interfacial tension between the studied fluids and their surface tension was determined by a force tensiometer using commercial instrumentation.

## 9.3.4. Total Organic Carbon and Source Rock Characterisation

Total organic carbon and source rock characterisation was determined on select samples used for wettability tests, using Rock Eval<sup>®</sup> methods on a HAWK<sup>®</sup> analyser, according to the method outlined in Espitalié et al. (1977),

## 9.3.5. Capillary Pressure

The capillary pressure was determined by mercury porosimetry utilising a Micrometrics Autopore IV 9520<sup>®</sup> porosimeter. Mercury porosimetry relies on the injection of mercury into a prepared sample at increasing pressure steps (up to 60,000 psi, 414.4 MPa). The technique is capable of directly measuring

pore volume by forcing mercury into the pore space. The technique is also capable of directly measuring pore (throat) diameters in the range of 0.003 to 360  $\mu$ m. The Washburn (1921) equation, which is the standard method to derive pore size distribution, has been used in this study.

$$D = -\left[\frac{1}{P}\right] 4\gamma \cos\varphi$$

Where D = pore diameter, P = applied pressure,  $\gamma$  = surface tension, and  $\varphi$  = contact angle. Triple distilled mercury is used to ensure optimum test conditions and consistent physical properties. Testing under these conditions assumes a mercury surface tension of 485 dynes/cm and a contact angle between mercury and air, of 130°. The irreducible water saturation from capillary pressure data is determined from the asymptote of the recalculated capillary pressure curves, based on the contact angles and interfacial tensions measured on the rocks and fluids.

In this study we make use of mercury intrusion capillary pressure (MICP) data to characterise pore throat size and distribution.

#### 9.3.6. Permeability

Gas permeability for samples with permeability less than 1E-3 md was measured using the pulse decay (Brace et al., 1968; Yamada & Jones, 1980; Trimmer, 1981; Hsieh et al., 1981; Neuzil et al., 1981; Bourbie & Walls, 1982; Dicker & Smits, 1988; Jones, 1997; Cui et al., 2009) method with a custom-built pulse-decay permeameter (PDP), consisting of two reservoirs of known volumes and a Hoek-type core cell holder, using helium as the probe fluid. The choice of helium as probe fluid may cause an overestimation of permeability relatively to more common in-situ gases, such as CH<sub>4</sub> and heavier alkanes, due to their smaller molecular diameter compared to hydrocarbon gases. The use of other gases, however, would require adsorption corrections that are impractical and introduce large uncertainties in the measurements. The plug samples designated for permeability measurements were cut with nitrogen, then cleaned of soluble hydrocarbons and any residual connate brine through distillation with Dean-Stark apparatuses using toluene or other solvents as needed. Each sample was cleaned for approximately one week, oven-dried at 110 °C for another week and kept at 60 °C until the beginning of the analysis. Sample mass was measured before and after solvent extraction as a means of quality control. The ends of all plugs were trimmed to minimise mud filtrate invasion effects. Plug end surfaces were then milled in a surface grinder, in order to create a right cylinder with smooth parallel faces on both ends. Permeability was obtained under at least three different confining pressures from approximately 17 to 45 MPa (2,500 to 6,500 psi), while maintaining a constant pore pressure of about 7 MPa (1,000 psi), in order to encompass the entire range of in-situ net confining stress (NCS) calculated for the samples. Due to the high pore pressure used in the experiments, gas slippage effects are minimised, as is the magnitude of gas compressibility variation with small pressure fluctuations (Dicker and Smits, 1988; Jones, 1997). A differential pressure of approximately 1 MPa (150 psi) was established between the upstream and

downstream ends of the core cell holder, and the permeability was calculated based on the pressure pulse decay method as described by Cui et al. (2009).

Samples with permeabilities higher than the upper threshold for the pulse-decay method were measured using a custom-built steady-state permeameter. Gas permeability is determined by solving the integrated form of the semi-empirical Darcy's law for compressible fluids (American Petroleum Institute, 1998; McPhee et al., 2015). Permeabilities were measured at three or more stresses and corrected for gas slippage (Klinkenberg, 1941). Unless otherwise stated when single permeability values are reported, the measurement is at an effective stress of 4800 psia (33 MPa).



Figure 9.1 - Outline of sampling handling and analyses of core and fluid systems.

# 9.4. Results

#### 9.4.1. Doig Formation

The petrophysics of the Doig Formation was determined as part of a basin wide study that comprised the PhD thesis at The University of British Columbia (UBC) by Pablo Lacerda Silva (Figure 9.2). The following text on the Doig Formation is an extract from his unpublished thesis which is available through UBC (Silva, 2021).

#### 9.4.1.1. Mineralogy

The mineralogy of the Doig Formation is highly variable. Although quartz, dolomite and calcite are the dominant minerals, their proportions vary widely from over 90 wt.% of quartz to over 80 wt.% of

carbonate minerals (Silva, 2021). Apatite is locally important as a major component of phosphorite beds (Silva and Bustin, 2020b), reaching 80 wt.%. The only significant clay mineral detectable by XRD is illite, which is present in relatively low amounts with a median value of 4.9 wt.% and reaching a maximum of up to 30 wt.%. The maximum concentration of K-feldspar and plagioclase are 23 and 30 wt.%, respectively. Accessory minerals include pyrite, which is present in most samples, with a median value of 1.2 wt.% and a maximum of 15.5 wt.%, and sparse occurrences of ankerite and siderite, as well as anhydrite and gypsum.

#### 9.4.1.2. Porosity and Pore Size Distribution

Unstressed helium pycnometry porosity of the Doig Formation samples in the dried state ranges from 0.97 to 17.83 PU<sup>6</sup>, with a median value of 3.85 PU. Porosities increased from the as-received state to oven-dried in almost all cases, albeit with an average increase of less than 4%. Stressed corrected porosities using the MIP compressibility curves, which more accurately represent in-situ conditions, range from 0.26 to 14.63 PU, with a median value of 2.77 PU. Porosity distribution is slightly bimodal. The first mode for stressed corrected porosity of approximately 2.3 PU corresponds to the centre of the distribution for most mudstones and bio-wackestones. The second group, with a mode of approximately 10.3 PU, represents quartz-rich siltstones of the upper Doig and phosphatic grainstones of the Doig phosphate zone (DPZ).

Porosity does not correlate well with any single variable, as the origins of porosity in the rocks analyzed are highly variable. Quartz has a weak positive correlation with porosity (Figure 9.3-A), which based on petrography, is both from primary intergranular porosity (Figure 9.4-A) and grain dissolution-enhanced (Figure 9.4-C) porosity of quartz-rich siltstones. Intergranular and moldic porosity in phosphatic grainstones is responsible for the strong correlation between apatite and porosity in rocks with a patite concentrations above 30 wt.% (Figure 9.3-C; Figure 9.5-E); in apatite-poor samples, no correlation between apatite and porosity exists.

<sup>&</sup>lt;sup>6</sup> Porosity values in the Doig are expressed in porosity units (PU), which correspond to percentage of void in a solid volume, or void volume in percentage as opposed to fraction.



Figure 9.2 - Location of wellbores samples and analysed, and public data used in this study on a map of the Doig subcrop area and shaded relief topographic backdrop map, with main structural lineaments (after Berger et al., 2008) and outline of fields on which the Doig sampled wells are located.



Figure 9.3 – Cross-plots of porosity at in-situ net confining stress versus minerals from XRD that show any degree of correlation with porosity, with marker shape by stratigraphic interval, linear regression line and r-squared value.

Calcite, K-feldspar and illite content, all correlate negatively with porosity (Figure 9.3-B, Figure 9.3-D, Figure 9.3-E). As calcite occurs primarily as cement, with exception of bio-wackestones and biopackstones, the negative correlation is a result of pore space occlusion. The correlation is obscured by porosity degradation due to dolomite cement (Figure 9.4-A, Figure 9.4-D), and high porosity preservation in phosphatic grainstones with relatively high degree of calcite cementation. The negative correlation between porosity and K-feldspar is likely a result of preferential dissolution of feldspars in siltstones with grain dissolution-enhanced porosity (Figure 9.4-E). The negative correlation between illite and porosity is caused by the intergranular porosity of clay-poor siltstones and phosphatic grainstones, and in the case of siltstones, enhanced grain and cement dissolution promoted by the large pore throat sizes.

Compaction has a significant influence in porosity, as shown by the negative correlation of porosity with paleo depth of burial, as proxied by Tmax, and strong positive correlation to pore throat diameter from MICP (Figure 9.6-A, Figure 9.6-B, Figure 9.6-C). Porosity also correlates negatively with TOC content, albeit with significant scatter in the lower porosity range (Figure 9.6-C). This suggests that organic porosity development from thermal maturation is not responsible for creating significant pore volume. Intercorrelation of quartz, TOC and porosity causes the negative correlation between TOC and porosity, due to the high intergranular porosity of quartz-rich siltstones.



Figure 9.4 - Photomicrographs of representative lithologies of the upper Doig Formation in planepolarized light. Porosity is blue in thin sections. Green box shows location of detailed image. Pie chart represents mineral volumes from XRD converted from weight using reference density values from Serra (1990) and normalized to include porosity and TOC content. (A) Sample TB1: siltstone with quartz (Qt), Kfeldspar (KF) and plagioclase grains with corroded borders, quartz overgrowth (QO), dolomite (Do) and siderite cement, interstitial pyrite (Py), and abundant intergranular porosity. (B) Sample CZ4: siltstone with grain dissolution and calcite and dolomite cementation and overlying laminated mudstone with quartz and feldspar grains in a clay (CI) matrix. (C) Sample HM2: very fine sandstone composed mostly of quartz grains with corroded borders, sparse apatite (Ap) grains, pervasive grain dissolution and interstitial dolomite cement. (D) Sample TG1: heterolithic laminated siltstone and mudstone with quartz, feldspar and sparse apatite grains, clay matrix, and calcite (Ca) and dolomite cement, as well as a calcite vein offset by a clay lamination (E) Sample CD9: bio-wackestone with quartz, and feldspar silt matrix, calcite, and dolomite cement, as well as almost complete dissolution of bioclasts, creating moldic porosity and partial filling by quartz. (F) Sample TG5: siltstone with quartz, feldspar, and sparse apatite grains, with calcite and dolomite cement, interlaminated with clay-rich laminae.



Figure 9.5 - Photomicrographs of representative lithologies of the Doug Phosphate Zone in plane-polarized light. Porosity is blue in thin sections. (A) Sample MH1: mudstone containing silt-sized quartz (Qt), K-feldspar (KF) and apatite (Ap) grains in a clay (CI) matrix. (B) Sample AA3: siltstone with bioturbated fabric containing quartz, feldspar, sparse apatite grains and intraclasts, grain dissolution, calcite and dolomite cement. (C) Sample SS8: bio-packstone composed almost exclusively of recrystallized bivalves, interlayered with detrital sediment composed of quartz, feldspar, and clay. (D) Sample CP8: laminated mudstone composed of quartz, feldspar, and clay, with pervasive substitution of grains by dolomite (Do), and nodules of intergrown anhydrite (An) and pyrite (Py). (E) Sample MH5: phosphatic grainstone composed of granule-sized apatite intraclasts, silt-sized apatite coated grains, often with quartz nuclei, cemented by calcite. (F) Sample CD8: mudstone composed of quartz and feldspar grains with corroded borders in a clay matrix, with extensive grain dissolution and substitution by dolomite, calcite cementation, as well as interstitial pyrite precipitation.


Figure 9.6 - Cross-plots of porosity at in-situ net confining stress versus TOC content, Tmax and common logarithm of median pore throat diameter from MICP in nanometres, illustrating influence of compaction and maturity on porosity, with marker shape by stratigraphic interval, linear regression line and r-squared value. Note the inverted vertical axis on the Tmax cross plot.

Pore size distributions span four orders of magnitude, with median pore throat diameter from MICP ranging from 5 to 2700 nm. Arranging the pore size distribution by lithotype based on the mudstones ternary mineralogy classification of Gamero-Diaz et al. (2012) provides insights as to the control of mineralogy on the pore size distributions (Figure 9.7). Quartz-rich siltstones contain mostly macropores, with median pore throat diameter ranging from 36 to 930 nm, and an average of 316 nm. Relatively small amounts of clay are sufficient to significantly affect pore size. The clay-rich, siliceous, mixed siliceous and mixed mudstones are mostly coarse mesoporous, with median pore throat diameters ranging from 7 to 136 nm, and an average of 27 nm.



Figure 9.7 - Cumulative distribution of normalized pore volumes by pore throat size for all samples colored by lithotypes of Gamero-Diaz (2012) based on mineralogy. Pore size classification according to IUPAC (Sing et al., 1985).

In relatively clay-rich facies, an increase in the proportion of carbonate at the expense of quartz has little influence on pore throat sizes. Mixed and carbonate siliceous mudstones are predominantly fine to coarse mesoporous, with median pore throat diameters ranging from 5 to 70 nm, and an average of 20 nm (Figure 9.7). The pore size distributions of clay-poor lithotypes with relatively high carbonate content is highly variable. Carbonate-rich siliceous mudstones range from macroporous to fine mesoporous, with median pore throat diameters ranging from 5 to 2700 nm, and an average of 174 nm, while mixed carbonate, silica-rich carbonate and carbonate mudstones range from 5 to 2220 nm, and an average of 136 nm. The largest pore sizes in carbonate-rich lithotypes are associated with dissolution enhanced-porosity siltstones partially cemented by dolomite, and phosphatic grainstones with calcite-recrystallized skeletal grains and calcite cement.

#### 9.4.1.3. Permeability

Absolute matrix permeability to gas of the Doig Formation ranges over six orders of magnitude from  $8 \times 10^{-6}$  to 14 mD, with a median of  $6.4 \times 10^{-4}$  mD, at in-situ net confining stress conditions (Figure 9.8). Permeability anisotropy is highly variable, with a kv/kh ratio ranging from 0.003 to 3.269. The median permeability parallel to bedding is  $1.1 \times 10^{-3}$  mD, while the median permeability perpendicular to bedding is  $3.3 \times 10^{-4}$  mD. Permeability is most strongly controlled by pore throat size and has a strong positive correlation ( $R^2 = 0.37$ ) with median pore throat size. Porosity has the second strongest control on permeability, with a moderate positive correlation ( $R^2 = 0.18$ ). Permeability has a weak positive correlation with quartz ( $R^2 = 0.04$ ) and a weak negative correlation with clay ( $R^2 = 0.08$ ). The highest permeabilities are associated with the relatively coarse silica-dominated siltstones, occasionally with grain dissolution and partial dolomitisation. Above a clay content of 15 wt.%, permeabilities are lower than  $1 \times 10^{-3}$  mD.



Figure 9.8 - Cross-plot of porosity versus absolute gas permeability at in-situ net confining stress, with marker colored by lithotypes of Gamero-Diaz (2012) based on mineralogy, size by common logarithm of median pore throat diameter from MICP and shape by plug orientation with respect to bedding. Lines of the relation between permeability and porosity based on the Kozeny-Carman equation for pore diameters with parallel pipe geometry are shown for reference (Mavko et al., 2009), assuming a tortuosity factor of unity.

Permeability anisotropy is lowest in quartz-rich siltstones, which have the most isotropic grain fabric of the studied samples. The kv/kh ratio has a weak positive relationship with quartz ( $R^2 = 0.11$ ) and a weak negative relationship with TOC ( $R^2 = 0.09$ ). The influence of net confining stress (NCS) on permeability reduction varies from half an order of magnitude of permeability reduction per 1000 psi increase in NCS, to a fiftieth of an order of magnitude per 1000 psi, with a median of a tenth of an order of magnitude per 1000 psi. Quartz, TOC, and clay are the main controls of permeability reduction with confining stress. The permeability of quartz-rich siltstones is the least sensitive to NCS (Figure 9.9). Permeability is most sensitive to stress in samples with relatively high organic and clay content. The amount of carbonate does not have a strong influence on permeability sensitivity to stress.



Figure 9.9 - Cross-plots of common logarithm of permeability versus net confining stress for all core plugs at different stresses, for the various lithotypes of Gamero-Diaz (2012) and colored accordingly. Measurements of the same sample at different net confining stresses are represented by the same symbols and connected by a linear regression line. The slope of the line is proportional to the sensitivity of permeability to stress. The same symbols connected by a line represent the same sample measured at different stresses.

#### 9.4.1.4. Geologic Controls on Reservoir Properties

Reservoir properties in the Doig Formation are controlled by a complex interplay between depositional environment, diagenesis, and mechanical compaction. Depositional environment had a major influence in determining the large-scale distribution of quartz, clay, apatite and to a lesser extent calcite. Due to their relatively coarser grain-size, low clay-content and greater degree of sorting, quartz-rich siltstones and phosphatic grainstones tend to be macroporous to coarse mesoporous and

correspond to the highest permeabilities found in the Doig Formation. The amount of clay, which is controlled by the depositional environment, has only a slight detrimental effect to total porosity. Due to bound water, particle shape and size however, the presence of clay significantly reduces effective porosity and the pore throat sizes, which limits the pore space available for hydrocarbons and lowers the permeability.

The primary intergranular porosity of quartz-rich siltstones is often enhanced by grain dissolution, which has been noted by Harris and Bustin (2000) as an important factor in reservoir quality. Secondary porosity created by early grain dissolution in the diagenetic sequence was later occluded by yet later dolomite cementation, according to Martin (2008). Most of the quartz-rich siltstones were only partially cemented by dolomite and preserved significant macro and mesoporosity. Another type of secondary porosity is related to partial or complete dissolution of calcitic and phosphatic skeletal grains in bio-packstones and bio-wackestones. This moldic porosity occurs mostly in the DPZ and is responsible for poorly connected macropores. Calcite occurs as skeletal fragments and rare veins, and most frequently as pore-filling cement, precipitated in multiple phases through a complex diagenetic history as also noted by Martin (2008). As such, calcite is responsible for occluding pore space, reducing pore throat sizes and permeability. In the DPZ however, there are phosphorites containing significant quantities of calcite while retaining macropores and thus, high permeabilities.

Compaction by grain rearrangement and pressure solution imposes a dominant control on porosity, with an observable trend of porosity reduction from the shallow northeastern edge towards the deeper southwest, despite local variations caused by depositional and diagenetic influences discussed above. The compaction influence in porosity reduction is also seen by the negative correlations of porosity to thermal maturity and pore throat sizes. The compaction trend affects matrix permeability across the basin, due to the compounding effect of pore throat size and porosity reduction. In the DPZ, the trend in porosity reduction with depth is reversed from the basin centre towards the western edge, which is likely related to phosphorite facies and preservation of their high intergranular porosity due to early calcite cementation and subsequent partial cement dissolution.

Permeability in the Doig Formation is extremely variable, and primarily controlled by pore throat size and porosity, and subordinately by quartz and clay volumes. The relatively coarse quartz-rich siltstones have the highest permeabilities, occasionally in the millidarcy range when enhanced by grain dissolution. Clay and TOC content have a detrimental effect on permeability due to their influence in inhibiting advective flow, although the correlation of permeability with clay and TOC shows significant scatter. The relationship between carbonate and permeability is obscured by dolomitisation, which is often associated with grain dissolution, and high permeability phosphorites with relatively high calcite content.

Mineralogy exerts a strong control on permeability reduction with stress and vertical to horizontal permeability anisotropy. Among the reservoir facies studied, quartz-rich siltstone is the facies that has the least anisotropic permeability and the least stress dependent permeability, due to its isotropic and rigid fabric. Lower permeabilities in the deepest and most compacted areas of the basin may have contributed

to the development of overpressure due to the low rates of advection and diffusion of generated hydrocarbons.

### 9.4.2. Montney Formation

There have been over 12,000 wells drilled and completed in the Montney, of which 4,000 produce variable amounts of liquid hydrocarbons (LHC<sup>7</sup>). The distribution of liquid hydrocarbons has been described and mapped in Chapter 3 of this report. At a large, first order scale, the occurrence of LHC mimics the distribution of the current Montney oil window as mapped by the thermal maturity indicators in Chapter 3. Inasmuch as most of the hydrocarbons in the Montney Formation are considered self-sourced or have undergone short distances of migration, this relationship is anticipated. Superimposed on this distribution is variable and complex production rates of LHC from wells that do not lend themselves to a straightforward interpretation. In some areas, hydrocarbon liquids and gases are vertically stratified contrary to that anticipated based on hydrocarbon density and gravity. This creates unique challenges in optimizing completions and production. In some areas the H<sub>2</sub>S distribution mimics the hydrocarbon liquid stratification suggesting a related causality whereas in other areas there is no obvious correlation.

In dry gas areas such as such as in Septimus, the upper, middle, and lower Montney produce equally dry gas whereas in wet gas areas such as Tower, all zones may produce wet gas although the amounts may vary with detailed variations in lithology. Overall, the upper Montney is preferentially and solely completed by most operators, but in some areas the middle Montney and in fewer areas the lower Montney have been completed and produces at economic rates. In detail, drawing conclusions from comparing production rates between wells, is difficult to impossible inasmuch as the drilling and completion strategies vary on a well-to-well basis. In most (all?) areas the variability of production between wells is significant; the variation between wells completed in one member is greater than the differences between members in the same well. Even wells completed in the same zone on the same pad by the same operator and with the same completion strategy are invariably found to have significant differences in drilling and completion. The impacts of variable drilling and completion methods on production metrics are thus difficult to isolate from variations in reservoir properties or fluid saturations.

Resolving the controls on LHC and  $H_2S$  production is confounded in that the produced fluids are not necessarily the same as the reservoired hydrocarbons, which is the result of selective retention due to sorption, capillary condensation of some phases, and selective production. Selective production and retention are in turn further complicated by the extreme capillary pressures that exist in the nanometer scale pores in these reservoirs that impacts the phase envelope(s) and hence PVT behavior of the fluids.

<sup>&</sup>lt;sup>7</sup> 'Liquid hydrocarbons' is used in reference to oil, natural gas liquids and condensate. Due to vagaries of how production is reported by industry it is not possible to separate natural gas liquids, condensate and oil

In order to establish the stratigraphic and aerial variation in the capillary pressures of the Montney Formation, we have performed MICP, wettability, interfacial and surface tensions on produced fluids and integrated our petrophysical data with the production histories of corresponding wells from key wells across the Montney subcrop (Figure 9.10). In this study, we have relied on analyses mainly carried out in our UBC laboratory. Although there is an enormous volume of third-party public data in the Montney well files available from the OGC and AGS, we have avoided using third-party analyses wherever possible unless the methods of analyses are fully described. In particular, much of the MICP data in the literature and public well files is not corrected for conformance and/or compressibility and permeability has been measured on unconfined, crushed samples and not at reservoir conditions.

In the following section, petrophysical analyses of a range of Montney producing wells from dry gas, wet gas, volatile oil, and black oil wells are presented and the results compared. The goal of this approach is to compare and contrast reservoir properties that contribute to reservoir performance.



# **Montney Well Location Map**

Figure 9.10 - Location of Montney wells described in this study, location of the Montney subcrop and main structural and tectonic elements.



Figure 9.11 - Variation in production of upper and lower Montney wells in the Septimus area. The wells are shown as examples only.



Figure 9.12 - Variation in production from the upper, middle, and lower Montney. The wells are show as examples only. The Montney Member picks are after Davies et al., (1998).

#### 9.4.2.1. Dry Gas Window

In the area of the north Montney, production is predominantly dry gas with little or no LHCs, which is consistent with the relatively high level of the thermal maturity and kerogen type of the strata.

In the Lily Lake area, operators have cored the entire Montney succession and have completed and produced the lower, middle, and upper Montney. In Figure 9.9 we plot the variation in porosity, pore size and mineralogy through the continuously cored Montney well from the 94-G-2 map sheet (Bustin, 2018). The mineralogy and petrophysical properties are relatively consistent through the entire interval (Figure 9.13, Figure 9.14). The mineralogy is mainly quartz, feldspar, illite (clay) and calcite and dolomite. Pyrite is a near ubiquitous minor mineral that occurs mainly in the range from 1 to 3%. Barite and ankerite occur rarely, and chlorite is present in minor amounts at depths below the base of the upper Montney<sup>8</sup>. The insitu (absolute) porosity varies from about 2% to 6% and from MICP the median pore size is less than 1 nm and averages about 6 nm and median pores size is about 10 nm (Figure 9.14). There are no consistent trends in the porosity or mineralogy through the sampled interval. The correlation between clay content (mainly illite) and the gamma ray is poor which reflects the heterogeneity of the mineralogy in the rock which is below the well log resolution.

There is a weak positive correlation between quartz and porosity ( $R^2$ =0.23; Figure 9.15). There is a similar correlation of porosity with orthoclase ( $R^2$ = 0.16) but a much weaker correlation with albite ( $R^2$ =0.1; not plotted). The weak albite correlation probably reflects the presence of authigenic (pore filling?) as well as detrital albite as described by Wust et al. (2018). At concentrations of calcite below about 15% there is a slight positive relationship, but high concentrations (limestones) have low porosity ( $\approx$ 2-3%). Overall, there is no correlation between dolomite and porosity — rocks rich in dolomite have both the highest and lower porosities in the data set.

#### 9.4.2.2. Capillary Pressures

In order to derive metrics for calculating the capillary pressures to the Montney fluids systems and lithologies, wettability was determined by measuring contact angles on representative samples and the surface and interfacial tensions was measured to the fluid. In Figure 9.16 the contact angles to produced Montney water, freshwater and slickwater completion fluids made with fresh and produced water and Montney produced oil are plotted vs depth. The contact angle measurements were performed at UBC by Lazaruk (2017) as part of an undergraduate honours thesis. Although there is considerable variability in the dataset there is an overall decrease in the contact angle for all fluids with depth. The decrease is most pronounced with the fresh and produced (connate) waters and least pronounced with Montney oil. In order to understand the origin of change in wettability with depth, the contacts angles are cross-plotted with mineralogy and TOC in Figure 9.17. The strongest correlation with wettability is the positive correlation with TOC content albeit the correlation is dominated by the three high TOC content samples.

<sup>&</sup>lt;sup>8</sup> The Montney Member picks are after Davies et al. 1998.

The correlation with mineralogy is very poor; however, there is a very weak negative trend with carbonate and very weak positive trend with quartz plus feldspar. It is assumed that the overall trend in wettability with depth reflects corresponds to lower TOC values. Organic matter is hydrophobic, so it has a marked impact on wettability to water. The TOC sample density is less than that of wettability which creates some ambiguity in correlating the TOC with depth.



Figure 9.13 - Variation in weight percent mineralogy by XRD through the Montney Formation.

The impact of the change wettability with depth in Figure 9.16 on capillary pressures to oil/brine, gas/brine and completion fluid brine systems are shown in Figure 9.18. The impact is largest for fresh water/gas at a wetting phase (water) saturation of 40%. There is 3000 psi (10.7 MPa) difference in capillary pressure due to change in wettability from 35 to 71° whereas the impact on oil capillary pressure is less than 100 psi (0.7 MPa).

#### 9.4.2.3. Production

There are ten producing wells on the Lily pad in the north Montney. The wells produce from the upper, middle, and lower Montney. The production history of representative wells — two upper, one

middle and one lower Montney well are show in Figure 9.19. The lower Montney wells had the highest initial production rates, followed by the middle Montney and upper Montney. The differences in production history between the wells cannot be commented on in detail without the knowledge of operational issues and details of the completion program. A minor amount of condensate was reported during the first few months of production for most wells, after which almost no condensate has been reported. The one exception is well 200D completed in the middle Montney which early 2018 to mid-2019 reported significant condensate production (Figure 9.19). Without knowledge of the well operations, drawing far-reaching conclusions based on this occurrence is not prudent. It is notable, and inexplicable that one in five wells in the middle Montney would experience a mid-life condensate production period when other wells, including wells higher and lower stratigraphically on the pad, report no or very little condensate.



Figure 9.14 - Variation in stressed and non-stressed permeability, compressibility of the rock and variation in average and median pore size through the Montney Formation.



Figure 9.15 - Variation in porosity with mineralogy from the 94-G-2 well.



Figure 9.16 - Wettability as measured by contact angles on samples through the Montney Formation. Using Montney connate water, fresh water and slickwater completion fluids with fresh and produced water bases and Montney-produced oil. Contact angles measured at UBC by K. Lazaruk as part of an undergraduate honours thesis (Lazaruk, 2017).



Figure 9.17 - Variation in wettability with TOC and mineralogy. Inset table provides the density and surface tension of the fluids and the interfacial tension between Montney-produced oil and Montney connate water.



Figure 9.18 - The impact on gas/water capillary pressure for the range of contact angles measured with depth in Figure 9.16 for the different fluids.



Figure 9.19 - Lily Pad wells, north Montney area. Note the condensate production in the 200D well.

## 9.4.2.4. Wet Gas in the Dry Gas Area

In the Monias and adjacent Groundbirch areas, the Montney Formation produces almost exclusively dry gas. The 13-35-81-21W6 well is an exception which has produced significant condensate since production commenced in 2016 and continues to produce about 50 m<sup>3</sup>/month of condensate. This well is thus of special interest in that it provides insights as to the controls on the distribution and production of LHCs.

The porosity, permeability, TOC content and mineralogy were analysed through the Montney succession (Figure 9.20; Table 9.1). In the limited data set, there is no correlation between petrophysical properties, mineralogy, or TOC content, nor any trends with depth. The pore throat diameter vs. porosity volume plots derived from MICP show a consistent trend with depth throughout the Montney Formation.

The producing wells (Figure 9.10) are completed in the upper Montney Formation. Based on the consistent lithology and petrophysical properties a second horizontal could be placed in the lower

Montney Formation. Dry Montney gas wells that are producing in the proximity of the 13-35 well have not been cored, so no comparisons can be drawn with adjacent producers based on detailed petrophysics.

Depth (m)	Ø %	K md	Mineralogy Wt. <del>%</del>							
			Quartz	Feldpar	Calcite	Dolomite	Apatitie	Illite	Pyrite	TOC
1911	2.26									
1912.8	2.91									
1917	5.47	2.95E-04	14.4	10.4	22	32.9	19	1.4		2.32
1922	5.28	5.08E-04	39.9	24.2	4.8	23.6		4.4	3	0.8
1928.5	5.05	2.04E-04	17.4	19.9	4.3	21.9		34	2.5	1.07
1935	5.02	2.35E-04	24	16.4	5.8	35.9		15.3	2.5	1.59
1942.8	3.73									
1946	3.79									
1952	5.26	1.86E-04	22.4	16.4	3.6	27.9		27.2	2.6	1.61
1962.3	5.09									
1968	4.29									
1974	5.11									
1978	6.05	3.01E-04	31.2	23.2	11.1	28.6		3.8	2	0.58
1982.5	4.59									
1994	4.99									
2001	4.80									
2014	4.92									
2023	3.80									
2037	4.10									
2051.8	5.31	4.07E-05	34.8	20.7	6.8	13.3		19.6	4.8	2.51
2060	3.70									
2069	5.51	5.54E-04	34.8	20.7	6.8	13.3		19.6	4.8	0.77
2085	3.28									
2116	3.07									

Table 9.1 - Mineralogy, porosity and permeability, Montney Formation, 13-35-81-21W5. Porosity and permeability values from public data (OGC) measured at overburden stress.



Figure 9.20 - Montney Formation, Monias. Pore size at P10, P50 and P90 in nanometers from MICP, porosity, confined permeability and reservoir stress, mineralogy, and TOC.



Figure 9.21 - Plots of pore throat diameter vs porosity volume derived from MICP with the P10, P50 and P90 pore size provided for sample of varying depth in metres. The graphs show how the sample void volume is distributed amongst pores of indicated size. Corresponding well log provided in Figure 9.20.



Figure 9.22 - The 13-35 well production history. The completed interval is shown on the well log in Figure 9.20.

#### 9.4.2.5. Wet Gas/Oil

In areas where the maturity transitions between wet gas and volatile oil, the Montney Formation produces variable amount of gas, condensate, volatile oil, and water. In the Karr strike area (Figure 9.10), coarser grained (proximal facies) of the upper Montney Formation occur. There is a distinct overall coarsening upward trend in lithology from the base to the top of Montney Formation that is evident on logs and core. The mineralogy is 30% to 50% quartz, 15% to 30% feldspar, 2% to 12% illite, and 20% to 50% dolomite. There is no consistent trend in mineralogy through the cored interval (Figure 9.23). Above about 2600 m the only apparent trend in mineralogy is an overall increase in quartz content that follows the declining gamma ray log towards the top of the Montney Formation. The porosity and permeability increase upward from about 2600 m (Figure 9.23). At the top of the analysed interval, the porosity approaches 10% and the corresponding permeability of 0.1 md. Although the dataset is limited, there is modest positive correlation between quartz content and porosity (R<sup>2</sup>= 0.6; Figure 9.24).



Figure 9.23 - Variation in porosity, permeability, and mineralogy through the cored interval.

#### Mineralogy vs Porosity



Figure 9.24 - Relationship between mineralogy and porosity. The trend line and correlation coefficient plotted is for quartz alone.

The capillary pressure curves show a marked change from the base to the top of the Montney Formation from poorly sorted fine pores to well sorted larger pores (Figure 9.25). The overall trend is thus of a significant increase in reservoir quality toward the top of the Montney Formation. The uppermost Montney has capillary pressures, permeability, and porosity values of a tight conventional reservoir whereas the middle and lower Montney Formation have reservoir properties of an unconventional reservoir.

The 12-29 well has not been produced. The closest Montney producing well (Figure 9.26) produced liquids with a high water cut and due to the high permeability at the top of the Montney. The 12-29 well would be anticipated to produce similarly to a conventional well and hence require a trap/seal to be productive. The 13-26-67-4W6 for example, produced with a water cut of over of 70% which has been a deterrent to further Montney development in this area. In contrast to the upper Montney Formation which has porosity and permeability high enough to require a trap/seal, the lower part of Montney has low porosity and permeability and remains a largely untested continuous unconventional reservoir that might be developable by suitably placed horizontally drilled and fraced wells.



Figure 9.25 - Gas-brine capillary pressure curves and corresponding saturation associated with the indicated pore throat size distribution.



Figure 9.26 - Production data for the 13-26 well. The well has produced significant condensate and gas but with an associated consistently high water cut ( $\approx$ 70%).

#### 9.4.2.6. Black Oil – Waskahigan

In the Waskahigan strike area, the Montney Formation is a hybrid reservoir inasmuch as there are zones of comparatively high permeability and porosity sands with variable oil saturation and an updip trap. Down-dip however, the permeability is low, and the reservoir is a continuous unconventional reservoir (Glemser et al., 2019). Within the upper Montney Formation in the Waskahigan area, reservoir facies with high oil saturation and porosity and permeability are locally interbedded with sandstones with a high-water saturation which creates challenges to exploration and development. Based on the Montney gas geochemistry (Figure 9.27) the associated gas is considered to have migrated updip along preferential permeable pathways (Glemser et al. 2019; Figure 9.28). The introduction of the migrating gas into the pooled oil resulted in de-asphalting which has led to solid bitumen precipitation and associated asphaltenes in solution in the oil.

The upper Montney Formation is currently being exploited by horizontal wells placed in the upper coarser grained facies. The stratigraphy comprises two or more coarsening upward cycles. The mineralogy (not plotted) shows minimal variation and is comprised of about 50% quartz, 20% feldspar, 10% to 30% iron rich dolomite to ankerite, less than 10% clay and 1% to 4% pyrite. At least some albite, quartz and dolomite is authigenic.



Ante Creek, Gold Creek, Kakwa, Elmworth Areas

Figure 9.27 - Gas composition plotted with the overlying Barnett Shale trend. Modified from Glemser et al. (2019).



Figure 9.28 - Presumed migration pathways of gas into the Ante Creek – Waskahigan pools based on gas iC4/nC4/methane ratios. Modified from Glemser et al. (2019).

#### 9.4.2.7. Porosity, Permeability and Capillary Pressure

The porosity, permeability and P10, P50 and P90 pore throat size from MICP show generally increasing upward cycles that generally follow the gamma and density log signature (Figure 9.29). There is a good correlation between porosity and log permeability particularly for the 13-23 well.

In the upper Montney Formation, subtle variations in grain size or abundance of more argillaceous or silty laminae have a marked impact on reservoir properties at a scale that is beyond the 15 cm resolution of most well logs. The variation in capillary pressure, porosity, and permeability at effective stress of 4800 psi (33 MPa) is shown together with photomicrographs of the rock fabric and mineralogy. The laminated, very fine-grained sandstone at depths of 2333.23 m and 2229.47 m have permeabilities of about 1E-3 md with about 7% porosity whereas the non-laminated, very fine-grained sandstones with similar mineralogy have twice the porosity (15.2%) and two orders of magnitude higher permeability (2E-1). The difference in pore throat size of samples through the cored interval is plotted in Figure 9.32 and the variation in permeability with stress in Figure 9.33.



Figure 9.29 - Variation in porosity, pore size (p10, p50 and p90 from MICP) and permeability in the upper Montney in the 103/13-23-63-24W5 well.



Figure 9.30 – Cross-plot of porosity and permeability. Colors correspond to different Waskahigan wells. The green dots are the 13-23 well data plotted in Figure 9.29.







Figure 9.31 - Upper Montney in Well 12-7-64-23W5 showing variation in lithology, mineralogy (XRD) and capillary pressure from MICP. Note the abundance of authigenic quartz and dolomites in the SEM images.



Figure 9.32 - Variation in pore throat distribution (cumulative and incremental from MICP) of samples for the 12-7 well.



Figure 9.33 - Variation in permeability with effectives stress following Dean Stark core plugs from the 12-7 well.

In order to calculate the in-situ capillary pressures with respect to the reservoir brine and oil, the wettability was measured by oil and water on a suite of samples from the 12-7 wells and the interfacial tension measured between oil and brine (Table 9.2). These data were used in conjunction with MICP to calculate the oil/brine interfacial tension and different degrees of saturation for two sandstones from the 12-7 well, one from 2231.75 m with 15.2% porosity and the other from 2224.5 m with 6.2% porosity. The differences in capillary pressure at all saturations are dramatic. At a brine saturation of 30%, the capillary entry pressure of the 15.2% samples is a less than 10 kPa and for the 6.2% porosity sample about 3.5 MPa (500 psi).

The Montney production from the Waskahegan and adjacent areas is highly variable reflecting the lateral changes in facies and hydrocarbon saturation. An example production plot from the 4-7-64-23W5 well (Figure 9.35) demonstrates the high water cuts that reflect the presence of wet porous and permeable sands within or adjacent to the completed interval. Inasmuch as it is difficult to predict the occurrence of, or isolate, the wet sandstone during completions, they create an ongoing challenge to development.

Table 9.2 - Upper - Interfacial tension between produced water and oil for various upper Montney. Waskahigan wells. Lower variation in contact angle of produced oil and produced water on samples from 12-7 well.

Interfacial Tension Produced Water with Oil							
Sample	Brine Density (g/cm3)	Mean (mN/m)					
102/11-15-64-23w5	1.09	16.20					
100/14-15-64-23w5	1.09	13.20					
2-23-64-23	1.09	12.25					
4-23-64-24	1.09	15.00					
4-23-64-24w5	1.08	12.60					

Well/Depth	Contact Angle°	Produced Oil		
12-7-64-23W5	Produced Water			
2231.75-2231.80	9 9	9		
2222.0-2222.05	8	8		
22224.50-2224.5	5 20	20		
22226.34-2226.3	9 11	11		
2228.47-2228.52	2 7	7		
2234.10-2234.15	5 8	8		



Figure 9.34 - Oil-Water capillary pressure vs saturation of the wetting phase (brine) and pressure translated to height above the free water level.



Figure 9.35 - Example of production profile of a Waskahigan well (4-7-64-23W4). The extreme water cuts are interpreted to reflect contribution from wet porous and permeable sands interbedded with sands with higher oil saturation.

#### 9.4.2.8. Conventional Gas – Kahntah

In the Chinchaga, Kahntah and Ring Border fields, the Montney Formation was developed as a conventional gas reservoir beginning in the late 1970s. The Ring Board field was the location of the first Montney gas production in British Columbia. The reservoir in these fields corresponds to the very fine-grained sandstone and siltstone facies of the upper Montney (Nassichuk, 2000). Data from the Kahntah field is included in this section because of the contrast it provides with respect to reservoir properties of the hybrid and unconventional reservoirs that are currently exploited. The detailed description of the lithofacies and corresponding reservoir facies are provided by Nassichuk (2000).

The stratigraphy of the upper Montney reservoir is an overall coarsening upward section (Figure 9.36). The upper coarser and cleaner sandstone unit comprises a conventional reservoir. The capillary pressure curves throughout the interval generally show well-sorted pores which are significantly larger than those described in the hybrid and unconventional reservoirs; overall capillary pressures for a given wetting phase saturation are an order(s) magnitude lower. A sampling of porosity values from core tests and permeability measured at reservoir stress (Figure 9.37) show porosity approaching 20%, mean pores sizes of 10,000 nm, and permeability up to 10 md. The P10, P50 and P90 pore (throat) sizes show weak positive trends with both porosity and permeability.

The production history of the B-74-D well (Figure 9.36) is provided here for contrast with the unconventional reservoirs. The well had high initial gas and water rates, both of which rapidly declined over about five years, attesting to compartmentalization of the reservoir due to the complex stratigraphy and associated reservoir facies.



Figure 9.36 - Montney Formation- conventional reservoir in Kahntah. Capillary pressure of gas-brine vs saturation of wetting phase, and porosity and permeability, production history and well log.





Figure 9.37 - Conventional Montney reservoir porosity and permeability vs the P10, P50 and P90 pore size diameter (pore throat) in nanometers.

## 9.4.3. Variability in Montney Reservoir Properties

The reservoir properties of the Montney Formation vary significantly, both regionally across an area of about 130,000 km square, and stratigraphically over a thickness that ranges up to 300 m. The lateral variability in the formation is a composite product of varying depositional facies, diagenesis, and burial, thermal, structural, deformation and tectonic history. The stratigraphic variation mainly reflects depositional environments through time which were in turn a response to regional and local tectonics, varying subsidence rates, varying sediment provenances (which contributed grains of varying mineralogy) and the subsequent overprint of diagenesis and deformation which did impact all facies equally. The wells and areas described in this study were selected for their contrasting reservoir properties and production in an attempt to document their diversity and commonalities. In this section we compare and contrast the reservoir properties.

#### 9.4.3.1. Porosity and Permeability

Porosity and permeability analyses of very low porosity and permeability rocks are challenging, and no standards have been adopted. The different major laboratories that perform commercial analyses for industry employ different methods of analyses including sample preparation. Since the porosity and permeability of the unconventional Montney Formation are very low, even small discrepancies in analytical methods translate to large percentage variations in the analytical data. In comparing the reservoir properties from different areas below it was necessary to use some publicly available analyses from the well log files of the OGC and AER and hence some of the variability in the datasets is undoubtably a product of the analytical methods employed.

The porosity and permeability from a suite of samples from the studied wells or adjacent wells are cross-plotted in Figure 9.38. The overall trend of permeability with declining porosity is similar between conventional Montney reservoirs (Chinchaga, Kahntah and Ring Border) through to unconventional reservoirs on a log permeability vs porosity plot. The cluster of low permeability green dots on Figure 9.37 are from the Doig Formation and the red dots which form an offset trend (lower right) are from the Waskahegan area. The trends are parallel but offset which we attribute to different mineralogy and/or fabric of the Doig Formation (measured at UBC). The increase in scatter in permeability for a given porosity in Figure 9.38 is apparent; a manifestation of permeability being plotted on a log scale (as usual for such plots). In terms of absolute permeability, the variation of permeability is greater at higher porosity. For most data in our study there is a well-developed trend of the log P50 pore diameter and porosity (Figure 9.39) and log P50 pore diameter and log permeability (Figure 9.40).

Samples of the relationship between permeability and effective stress for the sample suite are plotted in Figure 9.41 and Figure 9.42. Permeability measured parallel (Figure 9.41) and perpendicular (Figure 9.42) to bedding vary between one and two orders of magnitude with increasing effective stress. In terms of absolute permeability, the change with stress is much greater with stress for high permeability rocks. However, as a percentage of the existing permeability, the impact of stress is much greater on low permeability rocks. Hence higher stresses at greater depth or changing stress due to pore pressure reduction during production, have a greater proportional impact on production from low permeability
reservoirs. Three examples where permeability was measured on plugs cut parallel and perpendicular to bedding (Figure 9.43) show that permeability normal to bedding is one to two orders of magnitude less than parallel to bedding which is generally the case for laminated low permeability Montney and Doig strata.



Figure 9.38 - Absolute porosity versus permeability of samples from the Montney and Doig formations. Only confined permeability data is shown, which has been normalized to an effective stress of 33 MPa (4800 psi) where possible. The colours correspond to different wells. The low porosity green dots are from the Doig Formation in the Graham strike area.



Figure 9.39 - The variation of P50 pore throat diameter, in nanometers, from MICP with porosity.



Figure 9.40 - Variation in permeability with P50 pore throat diameter in nanometers from MCIP. Permeability measured at effective stress of 33 MPa (4800 psia).



Figure 9.41 - Variation in permeability parallel to bedding with effectives stress of Montney well samples. Examples from wells of this study.



Figure 9.42 - Variation in permeability parallel and perpendicular to bedding with varying effectives stress. Examples from Montney wells of this study.

#### 9.4.3.2. Capillary Pressure

The importance of capillary pressure and in particular the ratio of viscous forces to capillary pressure (the capillary number) and gravity force to capillary pressure (the Bond number) are well documented in conventional reservoirs (i.e., Vizika and Kalaydjian, 2003). Unconventional reservoirs are fundamentally reservoirs in which capillary pressures dominate over viscous and gravitational forces.

In this study, capillary pressures were determined to mercury, by mercury injection porosimetry and the pressure recalculated to fluids of interest based on measurement of the wettability (contact angle) and surface tension or interfacial tension between the fluids of interest. As we have shown for the north Montney, through high density sampling of the entire formation there is considerable variation in wettability through the Montney Formation that has significant impact on the reservoir capillary pressure. There is also considerable variability in the interfacial tension between reservoir brine (and completion fluid) and Montney NGLs and oil which impacts capillary pressure. Although variation in pore throat radius is the dominant factor controlling capillary pressure in the Montney Formation as shown earlier, both wettability and interfacial tension must be considered in any quantitative study. In some mudstones and, particular in the kerogen fraction, the pores are too small (<3 nm) to be accessed by mercury during MICP analyses hence does not capture the entire porosity of a mudstone. However, our data shows that when the total porosity, determined by helium pycnometry, is compared to porosity from MICP, it is apparent in all but the most unusual mudstones, that the majority of the porosity is accessed by mercury.

The capillary pressures of conventional versus unconventional reservoir facies are readily differentiated by MICP. The best reservoirs with the highest permeability and porosity are those with well-sorted large pore throats. The upper Montney Formation reservoir at Kahntah has very low entry pressures, but since equipped with a seal and trap, it was a successful conventional reservoir (Figure 9.43). At Karr, where the upper Montney also has low capillary pressures but in the absence of a seal and/or trap, it is anticipated that the reservoir would have a high water saturation (wet).

The sorting of the pore throats, which is manifested in the shape of the capillary pressure curve, is an important metric but cannot be considered independent of the pore throat size in evaluating reservoir quality. In Figure 9.44, the gas-water and oil-water capillary pressures required to displace 50% of the wetting phase (i.e., Sw= 0.5) are cross-plotted with the corresponding smallest pore throat size accessed at 50% saturation. For each MICP analyses and from the capillary pressure curve, two data points were obtained and are plotted in Figure 9.44 at the same pore size. One of these data points represents the pressure for gas-water (circle) system and the other for oil-water (square). The plot shows that as the smallest pore size accessed at 50% saturation approaches 10 nm, the pressure begins to increase towards an asymptote.



Figure 9.43 - Comparison of gas-brine capillary pressures in the upper most Montney facies at wells at Kahntah (left) and Karr (right). The dashed curves are from Kahntah and solid curves are from Karr.



Figure 9.44 - Gas-water and Oil-water capillary pressure at 50% saturation of the wetting phase and the corresponding pore throat size. Colors represent samples from the same area. For one MICP test there are two pressures plotted for the same pore throat size. The lower pressure (a square) is oil-water, and the higher pressure (a circle) is gas-water.

#### 9.4.3.3. Other Considerations

The capillary pressures, porosity, permeability, and fluid saturations cannot be considered in isolation of the stratigraphy and structure in categorising a reservoir. The entire Montney Formation, for example at Lily Lake, can be categorised as an unconventional reservoir and is being developed as such. Although there may be lower capillary pressure reservoir facies in the succession, they would be fully encapsulated in an over-pressured gas charged sandwich and as such it is a continuous self-sourced and sealed reservoir. If this would not be the case, the over-pressures could not be sustained at a geological time scale. At the opposite extreme is the upper Montney interval at Kahntah which is a conventional reservoir. At Kahntah, the capillary pressure is too low to self-seal the hydrocarbons in place and the hydrocarbons undoubtedly migrated into the reservoir and were sealed by a high capillary pressure facies. Hence a sealing unit with high capillary pressure is required to prevent gravitational and/or viscous forces from dispersing the hydrocarbons.

The Karr example presented in this study is an example in which the middle and lower Montney Formation have capillary pressures that would self-seal the generated hydrocarbons. The upper Montney Formation that has been completed is a tight sand compared to the Kahntah Montney, but the capillary pressures are still too low to self-seal the reservoir such that any generated hydrocarbons should not be anticipated unless an independent seal/trap exists. Hence, at this location in Karr, a continuous upper Montney resource play may not exist, whereas there may be, counter-intuitively, a better target in the high capillary pressure rocks in the middle and lower Montney, which is a more likely a candidate as continuous unconventional reservoir due to high capillary pressures.

The Waskahigan upper Montney Formation is being developed as a conventional tight oil play. This area has some sandstones with a high water saturation and is responsible for the higher water cuts, whereas other sandstones have significant oil saturation which likely reflect the lateral continuity of various stratigraphic units. The oil in these sands may have migrated up dip to their current position and were entrapped by a capillary pressure barrier (facies change or structure). The gas compositions suggest a later post-oil gas migration event. Whether or not lower intervals in the Montney Formation have resource potential is unknown.

### 9.5. Discussion and Conclusions

#### 9.5.1. Doig Formation

Reservoir properties in the Doig Formation are controlled by a complex interplay between depositional environment, diagenesis, and mechanical compaction. The depositional environment had a major influence in determining the large-scale distribution of quartz, clay, apatite and to a lesser extent calcite. Due to their relatively coarser grain size, low clay content and greater degree of sorting, quartz-rich siltstones and phosphatic grainstones tend to be macroporous to coarse mesoporous and correspond to the highest permeabilities found in the Doig Formation. The amount of clay, which is controlled by the

depositional environment, has only a slight detrimental effect to total porosity. Due to bound water, particle shape and size however, the presence of clay significantly reduces effective porosity and the pore throat sizes, which limits the pore space available for hydrocarbons and lowers the permeability.

The primary intergranular porosity of quartz-rich siltstones is often enhanced by grain dissolution, which has been noted by Harris and Bustin (2000) as an important factor in reservoir quality. Secondary porosity created by early grain dissolution in the diagenetic sequence, was later occluded by yet later dolomite cementation, according to Martin (2008). Most of the quartz-rich siltstones were only partially cemented by dolomite and preserved significant macro and mesoporosity. Another type of secondary porosity is related to partial or complete dissolution of calcitic and phosphatic skeletal grains in bio-packstones and bio-wackestones. This moldic porosity occurs mostly in the DPZ and is responsible for poorly-connected macropores. Calcite occurs as skeletal fragments, within rare veins and most frequently as pore-filling cement, precipitated in multiple phases through a complex diagenetic history as also noted by Martin (2008). As such, calcite is responsible for occluding pore space, reducing pore throat sizes and permeability. In the DPZ however, phosphorites containing significant quantities of calcite were able to retain macropores and thus, high permeabilities.

Compaction by grain rearrangement and pressure solution, imposes a dominant control on porosity, with an observable trend of porosity reduction from the shallow northeastern edge towards the deeper southwest, despite local variations caused by depositional and diagenetic influences discussed above (Silva, 2021). The compaction influence in porosity reduction is also seen by the negative correlations of porosity to thermal maturity and pore throat sizes (Figures 9.5, 9.6). The compaction trend affects matrix permeability across the basin, due to the compounding effect of pore throat size and porosity reduction. In the DPZ, the trend in porosity reduction with depth is reversed from the basin centre towards the western edge, which is likely related to phosphorite facies and preservation of their high intergranular porosity due to early calcite cementation and subsequent partial cement dissolution.

Permeability in the Doig Formation is extremely variable, and primarily controlled by pore throat size and porosity, and subordinately by quartz and clay volumes. The relatively coarse quartz-rich siltstones have the highest permeabilities, occasionally in the millidarcy range when enhanced by grain dissolution. Clay and TOC contents have a detrimental effect on permeability due to their influence in inhibiting advective flow, although the correlation of permeability with clay and TOC contents shows significant scatter. In this study area, the relationship between carbonate and permeability in the Doig Formation is obscured by dolomitisation, which is often associated with grain dissolution, and high permeability phosphorites with relatively high calcite content.

Mineralogy exerts a strong control on permeability reduction with stress and vertical to horizontal permeability anisotropy. Among the reservoir facies studied, quartz-rich siltstone is the facies that has the least anisotropic permeability and the least stress dependent permeability, due to its isotropic and rigid fabric. Lower permeabilities in the deepest and most compacted areas of the basin may have contributed to the development of overpressure due to the low rates of advection and diffusion of generated hydrocarbons.

#### 9.5.2. Montney Formation

The stratigraphy and sedimentology of the Montney Formation has been exhaustively studied befitting the reservoir's role as the main gas producing unit in Canada. Hydrocarbon liquid production at a large scale mimics the distribution of the current Montney oil window as mapped by thermal maturity. Where the Montney Formation is being developed as an unconventional continuous resource, the LHCs are considered self-sourced or have undergone short distances of migration and the reservoir is self-sealing and trapping due to the high capillary pressures. If the reservoir was not self-sealing, the pervasive areas of over-pressuring could not be sustained at geological times scales. Superimposed on the regional distribution of LHC, there are isolated areas where wells produce variable amounts of LHCs whereas as other surrounding wells do not. In some areas, LHCs and gases are vertically stratified contrary to that anticipated based on hydrocarbon density and gravity which creates unique challenges in optimizing completions and production. The reason for LHCs production in isolated wells, in areas where surrounding wells produce dry gas, remains inexplicable and invoking faulting and migration would require migration against the anticipated pressure gradient.

Correlating production performance with petrophysical measurements has proven difficult due to varying drilling and completion strategies on a well-to-well basis. In most areas, the variability between wells is significant and the variation between wells completed in one member of the Montney Formation is greater than the differences between members in the same well. Even wells completed in the same zone (member) on the same pad by the same operator and with the same completion program are invariably found on detailed examination to have significant differences in drilling and completion. The impact of such differences is difficult to isolate from variations in reservoir properties or fluid saturations.

Capillary pressures from MICP were recalculated to that of the produced fluids utilising measurement of the wettability (contact angle) and surface tension or interfacial tension between the fluids of interest and representative reservoir facies. High frequency wettability analyses of a continuous core through the entire Montney interval in the North Montney show an overall decrease in the contact angle of freshwater, completion fluid and Montney oil with depth. The trend in wettability is strongly correlated with the TOC content of the strata. There is also considerable variability in the interfacial tension between reservoir brine (and completion fluid) and Montney NGLs and oil. Variation in pore throat radius is the dominant factor controlling capillary pressure in the Montney Formation but both wettability and interfacial tension impacts capillary pressure and must be considered in any quantitative analyses of entry pressures or migration.

The capillary pressures of conventional versus unconventional reservoir facies are readily differentiated by capillary pressure. The upper Montney conventional reservoir at Kahntah has very low entry pressures and required a trap and seal to retain hydrocarbons. The entire Montney Formation is in many areas considered a lateral continuous unconventional reservoir even though the upper most Montney Formation is the preferred drilling and completion target. The Karr example presented in this study is an example in which the middle and lower Montney have capillary pressures that would self-seal the generated hydrocarbons whereas the upper Montney is a tight sandstone and capillary pressures are too low to self-seal the reservoir. The Waskahigan upper Montney Formation is being developed as a

conventional tight oil play and there is evidence for late-stage phase of gas migration into the oil resulting in de-asphalting of the oil. This has resulted in solid bitumen precipitation and asphaltenes being suspended in the oil.

## 10. Conclusions and Recommendations

In this study we have developed workflows that illustrate the complexity of the Montney-Doig petroleum system and the likely causes of the changes in the distribution of hydrocarbon composition and H<sub>2</sub>S. The hydrocarbon composition is complex due to first, second, and third-order variation across the basins. First-order variation is due to the basin-scaled maturation trends across the WCSB and the second- and third-order variations are due to regional structural changes, structural elements and coarser lithologies acting as conduits, changes in TOC content and types, heat flow fluctuations, and variations in depth and duration of burial. Basin modelling, coupled with mapping of organic maturation, reservoir thickness mapping, organic matter typing, hydrocarbon compositional mapping, hydrocarbon isomer ratio mapping and excess methane mapping provide workflow templates for operators to determine secondand third order-variations seen within their play areas, and this will aid the development of a customised geological model to predict hydrocarbon compositional changes for their development strategy. Chapter 5 illustrates the successful use of sulphur isotopic, SEM-EDX and XRD analyses to determine that the sulphur source is Triassic strata, with the Charlie Lake Formation the most likely candidate. The sulphate is most likely migrated from the Charlie Lake Formation through conduits (fractures/faults) and deposited as anhydrite within the Montney Formation, similar to what is seen in the Halfway and Doig formations. This migration created discrete lateral sulphate-rich zones (i.e., with fractured zones) that, when in contact with hydrocarbons, generated H<sub>2</sub>S; the gas has strong sorption affinity and once formed in-situ will bind to the organic matter surface and not migrate. This model of sulphate migration through fractures fits the observation of laterally discrete zones of H<sub>2</sub>S gas which results in both sweet and sour wells producing on the same multi-well pad. The sulphur analyses also revealed several wells with heavier isotopic signatures compared to the rest of the sample suite, which may indicate the sulphate has been sourced from deeper strata. Researchers have shown the deeper strata (Mississippian and Devonian rocks) have a heavier sulphur isotopic signature than sulphur from Triassic rocks. Operators should develop their own H<sub>2</sub>S concentration and sulphur isotope maps together with maps of the Charlie Lake Formation distribution, sulphate-ion concentration in Montney pore water and structural elements derived from three-dimensional seismic data. Due to propriety reasons, we could not use seismic data in this project and seismic data purveyors should consider release of seismic data to the science community if these complex systems are to be better understood.

Recommendations from this project include:

- Carbon isotopic analyses of hydrocarbons in areas of changing hydrocarbon composition to determine secondary cracking and fractionation rates from migration of deeper, more mature gases
- Carbon isotopic analyses of CO<sub>2</sub> gases coupled with carbon isotopic analyses of kerogen, limestone, and other carbon sources to create a geological model for CO<sub>2</sub> generation within the Montney Formation
- The public release of three-dimensional seismic data to the science community to provide more robust structural mapping to help determine changes in hydrocarbon composition and H<sub>2</sub>S concentration
- In-situ laser ablation to determine the sulphur isotopic signature of anhydrite in British Columbian Montney producing wells to help determine the sulphur isotopic signatures within areas that have heavier sulphur isotopic signatures near the deformation front, and determine the sources of sulphur (shallow versus deeper sulphur-rich strata)
- Run SEM-EDX on Montney Formation core to determine the relationship between anhydrite and surrounding minerals (i.e., fracture fill, in-situ deposition)
- Continued collection of anhydrite samples, connate water, and H<sub>2</sub>S gas as additional souring Montney wells are observed across the British Columbia play area to confirm that Triassic sulphate is the major source and cause of souring

## 11. References

Adams. M., 2016. A Progress Energy Montney case study in risk identification grouping and mitigation. *In: Geoconvention, 2016, Optimizing Resources*. Calgary, Alberta.

Agilent, 2011. Hydrocarbons C3–C32 thermal desorption of rock samples: Agilent TechnologiesApplicationNoteEnergyandFuels.Retrievedfromhttp://www.chem.agilent.com/Library/applications/A00059.pdf,accessed on Dec 2nd, 2021.

AGS (Alberta Geological Survey), 2012. Adsorption isotherm analyses of Alberta geological units for shale- and siltstone-hosted hydrocarbon evaluation (tabular data, tab-delimited format to accompany Open File Report 2012-06): Edmonton, Alberta, Alberta Geological Survey.

Allen, P.A., and Allen, J.R., 1990. *Basin Analysis: Principles and Applications*: Malden, Massachusetts, Blackwell Scientific Publications, 451 pp.

Algeo, T.J., Luo, G.M., Song, H.Y., Lyons, T.W., and Canfield, D.E., 2015. Reconstruction of secular variation in seawater sulfate concentrations. Biogeosciences, 12, p.2131–2151. doi: 10.5194/bg-12-2131-2015.

American Petroleum Institute, 1998. Recommended Practices for Core Analysis RP 40, 2nd ed.: Washington, D.C., American Petroleum Institute, 236 pp. doi:10.1108/eb054465.

Bachu, S., and Cao, S., 1992. Present and past geothermal regimes and source rock maturation, Peace River Arch Area, Canada. *AAPG Bulletin*, 76(10), p.1533–1549. doi:10.1306/BDFF8A38-1718-11D7-8645000102C1865D.

Balashov, V.N., Engelder, T., Gu, X., Fantle, M.S., and Brantley, S.L., 2015. A model describing flowback chemistry changes with time after Marcellus Shale hydraulic fracturing. *AAPG Bulletin*, 99(1), p.143-154. doi: 10.1306/06041413119.

Barbot, E., Vidic, N.S., Gregory K.B., and Vidic, R.D., 2013. Spatial and temporal correlation of water quality parameters of produced waters from Devonian-age shale following hydraulic Fracturing. *Environmental Science & Technology*, 47, p.2562-2569. doi: 10.1021/es304638h.

Barclay, J.E., Krause, F.F., Campbell, R.I., and Utting, J., 1990. Dynamic casting of the Dawson Creek Graben Complex: Carboniferous-Permian Peace River Embayment, western Canada. *Bulletin of Canadian Petroleum Geology*, 38(A), p.115–145. doi:10.35767/gscpgbull.38a.1.115.

BC Government (Government of British Columbia), 2005. Environmental Management Act: Oil andGasWasteRegulation.Retrievedfromhttps://www.bclaws.gov.bc.ca/civix/document/id/complete/statreg/32\_254\_2005, accessed on Dec13th, 2020.

BC Government (Government of British Columbia), 2016. Fact Sheet 1: The Northeast Air Quality Monitoring Project. Retrieved from http://farmersadvocate.ca/wp-content/uploads/2016/06/pog-factsheets.pdf, accessed on Dec 13th, 2020.

BC Oil and Gas Commission (BC OGC), 2008. Hydrocarbon and by-product reserves in British Columbia: Victoria, British Columbia, Oil and Gas Commission, 31pp.

BC Oil and Gas Commission (BC OGC), 2012. *Montney Formation Play Atlas NEBC*. Victoria, British Columbia, Oil and Gas Commission, 35 pp.

Bearinger, D., 2013. Message in a bottle. SPE 168891/URTeC 1618676. *In: Unconventional Resources Technology Conference*. Denver, Colorado. doi: 10.1190/urtec2013-148.

Berger, Z., Boast, M., and Mushayandebvu, M., 2008. The contribution of integrated HRAM studies to exploration and exploitation of unconventional plays in North America. Part 1: The Peace River Arch. *Reservoir*, 35(10), p.42–47.

Berger, Z., Boast, M., and Mushayandebvu, M., 2009. The contribution of integrated HRAM studies to exploration and exploitation of unconventional plays in North America. Part 2: Basement structures control on the development of the Peace River Arch's Montney/Doig resource plays. *Reservoir*, 36(2), p.40–45.

Bernasconi, S.M., Meier, I., Wohlwend, S., Brack, P., Hochuli, P.A., Bläsi, H., Wortmann, U.G., and Ramseyer, K., 2017. An evaporite-based high-resolution sulfur isotope record of Late Permian and Triassic seawater sulfate. *Geochimica et Cosmochimica Acta*, 204(1), pp.331-349. doi: 10.1016/j.gca.2017.01.047.

Blauch, M.E., Myers, R.R., Moore, T.R., Lipinski, B.A., and Houston, N.A., 2009. Marcellus Shale postfrac flowback waters – Where is all the salt coming from and what are the implications? SPE 125740. *In: SPE Eastern Regional Meeting*. Charleston, West Virginia. doi: 10.2118/125740-ms.

Blount, C.W., 1977. Barite solubilities and thermodynamic quantities up to 300°C and 1400 bars. American Mineralogist, 62, p. 942-957.

Boschetti, T., Cortecci G., Toscani, L., and Iacumin, P., 2011. Sulfur and oxygen isotope compositions of Upper Triassic sulfates from northern Apennines (Italy): paleogeographic and hydrogeochemical implications. *Geologica Acta*, 9, p.129-147.

Brace, W.F., Walsh, J.B., and Frangos, W.T., 1968. Permeability of granite under high pressure. *Journal of Geophysical Research*, 73(6), p.2225–2236. doi: http://dx.doi.org/10.1029/JB073i006p02225; doi:10.

Brack, L., Abbott, G.M., Noble, I.A., and Tang, C.W., 1987. Triassic/Jurassic fields. *In:* Anderson, N.L., Hills, L.V., and Cederwall, D.A., (eds.) *Geophysical Atlas of Western Canadian Hydrocarbon Pools*. Calgary, Alberta, Canadian Society of Exploration Geophysicists and Canadian Society of Petroleum Geologists, pp.187–215.

Bourbie, T., and Walls, J., 1982. Pulse decay permeability: Analytical solution and experimental test. *Society of Petroleum Engineers Journal Forum*, 22(5), p.719–721. doi:10.2118/9744-pa.

Burke, L.H., and Nevison, G.W., 2011. Improved hydraulic fracturing with energised fluids: a Montney example. *In: CSPG CSEG CWLS 2011 Convention*. Calgary, Alberta.

Bustin, R.M., 2002. Research activities on carbon dioxide, hydrogen sulphide and sulphur dioxide sequestration. *In: First International Forum on Geological Sequestration of Carbon Dioxide in Deep, Unmineable Coal seams (Coal-Seq I)*. Houston, Texas.

Bustin, R.M., 2001, Hydrogen sulphide sorption on coals: implications for sequestration of acid gas, in-situ sweetening of sour gas and co-production of methane. *In: Coalbed Methane Symposium Proceedings*, Tuscaloosa, Alabama.

Bustin, R.M., 2000 Hydrogen sulphide sorption on coal with comparison to methane, carbon dioxide, nitrogen and hydrogen sorption: Implications for acid gas sequestering and co-production of methane. *In: The Society of Organic Petrology Annual Meeting.* Bloomington, Indiana. p.15.

Bustin, R.M., and Bustin, A.M.M., 2016. Potential for natural-gas liquid from western Canadian shales: regional variation in thermal maturity and gas composition, northeastern British Columbia. *Geoscience BC Summary of Activities*, p.49–54.

Bustin, R.M., and Clarkson, C.R., 1998 Geological controls on coalbed methane reservoir capacity and gas content. *International Journal of Coal Geology*, 38, pp.3-26.

Carmody, R.W., Plummer, L.N., Busenberg, E., and Coplen, T.B., 2009. *Methods of collection of dissolved sulphate and sulphide and analysis of their sulphur isotopic composition: Open-file report 97-234:* Reston, Virginia, United States Geological Survey, 91 pp. doi: 10.3133/ofr97234.

Carpenter, A.B., 1978. Origin and chemical evolution of brines in sedimentary basins: SPE 7504. *In:* 53<sup>rd</sup> Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers. Houston, Texas, doi: 10.2523/7504-ms.

Carpenter, A.B., and Trout, M.A., 1978. Geochemistry of bromide-rich brines of the Dead Sea and Southern Arkansas. *Oklahoma Geological Survey Circular*, 79, p.78-88.

Carpentier, B., Huc, A.Y., and Bessereau, G., 1991. Wireline logging and source rocks - Estimation of organic carbon content by the CARBOLOG method. *The Log Analyst*, 32(3), p.279–297.

Chafin, D.T., 1994. Sources and migration pathways of natural gas in near-surface ground water beneath the Animas River Valley, Colorado and New Mexico. Open-file report 9-4006: Denver, Colorado, United States Geological Survey, 56 pp. doi: 10.3133/wri944006.

Chalmers, G.R.L., 2016. Souring of Kaybob Duvernay wells: Investigation of hydraulic fracturing barrier effectiveness, completions design and pre-Duvernay structural features. AAPG Search & Discovery, Article #10864.

Chalmers, G.R.L., and Bustin, R.M., 2012. Geological evaluation of Halfway-Doig-Montney hybrid gas shale-tight gas reservoir, northeastern British Columbia. Marine and Petroleum Geology, 38, p.53-72. doi: 10.1016/j.marpetgeo.2012.08.004.

Chalmers, G.R.L., Bustin, R.M. and Bustin, A.A. (2019): Stratigraphic and lateral distribution of hydrogen sulphide within the Triassic Montney Formation, northern regional play area, northeastern British Columbia and northwestern Alberta; in Geoscience BC Summary of Activities 2018: Energy and Water, Geoscience BC, Report 2019-2, p. 43–46.

Chapman, E.C., Capo, R.C., Stewart, B.W., Kirby, C.S., Hammack, R.W., Schroeder, K.T., and Edenborn, H.M., 2012. Geochemical and strontium isotope characterization of produced water from Marcellus Shale natural gas extraction. Environmental Science & Technology, 46, p.3545-3553. doi: 10.1021/es204005g.

Chayes, F., 1960. On correlation between variables of constant sum. *Journal of Geophyical Research*, 65, pp.4185–4193.

Claypool, G., Holser, W., Kaplan, I., Sakai, H., and Zak, I., 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology*, 28, 199-260.

Comisky, J.T., Santiago, M., McCollom, B., Buddhala, A., and Newsham, K.E., 2011. Sample size effects on the application of mercury injection capillary pressure for determining the storage capacity of tight gas and oil shales. *In: Canadian Unconventional Resources Conference*. Calgary, Alberta. doi:10.2118/149432-MS.

Compton, A., Bincaz, I., and Bermel, C., 2017. Comparative H<sub>2</sub>S economics for shale gas. Retrieved from www.merichem.com/index.php?option=com\_content&view=article&id=312:comparative-h2s-economics-shale-gas&catid=29:technical-papers&Itemid=101, accessed on Nov 2<sup>nd</sup>, 2017.

Connolly, C.A., Walter, L.M., Baadsgaard, H., and Longstaffe, F.J., 1990. Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. *Applied Geochemistry*, 5, p.375-395. doi: 10.1016/0883-2927(90)90016-X.

Crisp, P.T., Ellis, J., De Leeuw, H.W. and Schenck, P.A., 1986. Flash thermal desorption as an alterative to solvent extraction for the determination of C8-C35 hydrocarbons in oil shales. *Analytical Chemistry*, 58, p.258-261.

Crombez, V., Rohais, S., Baudin, F., Euzen, T., and Petrovic, M., 2014. Organic content variations and links to sequence stratigraphy in the Montney and Doig formations (Alberta/British Columbia). *In: Geoconvention 2014: FOCUS*. Calgary, Alberta.

Crombez, V., Baudin, F., Rohais, S., Riquier, L., Euzen, T., Pauthier, S., Ducros, M., Caron, B., and Vaisblat, N., 2017. 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. *Marine and Petroleum Geology*, 83, p.382–401. doi: 10.1016/j.marpetgeo.2016.10.013.

Cui, X., Bustin, R.M., and Laxminarayana, C., 2007, Adsorption-induced coal swelling and stress: Implications for methane production and acid gas sequestration into coal seams. *Journal of Geophysical Research*, 112. doi: 10.1029/2004JB003482.

Cui, X., Bustin, A.M.M., and Bustin, R.M., 2009. Measurements of gas permeability and diffusivity of tight reservoir rocks: Different approaches and their applications. *Geofluids*, 9, p.208–223. doi: 10.1111/j.1468-8123.2009.00244.x.

Cui, X., Nassichuk, B., 2018. Permeability of the Montney Formation in the Western Canada Sedimentary Basin: Insights from different laboratory measurements. *Bulletin of Canadian Petroleum Geology*, 66(2), p.394–424.

Davies, G., 1997. The Triassic of the Western Canada Sedimentary Basin: Tectonic and stratigraphic framework, paleogeography, paleoclimate and biota. *Bulletin of Canadian Petroleum Geology*, 45, p.434-460. doi: 10.35767/gscpgbull.45.4.434.

Davies, G.R., Moslow, T.F., and Sherwin, M.D., 1997. The Lower Triassic Montney Formation, westcentral Alberta. *Bulletin of Canadian Petroleum Geology*, 45, p.474-505.

Dehghanpour, H., Lan, Q., Saeed, Y., Fei, H., and Qi, Z., 2013. Spontaneous imbibition of brine and oil in gas shales: effect of water adsorption and resulting microfractures. *Energy Fuels*, 27, p.3039-3049. doi: 10.1021/ef4002814.

Desrocher, S., 1997. Isotopic and compositional characterization of natural gases in the Lower and Middle Triassic Montney, Halfway, and Doig formations, Alberta Basin. M.Sc. Dissertation, University of Calgary, 218 pp.

Desrocher, S., Hutcheon, I., Kirste, D., and Henderson, C.M., 2004. Constraints on the generation of  $H_2S$  and  $CO_2$  in the subsurface Triassic, Alberta Basin, Canada. *Chemical Geology*, 204, p.237-254. doi: 10.1016/j.chemgeo.2003.11.012.

Dicker, A.I., and Smits, R.M., 1988. A practical approach for determining permeability from laboratory pressure-pulse decay measurements. *In: SPE International Meeting on Petroleum Engineering*. Tianjin, China, p.285–292. doi: 10.1016/j.tem.2010.02.006.

Dixon, J., 2008. Stratigraphic relationships of the Triassic Halfway Formation in the Western Canada Sedimentary Basin. *Bulletin of Canadian Petroleum Geology*, 56, pp.62-68.

Dixon, J., 2009. Triassic stratigraphy in the subsurface of the plains area of Dawson Creek (94A) and Charlie Lake (94A) map areas, northeast British Columbia. *Bulletin of the Geological Survey of Canada*, 595, 78 pp. doi: 10.4095/226367.

Dixon, J., 2000. Regional lithostratigraphic units in the Triassic Montney Formation of western Canada. *Bulletin of Canadian Petroleum Geology*, 48, p.80–83.

Do, N.T., Yoshimura, Y., Harada, M., and Hiramatsu, K., 2015. Generation of hydrogen sulphide in the deepest part of the reservoir under anoxic water conditions. *Paddy and Water Environment*, 13(1), p.101-113. doi: 10.1007/s10333-013-0412-0.

Dow, W.G., 1977. Kerogen studies and geological interpretations. *Journal of Geochemical Exploration*, 7, p.79–99. doi:10.1016/0375-6742(77)90078-4.

Dresel, P.E., and Rose, A.W., 2010. *Chemistry and origin of oil and gas well brines in western Pennsylvania: Open-File Report OFOG 10-01.0:* Pennsylvania Geological Survey, 48 pp. doi: 10.3996/052013-JFWM-033.S11.

DuBois, P.F., Rogers, J.B., and Lamond, R.E., 2014. Correlation of high hydrogen sulphide concentration to deep features in Eagle Ford Shale Wells, McMullen County, Texas: Paper SPE-171624-MS. *In: SPE/CSUR Unconventional Resources Conference*. Calgary, Alberta. doi: 10.2118/171624-MS.

Eaton, D.W., Ross, G.M., and Hope, J., 1999. The rise and fall of a cratonic arch: A regional seismic perspective on the Peace River Arch, Alberta. *Bulletin of Canadian Petroleum Geology*, 47(4), p.346–361. doi: 10.35767/gscpgbull.47.4.346.

Edwards, D.E., Barclay, J.E., Gibson, D.W., Kvill, G.E., and Halton, E., 1994. Triassic strata of the Western Canada Sedimentary Basin. *In:* Mossop, G.D., and Shetsen, I., (eds.) *Geological Atlas of the Western Canada Sedimentary Basin*. Calgary, Alberta, Canadian Society of Petroleum Geologists and the Alberta Research Council, pp.259–275.

Engelder, T., Cathles, L.M., and Bryndzia, L.T., 2014. The fate of residual treatment water in gas shale. *Journal of Unconventional Oil and Gas Resources*, 7, p.33-48. doi: 10.1016/j.juogr.2014.03.002.

Engle, M.A., Reyes, F.R., Varonka, M.S., Orem, W.H., Ma, L., Ianno, A.J., Schell, T.M., Xu, P., and Carroll, K.C., 2016. Geochemistry of formation waters from the Wolfcamp and "Cline" shales: Insights into brine origin, reservoir connectivity, and fluid flow in the Permian Basin, USA. *Chemical Geology*, 425, p.76-92. doi: 10.1016/j.chemgeo.2016.01.025.

Engle, M., and Rowan, E.L., 2014. Geochemical evolution of produced waters from hydraulic fracturing of the Marcellus Shale, northern Appalachian Basin: A multivariate compositional data analysis approach. *International Journal of Coal Geology*, 126, p.45-56. doi: 10.1016/j.coal.2013.11.010.

Espitalie, J., Laporte, L.J., Madec, M., Marquis, F., Leplat, P., Paulet, J., and Boutefeu, A., 1977. Methode rapide decaracterisation des roches mères, de leur potential petrolier et de leur degré d'evolution. *Revue Institut Français du Pétrole*, 32, p.32-42.

Euzen, T., Watson, N., Fowler, M., Mort, A., and Moslow, T., 2021. Petroleum distribution in the Montney hybrid play: Source, carrier bed, and structural controls. *AAPG Bulletin*, 105, p.1867-1892. doi: 10.1306/1222020088.

Evoy, R.W., 1998. Reservoir sedimentology of the Doig Formation, Buick Creek Field, northeastern British Columbia. *In:* Hogg, J.R., (ed.) *Oil and Gas Pools of the Western Canada Sedimentary* Basin. Calgary, Alberta, Canadian Society of Petroleum Geologists, Special Publication S-51, pp.127–135.

Falode, O., and Manuel, E., 2014: Wettability effects on capillary pressure, relative permeability, and irreducible saturation using porous plate. *Journal of Petroleum Engineering*, 2014(465418). doi: 10.1155/2014/465418.

Faraj, B., Harold, W., Addison, G., McKinstry, B., Donaleshen, R., Sloan, G., Lee, J., Anderson, T., Leal, R., Anderson, C., Lafleur, C., and Ahlstrom, A., 2002. Shale gas potential of selected Upper Cretaceous, Jurassic, Triassic and Devonian shale formations in the Western Canada Sedimentary Basin of Western Canada: Implications for shale gas production: GRI-02/0233: Des Plaines, Illinois, Gas Technology Institute, 258 pp.

Ferri, F., Hayes, M., and Goodman, E., 2013. 2007-2011 Core and cuttings analyses: Petroleum geology open file 20013-1: Victoria, British Columbia, BC Ministry of Natural Gas Development

Fowler, M.G., Obermajer, M., and Snowdon, L.R., 2007. Rock- Eval/TOC data for eight NE British Columbia boreholes (map areas 93-O to 94-H): Open file 5673: Geological Survey of Canada. doi:10.4095/224584

Fowler, M.G., and Snowdon, L.R., 1998. Rock-eval/TOC data for nine west central Alberta wells (township 58 to 69, ranges 18W5 to 12W6): Open file 3591: Ottawa, Ontario, Geological Survey of Canada, 89 pp. doi:10.4095/209889.

Fowler, M.G., and Snowdon, L.R., 2001. Rock-Eval/TOC data for ten northern Alberta and British Columbia wells: Open file 4124: Ottawa, Ontario, Geological Survey of Canada. doi:10.4095/212981.

FracFocus, 2016. What chemicals are used: FracFocus chemical disclosure registry (Canada). Retrieved from http://fracfocus.ca/chemical-use/what-chemicals-are-used, accessed on February 15<sup>th</sup>, 2017.

Franks, S.G, 2016. Geochemistry of formation waters from the subsalt Tubular Bells Field, offshore Gulf of Mexico: Implications for fluid movement and reservoir continuity. *AAPG Bulletin*, 100, p.943-967. doi: 10.1306/02101615027.

Furlong, C.M., Gingras, M.K., Moslow, T.F., and Zonneveld, J.-P., 2018. The Sunset Prairie Formation: Designation of a new Middle Triassic formation between the Lower Triassic Montney Formation and Middle Triassic Doig Formation in the Western Canada Sedimentary Basin, northeast British Columbia. *Bulletin of Canadian Petroleum Geology*, 66(1), p.193–214.

Gamero-Diaz, H., Miller, C., and Lewis, R., 2012. sCore: A classification scheme for organic mudstones based on bulk mineralogy. *AAPG Search & Discovery*, Article #40951.

Ghanbari, E., Abbasi, M.A., Dehghanpour, H., and Bearinger, D., 2013. Flowback volumetric and chemical analysis for evaluating load recovery and its impact on early-time production: SPE 167165-MS. *In: SPE Unconventional Resources Conference*, Calgary, Alberta. doi: 10.2118/167165-ms.

Ghanizadeh, A., Clarkson, C.R, Vahedian, A., Ardakani, O., Wood, J.M., and Sanei, H., 2018. Laboratory-based characterization of pore network and matrix permeability in the Montney Formation: Insights from methodology comparisons. *Bulletin of Canadian Petroleum Geology*, 66(2), p.472–498.

Gibson, D.W., and Barclay, J.E., 1989. Middle Absaroka Sequence - The Triassic stable craton. *In:* Ricketts, B.D., (ed.) *Western Canada Sedimentary Basin - A case history*. Calgary, Alberta, Canadian Society of Petroleum Geologists, pp.219–232.

Golding, M.L., Orchard, M.J., Zonneveld, J.-P., and Wilson, N.S.F., 2015. Determining the age and depositional model of the Doig phosphate zone in northeastern British Columbia using conodont biostratigraphy. *Bulletin of Canadian Petroleum Geology*, 63(2), p.143–170. doi: 10.2113/gscpgbull.63.2.143.

Goldstein, T.P., and Aizenshtat, Z., 1994. Thermochemical sulfate reduction: A review. *Journal of Thermal Analysis*, 42(1), p.241–290. doi:10.1007/BF02547004.

Gregg, S.J., and Sing, K.S.W., 1982. *Adsorption, Surface Area and Porosity*, 2nd ed.: London, UK, Academic Press, 303 pp.

Gupta, I., Wilson, A.M., and Rostron, B.J., 2012. Cl/Br compositions as indicators of the origin of brines: Hydrogeologic simulations of the Alberta Basin, Canada: *GSA Bulletin*, 124(1-2), p.200-212. doi: 10.1130/B30252.1.

Habeeb, O.A, Ramesh, K., Ali, G.A.M., Yunus, R.M., Thanusha, T.K., and Olalere, O.A., 2016. Modelling and optimization for H<sub>2</sub>S adsorption from wastewater using coconut shell based activated carbon. *Australian Journal of Basic and Applied Sciences*, 10(17), p.136-147.

Haluszczak, L.O., Rose A.W., and Kump L.R., 2013. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry*, 28, p.55-61. doi: 10.1016/j.apgeochem.2012.10.002.

Harris, R.G., 2000. Sedimentology and reservoir characteristics of Triassic Doig sand bodies at West Stoddart and Cache Creek in northeastern British Columbia. M.Sc. Dissertation, University of British Columbia, 205 pp.

Harris, R.G., and Bustin, R.M., 2000. Diagenesis, reservoir quality, and production trends of Doig Formation sand bodies in the Peace River area of Western Canada. *Bulletin of Canadian Petroleum Geology*, *48*(4), p.339–359. doi: 10.2113/48.4.339.

Harrison A.L., Jew, A.D., Dustin, M.K., Thomas, D.L., Joe-Wong, C.M., Bargar, J.R., Johnson, N., Brown Jr., G.E., and Maher, K., 2017. Element release and reaction-induced porosity alteration during shale-hydraulic fracturing fluid interactions. *Applied Geochemistry*, 82, p.47-62. doi: 10.1016/j.apgeochem.2017.05.001.

He, C., Li., M., Liu, W., Barbot, E., and Vidic, R.D., 2014. Kinetics and equilibrium of barium and strontium sulfate formation in Marcellus Shale flowback water. *Journal of Environmental Engineering*, 140(5). doi: 10.1061/(ASCE)EE.1943-7870.0000807.

Hsieh, P.A., Tracy, J.V., Neuzil, C.E., Bredehoeft, J.D., and Silliman, S.E., 1981. Transient laboratory method for determining the hydraulic properties of 'tight' rocks - 1. Theory. *International Journal of Rock Mechanics and Mining Sciences & Geomechanics Abstracts*, 18(5), p.89–89. doi:10.1016/0148-9062(81)90090-5.

Hubbard, C.G., Cheng, Y., Engelbrekston, A., Druhan, J.L., Li, L., Ajo-Franklin, J.B., Coates J.D. and Conrad, M.E., 2014. Isotopic insights into microbial sulfur cycling in oil reservoirs. *Frontiers in Microbiology*, 5(480).\_doi: 10.3389/fmicb.2014.00480.

Hunt A., and Ratcliffe, J., 1959. Triassic stratigraphy, Peace River Area, Alberta and British Columbia, Canada. *AAPG Bulletin*, 43, p.563–589.

Hunt, J.M., 1996. *Petroleum Geochemistry and Geology* 2nd ed.: New York, USA, W.H. Freeman and Co., 743 pp.

Hutcheon, I., 1999. Controls on the distribution of non-hydrocarbon gases in the Alberta Basin. *Bulletin of Canadian Petroleum Geology*, 47, p. 573-593.

Hutcheon, I., Krouse, H.R., and Abercrombie, H., 1995. Geochemical transformations of sedimentary sulfur: controls of the origin and distribution of elemental sulfur, H<sub>2</sub>S and CO<sub>2</sub>, in Paleozoic reservoirs of western Canada. *In:* Vairavamurthy, M.A., and Schoonen, M.A.A., (eds.) *Geochemical Transformations of Sedimentary Sulfur*, ACS Symposium Series vol. 612. Washington, DC, American Chemical Society, pp. 426–438.

Ibrahimbas, A., and Riediger, C., 2004. Hydrocarbon source rock potential as determined by Rock-Eval pyrolysis, northeast British Columbia and northwest Alberta. *British Columbia Ministry of Energy and Mines Resource Development and Geoscience Branch Summary of Activities*, p.7-18.

Johnson, R.J. Folwell, B.D., Wirekoh, A., Frenzel, M., and Skovhus, T.L., 2017. Reservoir souring -Latest development for application and mitigation. *Journal of Biotechnology*, 256, p.57-67. doi: 10.1016/j.jbiotec.2017.04.003.

Jones, S.C., 1997. A technique for faster pulse-decay permeability measurements in tight rocks. *SPE Formation Evaluation*, 12(01), p.19–26. doi:10.2118/28450-PA.

Kampschulte, A., and Strauss, H., 2004. The sulfur isotopic evolution of Phanerozoic seawater based on the analysis of structurally substituted sulfate in carbonates. *Chemical Geology*, 204(2004), p.255–286

Kent, D.M., 1994. Paleogeographic evolution of the cratonic platform-Cambrian to Triassic. *In:* Mossop, G.D., and Shetsen, I., (eds.) *Geological Atlas of the Western Canada Sedimentary Basin*. Calgary, Alberta, Canadian Society of Petroleum Geologists and the Alberta Research Council, pp.69–86.

Kirste, D., Desrocher, S., Spence, B., Hoyne, B., Tsang, B., and Hutcheon, I., 1997. Fluid flow, water chemistry, gas chemistry and diagenesis in the subsurface Triassic in Alberta and British Columbia. *Bulletin of Canadian Petroleum geology*, 45, p.742-764.

Klinkenberg, L.J., 1941. The permeability of porous media to liquids and gases. In: *Drilling and Production Practice*. New York, New York, pp. 200–213.

Laxminarayana, C., Cui, X., and Bustin, R.M., 2004. Implications of volumetric swelling/shrinkage of coal in sequestration of acid gases: Paper #0435 *In: International Coalbed Methane Symposium*, Tuscaloosa, Alabama.

Laxminarayana, C., and Bustin, R.M., 2003. Sequestration potential of acid gases in Western Canadian coal: Paper #0360 *In: International Coalbed Methane Symposium*, Tuscaloosa, Alabama.

Liseroudi, M., Ardakani, O., Sanei, H., Pedersen, P., Stern, R., and Wood, J., 2020. Origin of sulfaterich fluids in the Early Triassic Montney Formation, Western Canadian Sedimentary Basin. *Marine and Petroleum Geology*, 114, p.1-17. doi: 10.1016/j.marpetgeo.2020.104236.

Luther IIII, G. W., Findlay, A.J., MacDonald, D.J., Owings, S.M., Hanson, T.E., Beinart, R.A., and Girguis, P.R., 2011. Thermodynamics and kinetics of sulphide oxidation by oxygen: A look at inorganically controlled reactions and biologically mei8dated processes in the environment. *Frontiers in Microbiology*, 2(62). doi: 10.3389/fmicb.2011.00062.

Machel, H.G., 1985. Facies and diagenesis of the Upper Devonian Nisku Formation in the subsurface of central Alberta. Ph.D. Thesis, McGill University, 392 pp.

Machel, H.G., 1987. Some aspects of diagenetic sulphate-hydrocarbon redox reactions. *In:* Marshall, J.D., (ed.) *Diagenesis of Sedimentary Sequences, Geological Society Special Publication No.* 36, Oxford, UK, The Geological Society, pp.15-28.

Machel, H.G., 2001. Bacterial and thermochemical sulfate reduction in diagenetic settings – old and new insights. *Sedimentary Geology*, 140, p.143-175. doi: 10.1016/s0037-0738(00)00176-7.

Machel, H.G., Krouse, H.R., Riciputi, L.R., and Cole, D.R., 1995. Devonian Nisku sour gas play, Canada: a unique natural laboratory for study of thermochemical sulfate reduction. *In:* Vairavamurthy, M.A., and Schoonen, M.A.A., (eds.) *Geochemical Transformations of Sedimentary Sulfur*, ACS Symposium Series vol. 612. Washington, DC, American Chemical Society, pp. 439–454.

Majorowicz, J.A., Jessop, A.M., and Lane, L.S., 2005. Regional heat flow pattern and lithospheric geotherms in northeastern British Columbia and adjacent Northwest Territories, Canada. *Bulletin of Canadian Petroleum Geology*, 53(1), p.51–66. doi:10.2113/53.1.51

Maghsoudi, H., Soltanieh, M., Bozorgzadeh, H., and Mohamadalizadeh, A., 2013. Adsorption isotherms and ideal selectivities of hydrogen sulfide and carbon dioxide over methane for the Si-CHA zeolite: Comparison of carbon dioxide and methane adsorption with the all-silica DD3R zeolite. *Adsorption*, 19, p.1045–1053. doi: 10.1007/s10450-013-9528-1.

Marcon, V., Joseph, C., Carter, K.E., Hedges, S.W., Lopano, C.L., Guthrie, G.D., and Hakala, J.A., 2017. Experimental insights into geochemical changes in hydraulically fractured Marcellus Shale. *Applied Geochemistry*, 76, p.36-50. doi: 10.1016/j.apgeochem.2016.11.005.

Markhasin, B., 1997. Sedimentology and stratigraphy of the Lower Triassic Montney Formation, subsurface of northwestern Alberta. M.Sc. Dissertation, University of Calgary, 153 pp.

Marriott, R.A., Pirzadeh, P., Marrugo-Hernandez, J., and Raval, S., 2016. Hydrogen sulphide formation in oil and gas. *Canadian Journal of Chemistry*, 94, p.406-413. doi: 10.1139/cjc-2015-0425.

Martin, R., 2008. Sedimentology, diagenetic history, and petroleum potential of the Middle Triassic Middle Doig Member, Blueberry/Inga area, northeastern British Columbia. B.Sc. Dissertation, University of Manitoba, 85 pp.

Mavko, G., Mukerji, T., and Dvorkin, J., 2009. *The Rock Physics Handbook: Tools for Seismic Analysis of Porous Media*, 2nd ed.: Cambridge, UK, Cambridge University Press, 524 pp.

McPhee, C., Reed, J., and Zubizaretta, I., 2015. *Core Analysis: A Best Practice Guide, Developments in Petroleum Science Volume 64*, 1st ed.: Amsterdam, Netherlands, Elsevier, 852 pp.

Menouar, H., Aman, H.M., Al-Majed, A.A., Khan, M.A., and Jilani, S.Z., 2002. Use of a nondestructive method to estimate drilling fluid invasion depths in core, application to formation damage. *In: International Symposium of the Society of Core Analysts*, Monterey, California.

Meshoulam, A., Ellis, G.S., Ahmad, W.S., Deev, A., Sessions, A.L., Tang, Y., Adkins, J.F., Liu, J., Gilhooly III, W.P., Aizenshtat, Z., and Amrani, A., 2016. Study of thermochemical sulfate reduction mechanism using compound specific sulphur isotope studies. *Geochemica et Cosmochimica Acta*, 188, p.73-92. doi: 10.1016/j.gca.2016.05.026.

Miles, W., and Oneschuk, D., 2016. *Magnetic anomaly map, Canada: Open file 7799*: Ottawa, Ontario, Geological Survey of Canada, 1 pp. doi: 10.4095/297337.

Moslow, T.F., 2000. Reservoir architecture of a fine-grained turbidite system: Lower Triassic Montney Formation, Western Canada Sedimentary Basin. *In:* Weimer, P., Slatt, R.M., Coleman, J., Rosen, N.C., Nelson, H., Bouma, A.H., Styzen, M.J., and Lawrence, D.T., (ed.) *Deep-Water Reservoirs of the World*. Houston, Texas, Society of Economic Paleontologists and Mineralogists, Gulf Coast Section, pp.686–713. doi: 10.5724/gcs.00.15.0686.

Mougin, P., Lamoureux-Var, V., Bariteau, A., and Huc, A.Y., 2007. Thermodynamic of thermochemical sulphate reduction. *Journal of Petroleum Science and Engineering*, 58(3–4), p.413–427. doi: 10.1016/j.petrol.2007.01.005.

Munson, E.O., 2015. *Reservoir characterization of the Duvernay Formation, Alberta: a pore- to basin-scale investigation*. Ph.D. Thesis, University of British Columbia, 266 pp.

Munson, E.O., Chalmers, G.R.L., Bustin, R.M., and Li, K., 2016. Utilizing smear mounts for X-ray diffraction as a fully quantitative approach in rapidly characterizing the mineralogy of shale gas reservoirs. *Journal of Unconventional Oil and Gas Resources*, 14, p.22-31. doi: 10.1016/j.juogr.2016.01.001.

NGI (Natural Gas Intelligence), 2017. Montney shale to gain more sour gas processing with SemCAMS proposal. Retrieved from http://www.naturalgasintel.com/articles/111382-montney-shale-to-gain-more-sour-gas-processing-with-semcams-proposal, accessed on Nov 22<sup>nd</sup>, 2020.

NEB (National Energy Board), 2013. *The Ultimate potential for unconventional petroleum from the Montney Formation of British Columbia and Alberta*. Calgary, Alberta, National Energy Board, 17pp.

NEB (National Energy Board), 2018. *Canada's energy future 2018 supplement: Natural gas production*. Calgary, Alberta, National Energy Board, 12 p.

Neuzil, C.E., Cooley, C., Silliman, S.E., Bredehoeft, J.D., and Hsieh, P.A., 1981. A transient laboratory method for determining the hydraulic properties of "tight" rocks-II. Application. *International Journal of Rock Mechanics and Mining Sciences & Geomechanics Abstracts*, 18(3), p.253–258. doi:10.1016/0148-9062(81)90980-3.

Newton, R., and Bottrell, S., 2007. Stable isotopes of carbon and sulphur as indicators of environmental change: Past and present. *Journal of the Geological Society*, 164, p.691–708. doi: 10.1144/0016-76492006-101.

Nixon, S.L., Walker, L., Streets, M.D.T., Eden, B., Boothman, C., Taylor, K.G., and Lloyd, J.R., 2017. Guar gum stimulates biogenic sulphide production at elevated pressures: Implications for shale gas extraction. *Frontiers in Microbiology*, 8. doi: 10.3389/fmicb.2017.00679

Osselin, F., Saad, S., Nightingale, M., Hearn, G., Desaulty, A-M., Gaucher, E.C., Clarkson, C.R., Kloppmann, W., and Mayer, B., 2019. Geochemical and sulfate isotopic evolution of flowback and produced waters reveals water-rock interactions following hydraulic fracturing of a tight hydrocarbon reservoir. *Science of the Total Environment*, 687, p.1389-1400. doi: 10.1016/j.scitotenv.2019.07.066.

Owen, J., 2017. An investigation into the controls and variability of the flowback water inorganic geochemistry of the Montney Formation, northeastern British Columbia and northwestern Alberta, Canada. M.Sc. Dissertation, The University of British Columbia, 207 pp.

Owen J., and Bustin M.R., 2017. Implications of the inorganic geochemistry of flowback water from the Montney Formation, northeastern British Columbia and northwestern Alberta: Progress report. *Geoscience BC Summary of Activities*, p.49–54.

Owen, J., Bustin, R.M., and Bustin, A.M.M, 2020. Insights from mixing calculations and geochemical modeling of Montney Formation post hydraulic fracturing flowback water chemistry. *Journal of Petroleum Science and Engineering*, 195. doi :10.1016/J.PETROL.2020.107589.

Parkhurst, D.L., and Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2) — A computer program for speciation, batch-reaction, one- dimensional transport, and inverse geochemical calculations: Water-Resources Investigations Report 99-4259: Denver, Colorado, United States Geological Survey, 310 pp.

Parkhurst, D.L., and Appelo, C.A.J., 2013. Description of Input and Examples for Phreeqc Version 3 – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations: Techniques and Methods 6-A43: Denver, Colorado, United States Geological Survey, 497 pp.

Pearson, K., 1897. Contributions to the mathematical theory of evolution. — On a form of spurious correlation which may arise when indices are used in the measurement of organs. *Proceedings of the Royal Society of London*, 60, p.489–98. doi: 10.1098/rspl.1896.0076

Petersen, H.I., 2002. A reconsideration of the "oil window" for humic coal and kerogen Type III source rocks. *Journal of Petroleum Geology*, 25(4), p.407–432. doi:10.1016/s0140-6701(03)92280-6.

Phan, T.T., Capo, R.C., Stewart, B.W., Macpherson, G.L., Rowan, E.L., and Hammack, R.W., 2016. Factors controlling Li concentration and isotopic composition in formation waters and host rocks of Marcellus Shale, Appalachian Basin. *Chemical Geology*, 420, p.162-179. doi: 10.1016/j.chemgeo.2015.11.003.

Pirzadeh, P., Lesage, K.L., and Marriott, R.A., 2014. Hydraulic fracturing additives and the delayed onset of hydrogen sulphide in shale gas. *Energy and Fuels*, 28, p.4993-5001.

Pirzadeh, P., Raval, S., and Marriott, R.A., 2015. On the fate of hydraulic fracturing fluid additives: Thermochemical sulfate reduction reaction of sodium dodecyl sulfate. *Organic Geochemistry*, 83–84, p.94-100. doi: 10.1016/j.orggeochem.2015.03.011.

Pooladi, M., Hong, H., Stocker, R.K., Theys, S., and Bachu, S., 2009. Chromatographic partitioning of H<sub>2</sub>S and CO<sub>2</sub> in acid gas disposal. *Journal of Canadian Petroleum Technology*, 48, p.51-57.

Reis, M.A.M., Almeida, J.S., Lemos, P.C. and Carrondo, M.J.T. 1992. Effect of hydrogen sulfide on growth of sulfate reducing bacteria. *Biotechnology and Bioengineering*, 40: p. 593-600. doi: 10.1002/bit.260400506

Ren, G.M., Pan, Y., Yang, X. M., Qiao, Y.Y., Li, H.W., Meng, C., and Xu, D.Y., 2014. Experimental study on treatment of wastewater containing oil and polyacrylamide by aerobic and anaerobic bacteria. *Applied Mechanics and Materials*, 675-677, p.539-542. doi: 10.4028/www.scientific.net/AMM.675-677.539.

Renock, D., Landis, J.D., and Sharma, M., 2016. Reductive weathering of black shale and release of barium during hydraulic fracturing. *Applied Geochemistry*, 65, p.73-86. doi: 10.1016/j.apgeochem.2015.11.001.

Riediger, C.L., 1990. Rock-eval/TOC data from the lower Jurassic "Nordegg Member" and from the lower and middle Triassic Doig and Montney formations, Western Canada Sedimentary Basin, Alberta and British Columbia: Open file 2308: Geological Survey of Canada, 27 pp. doi:10.4095/128197.

Riediger, C.L., Fowler, M.G., Brooks, P.W., and Snowdon, L.R., 1990. Triassic oils and potential Mesozoic source rocks, Peace River Arch area, Western Canada Basin. *Organic Geochemistry*, 16(1), p.295–305. doi: 10.1016/0146-6380(90)90049-6.

Rietveld, H.M., 1967. Line profiles of neutron powder-diffraction peaks for structure refinement. *Acta Crystallographica*, 22(1), p.151-152. doi: 10.1107/S0365110X67000234.

Rietveld, H.M., 1969. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*, 2(2), p.65-71. doi: 10.1107/s0021889869006558.

Rohais, S., Crombez, V., Euzen, T., and Baudin, F., 2016. The Lower and Middle Triassic of Western Canada: Passive margin, back-arc or fore-arc geodynamic setting? *In: Geoconvention 2016: Optimizing Resources*, Calgary, Alberta.

Rokhforouz, M.R., and Amiri, H.A.A., 2017. Phase-field simulation of counter-current spontaneous imbibition in a fractured heterogeneous porous medium: *Physics of Fluids*, 29(062104), p.1-9. doi: 10.1063/1.4985290.

Rokosh, C.D., Lyster, S., Anderson, S.D.A., Beaton, A.P., Berhane, H., Brazzoni, T., Chen, D., Cheng, Y., Mack, T., Pana, C., and Pawlowicz, J.G., 2012. *Summary of Alberta's shale- and siltstone-hosted hydrocarbon resource potential: ERCB/AGS Open File Report 2012-06*: Edmonton, Alberta, Energy Resources Conservation Board of Alberta and Alberta Geological Survey, 327 pp.

Romero-Sarmiento, M.-F., Euzen, T., Rohais, S., Jiang, C., and Littke, R., 2016. Artificial thermal maturation of source rocks at different thermal maturity levels: Application to the Triassic Montney and Doig formations in the Western Canada Sedimentary Basin. Organic Geochemistry, 97(97), p.148–162. doi:10.1016/j.orggeochem.2016.05.002

Seeking Alpha, 2017. Advantage ride along - Part 2. Retrieved from https://seekingalpha.com/article/4113528-advantage-ride-along-part-2, accessed on Oct, 7th, 2020.

Seven Generations Energy, 2020. Montney operations. Retrieved from https://www.7genergy.com/operations/montney, accessed on Dec 22<sup>nd</sup>, 2020.

Silva, P.L., 2021. Petroleum system analysis of the Triassic Doig Formation, Western Canada Sedimentary Basin. PhD Thesis, The University of British Columbia. 245 pp. doi: 10.14288/1.0400893.

Silva, P.L., and Bustin, R.M., 2020a. Hydrocarbon-generation kinetics of the Doig Formation, northeastern British Columbia and west-central Alberta. *Geoscience BC Summary of Activities*, p.65–76.

Silva, P.L., and Bustin, R.M., 2020b. Significance and distribution of apatite in the Triassic Doig Phosphate Zone, Western Canada Sedimentary Basin. *Minerals*, 10(904), p.1–26. doi: 10.3390/min10100904.

Sing, K., Everett, D., Haul, R., Moscou, L., Pierotti, R., Rouquérol, J., and Siemieniewska, T., 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (recommendations 1984). *Pure and Applied Chemistry*, 57, p.603–619. doi: 10.1351/pac198557040603.

Sharma, G., 1969. Paragenetic evolution in Peejay Field, British Columbia, Canada. *Mineral Deposits*, 4, p.346-354.

Snowdon, L.R., 1997. Rock-eval/TOC data for six wells in the Worsley area of Alberta (townships 80 to 87 and ranges 3W6 to 10W6): Open file 3492: Ottawa, Ontario, Geological Survey of Canada, 51 pp. doi:10.4095/209157.

Tamimi, A., Rinker, E.B., and Sandall, O.C., 1994. Diffusion coefficients fore hydrogen sulfide, carbon dioxide, and nitrous oxide in water over the temperature range 293-368 K. *Journal of Chemical & Engineering Data*, 39, p.330-332.

The Globe and Mail, 2009. EnCana's ticking timebomb. Retrieved from https://www.theglobeandmail.com/report-on-business/rob-magazine/encanas-ticking-timebomb/article4320509, accessed on Nov, 27th, 2020.

Torghabeh, A.K., Kalantariasl, A., Ghorbani, M.R., and Nematollahi, H., 2021. Multivariate thermochemical sulphate reduction (TSR) low temperature origin for H<sub>2</sub>S production: A Fars Provinance gas field. *Journal of Natural Gas Science and Engineering*, 88. doi: 10.1016/j.jngse.2021.103795.

Trimmer, D.A., 1981. Design criteria for laboratory measurements of low permeability rocks. *Geophysical Research Letters*, 8(9), p.973–975. doi:10.1029/GL008i009p00973.

Tuya Terra Geo Corp, and Geothermal Management Company, 2016. Direct-use geothermal resources in British Columbia: Report 2016-07 (Section A): Burnaby, British Columbia, Tuya Terra Geo Corp, Geothermal Management Company Inc. & Geoscience, 38 pp.

Utting, J., MacNaughton, R.B., Zonneveld, J.-P., and Fallas, K.M., 2005. Palynostratigraphy, lithostratigraphy and thermal maturity of the Lower Triassic Toad and Grayling, and Montney formations of western Canada, and comparisons with coeval rocks of the Sverdrup basin, Nunavut. *Bulletin of Canadian Petroleum Geology*, 53, p.5–24.

Vaisblat, N., Harris, N.B., Ayranci, K., Power, M., DeBhur, C., Bish, D.L., Chalaturnyk, R., Krause, F., Crombez, V., Euzen, T., and Rohais, S., 2011. Compositional and diagenetic evolution of a siltstone, with implications for reservoir quality; an example from the Lower Triassic Montney Formation in western Canada. *Marine and Petroleum Geology*, 129. doi: 10.1016/j.marpetgeo.2021.105066.

Veshareh, M.J., and Nick, H.M., 2021. Biased samples to study reservoir souring processes: A numerical analyses. *Journal of Cleaner Production*, 315. doi: 10.1016/j.jclepro.2021.127944.

Vizika, O., and Kalaydjian, F., 2003. Effect of capillary, viscous and gravity forces on gas-condensate mobility. *Petrophysics*, 44.

Walsh, W., Adams, C., Kerr, B., and Korol, J., 2006. *Regional "shale gas" potential of the Triassic Doig and Montney formations, northeastern British Columbia: Petroleum geology open file 2006-02*: Victoria, British Columbia, British Columbia Ministry of Energy Mines and Petroleum Resources, 19 pp.

Walsh, W., and McPhail, S., 2007. *Shale gas potential: core and cuttings analysis, northeast British Columbia: Petroleum Geology: Open file 2007-01*: British Columbia Ministry of Energy, Mines and Petroleum Resources, Resource Development and Geoscience Branch, 10 pp.

Wang, F., Pan, Z., and Zhang, S., 2016. Modelling fracturing-fluid flowback behavior in hydraulically fractured shale gas under chemical potential dominated conditions. *Applied Geochemistry*, 74, p.194-202. doi: 10.1016/j.apgeochem.2016.10.008.

Wang, F., Pan, Z., and Zhang, S., 2017. Impact of chemical osmosis on water leakoff and flowback behavior from hydraulically fractured gas shale. Journal of Petroleum Science and Engineering, 151, p.264-274. doi: 10.1016/j.petrol.2017.01.018.

Warren, J., 2016. Evaporites, 2nd ed.: Cham, Switzerland, Springer, 1807 pp.

Washburn, E.W., 1921. Note on a method of determining the distribution of pore sizes in a porous material. In: *National Academy of Sciences of the United States of America*. pp. 115–116. doi:10.1073/pnas.7.4.115.

Wilke, F.D.H., Vieth-Hillebrand, A., Naumann, R., Erzinger, J. and Horsfield, B., 2015. Induced mobility of inorganic and organic solutes from black shales using water extraction: Implications for shale gas exploitation. Applied Geochemistry, 63, p.158-168. doi: 10.1016/j.apgeochem.2015.07.008.

Wood, J., and Sanei, H., 2016. Secondary migration and leakage of methane from a major tight-gas system. Nature Communications, 7(13614). doi: 10.1038/ncomms13614.

Wüst, R.A.J., Tu, S., Nassichuk, B., Bozarth, T., Tucker, J., Cui, A., 2018. Chemostratigraphy, petrography, and SEM investigations of the Lower Triassic Montney Formation in Alberta: Implications for a new and revised diagenetic and depositional model. Bulletin of Canadian Petroleum Geology, 66(2), p.436–471.

Yamada, S.E., and Jones, A.H., 1980. A review of a pulse technique for permeability measurements. *Society of Petroleum Engineers Journal Forum*, 20(05), p.357–358. doi:10.2118/8760-pa.

Xia, X., and Ellis, G.S., 2016. Coupled kinetic and fluid dynamic models to understand H2S occurrence in unconventional petroleum systems: Paper #2460230. In: SPE/AAPG/SEG Unconventional Resources Technology Conference, San Antonio, Texas.

Xia, X., and Ellis, G.S., 2017. Hydrogen sulphide in the Permian Basin. AAPG Search & Discovery, Article #10950.

Yang, C., Hutcheon, I., and Krouse, H., 2001. Fluid inclusion and stable isotopic studies of thermochemical sulphate reduction from Burnt Timber and Crossfield East gas fields in Alberta, Canada. Bulletin of Canadian Petroleum Geology, 49(1), p.149-164. doi: 10.2113/49.1.149

Zeebe, R.E., and Tyrrell, T., 2019. History of carbonate ion concentration over the last 100 million years II: Revised calculations and new data. Geochemica et Cosmochimica Acta, 68(17), p. 3521-3530. doi: 10.1016/j.gca.2019.02.041.

Zhu, G., Zhang, S., Liang, Y., Dai, J., and Li, J., 2005, Isotopic evidence of TSR origin for natural gas bearing high H2S contents with the Feixianguan Formation of the northeastern Sichuan Basin, southwestern China. Science in China Series D: Earth Sciences, 48, p.1960-1971.

Ziemkiewicz, P.F., and He, Y.T., 2015. Evolution of water chemistry during Marcellus Shale gas development: A case study in West Virginia. *Chemosphere*, 134, p.224-231. doi: 10.1016/j.chemosphere.2015.04.040.

Zolfaghari, A., Dehghanpour, H., Ghanbari, E., and Bearinger, D., 2015. Fracture characterization using flowback salt-concentration transient. *In: SPE Hydraulic Fracturing Technology Conference*, The Woodlands, Texas, USA.

Zonneveld, J.-P., Carrelli, G., and Riediger, C., 2004. Sedimentology of the Upper Triassic Charlie Lake, Baldonnel and Pardonet Formations from Outcrop Exposures in the Southern Trutch Region, Northeastern British Columbia. *Bulletin of Canadian Petroleum Geology*, 52, p.343-375.

Zonneveld, J.-P., Golding, M., Moslow, T.F., Orchard, M.J., Playter, T., and Wilson, N., 2011. Depositional framework of the Lower Triassic Montney Formation, west-central Alberta and northeastern British Columbia. *In: CSPG CSEG CWLS Convention*, Calgary, Alberta.

# 12. Appendices

Appendix A: Sulphur and Oxygen Isotopic data for minerals and organic matter from this study and other studies.

Formation	Age	Sample ID	Well Authorization	Location	634S (VCDT)	δ180 (SMOW)	Sulphur Source	Data Source
Charlie Lake	Triassic	PBN - 1	30876	WCSB	14.2	7.69	anhydrite	This Study
Charlie Lake	Triassic	PBN - 2	30876	WCSB	14.6	8.75	anhydrite	This Study
Charlie Lake	Triassic	PBN - 3	30876	WCSB	14.7	7.94	anhydrite	This Study
Charlie Lake	Triassic	PBN - 4	30876	WCSB	15	8.86	anhydrite	This Study
Charlie Lake	Triassic	29453-1	29453	WCSB	16.22	12.38	anhydrite	This Study
Charlie Lake	Triassic	29453-2	29453	WCSB	13.59	11.55	anhydrite	This Study
Charlie Lake	Triassic	3944-1	3944	WCSB	14.84	10.78	anhydrite	This Study
Charlie Lake	Triassic	3944-2	29453	WCSB	15.02	10.88	anhydrite	This Study
Charlie Lake	Triassic	3944-3	29453	WCSB	15.77	12.26	anhydrite	This Study
Charlie Lake	Triassic	8183-1	8183	WCSB	14.77	10.91	anhydrite	This Study
Halfway	Triassic	PBN - 5	30876	WCSB	17	8.14	anhydrite	This Study
Halfway	Triassic	29453-3	29453	WCSB	15.51	14.16	anhydrite	This Study
Halfway	Triassic	3944-4	29453	WCSB	20.73	12.88	anhydrite	This Study
Doig Silt	Triassic	PBN - 6	30876	WCSB	13.2	3.96	anhydrite	This Study
Doig Silt	Triassic	29453-4	29453	WCSB	15.5	8.85	anhydrite	This Study
Doig Silt	Triassic	3944-5	29453	WCSB	20.98	13.45	anhydrite	This Study
Doig Shale	Triassic	PBN - 7	30876	WCSB	9.9	-3.69	anhydrite	This Study
Doig Shale	Triassic	29453-5	29453	WCSB	15.41	8.56	anhydrite	This Study
Montney (upper)	Triassic	32908-1	32908	WCSB	9.42	-	anhydrite	This Study
Montney (upper)	Triassic	26668-1	26668	WCSB	8.92	-2.87	anhydrite	This Study
Montney (upper)	Triassic	3944-6	3944	WCSB	13.94	7.56	anhydrite	This Study
Montney (upper)	Triassic	PBN - 10	30876	WCSB	14.5	-1	anhydrite	This Study
Montney (upper)	Triassic	29483-6	29453	WCSB	14.7	8.73	anhydrite	This Study
Montney (upper)	Triassic	PBN - 11	30876	WCSB	13.5	-	anhydrite	This Study
Montney (upper)	Triassic	PBN - 12A	30876	WCSB	15.5	-	anhydrite	This Study

Montney (middle)	Triassic	29453-7	29453	WCSB	15.55	4.46	anhydrite	This Study
Montney (middle)	Triassic	3944-7	3944	WCSB	16.96	2.95	anhydrite	This Study
Montney (lower)	Triassic	PBN - 13	30876	WCSB	13.3	0.2	anhydrite	This Study
Montney (lower)	Triassic	29453-8	29453	WCSB	11.59	18.37	anhydrite	This Study
Montney (lower)	Triassic	3944-8	3944	WCSB	10.92	-4.04	anhydrite	This Study
Belloy	Permian	3944-9	3944	WCSB	3.91	10.19	anhydrite	This Study
Muskeg	Devonian	8183-2	8183	WCSB	18.6	12.29	anhydrite	This Study
Muskeg	Devonian	8183-3	8183	WCSB	18.62	14.05	anhydrite	This Study
Muskeg	Devonian	8183-4	8183	WCSB	18.02	14.72	anhydrite	This Study
Muskeg	Devonian	8183-2 repeat	8183	WCSB	18.6	-	anhydrite	This Study
Muskeg	Devonian	8183-3 repeat	8183	WCSB	18.7	-	anhydrite	This Study
Muskeg	Devonian	8183-4 repeat	8183	WCSB	17.7	-	anhydrite	This Study
Montney (upper)	Triassic	32908-2	32908	WCSB	-4.68	5.26	Organic Matter	This Study
Montney (upper)	Triassic	32908-3	32908	WCSB	1.8	12.2	Organic Matter	This Study
Montney (upper)	Triassic	26668-2	26668	WCSB	-6.92	20.28	Organic Matter	This Study
Montney (upper)	Triassic	PBN9-1	30876	WCSB	-3.6	7.3	Organic Matter	This Study
Montney (upper)	Triassic	PBN9-2	30876	WCSB	6.39	17.82	Organic Matter	This Study
Montney (upper)	Triassic	PBN9-3	30876	WCSB	49.9	-	pyrite	This Study
Montney (upper)	Triassic	32908-4	32908	WCSB	2.9	-	pyrite	This Study
Montney (upper)	Triassic	26668-4	26668	WCSB	21.64	-	pyrite	This Study
Nisku	Devonian	n/a	n/a	WCSB	26.8	18.7	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	27.8	19.5	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.9	17.7	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	27.4	20.9	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	26.7	28.3	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	24.2	18.7	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	23.8	16.7	sulphate	Machel, H. (1985)

Nisku	Devonian	n/a	n/a	WCSB	26.3	19.2	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	27.1	21.2	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	28.1	17.8	sulphate	Machel, (1985)	Н.
Nisku	Devonian	n/a	n/a	WCSB	24.8	16.9	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.8	14.7	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.7	15.8	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.4	15.3	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	24.8	18.7	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	27.8	19.5	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	25.9	17.7	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	27.4	20.8	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.7	20.3	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	24.2	18.7	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	23.8	16.7	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.3	17.2	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	27.1	21.2	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	22.8	14.8	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	24.8	16.9	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.8	14.7	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.7	15.8	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	21.2	17.3	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	24.9	19.7	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	24.8	16.8	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	22.8	15.3	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	24.3	16.3	sulphate	Machel, (1985)	H.

Nisku	Devonian	n/a	n/a	WCSB	24.8	18.8	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.9	17.8	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	23.8	16.6	sulphate	Machel, (1985)	Н.
Nisku	Devonian	n/a	n/a	WCSB	23.7	14.3	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	24	16.3	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	23.8	15.7	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	29.5	14.7	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	24.1	15.5	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	25.6	16.3	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	23.2	16.1	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	27.6	19.2	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	28.8	17.9	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	28.4	16.2	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.3	18.4	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	25.8	17.9	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	25.5	19.3	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	25	19.3	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.6	17.7	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	27.8	18.3	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	26.7	17.1	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	27.8	17.6	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	25.9	18.4	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	25.4	18.2	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	22.6	17.8	sulphate	Machel, (1985)	H.
Nisku	Devonian	n/a	n/a	WCSB	23.9	17.5	sulphate	Machel, (1985)	H.

Nisku	Devonian	n/a	n/a	WCSB	26.3	19.4	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	24.6	17.9	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.2	18	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	24.6	18.2	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	26.3	17.4	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.5	17.9	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.9	16.7	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.4	14.9	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.2	13.2	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.8	19.5	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.7	20	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.3	17.8	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.7	17.5	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.3	18.9	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.5	17.8	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	25.5	17.1	sulphate	Machel, H. (1985)
Nisku	Devonian	n/a	n/a	WCSB	24	n/a	sulphate	Claypool et al. (1980)
Nisku	Devonian	n/a	n/a	WCSB	24.6	n/a	sulphate	Claypool et al. (1980)
Camrose Fm	Devonian	n/a	n/a	WCSB	24.2	12.9	sulphate	Claypool et al. (1980)
Peechee Fm	Devonian	n/a	n/a	WCSB	25.7	14	sulphate	Claypool et al. (1980)
Prairie Evaporite	Devonian	n/a	n/a	WCSB	19.4	14.3	sulphate	Claypool et al. (1980)
Watt Mtn Fm	Devonian	n/a	n/a	WCSB	21.8	14.5	sulphate	Claypool et al. (1980)
Prairie Evaporite	Devonian	n/a	n/a	WCSB	21.3	14.7	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB	29.1	15.3	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB	30.5	15.4	sulphate	Claypool et al. (1980)

Muskeg	Devonian	n/a	n/a	WCSB	20.5	15.5	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	31.6	15.7	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.5	16.6	sulphate	Claypool et al. (1980)
N/A	Devonian	n/a	n/a	Australia	21.8	17.1	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.2	17.3	sulphate	Claypool et al. (1980)
N/A	Devonian	n/a	n/a	Australia	22.7	17.8	sulphate	Claypool et al. (1980)
Wabamun	Devonian	n/a	n/a	WCSB	27	n/a	sulphate	Claypool et al. (1980)
Wabamun	Devonian	n/a	n/a	WCSB	28.2	n/a	sulphate	Claypool et al. (1980)
Wabamun	Devonian	n/a	n/a	WCSB	27.5	n/a	sulphate	Claypool et al. (1980)
Wabamun	Devonian	n/a	n/a	WCSB	26.3	n/a	sulphate	Claypool et al. (1980)
Slave Point Fm	Devonian	n/a	n/a	WCSB (Ab)	18.8	n/a	sulphate	Claypool et al. (1980)
Elk Point	Devonian	n/a	n/a	WCSB (Ab)	17.1	n/a	sulphate	Claypool et al. (1980)
Cooking Lake Fm	Devonian	n/a	n/a	WCSB	34	n/a	sulphate	Claypool et al. (1980)
Crowfoot Fm	Devonian	n/a	n/a	WCSB	24.2	n/a	sulphate	Claypool et al. (1980)
Camrose Fm (~Nisku)	Devonian	n/a	n/a	WCSB	24.6	n/a	sulphate	Claypool et al. (1980)
Cairn Fm	Devonian	n/a	n/a	WCSB	30.5	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	30	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	30	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.5	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	29.2	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.9	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.5	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.5	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	25.1	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28	n/a	sulphate	Claypool et al. (1980)

Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	29.3	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.4	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	27.9	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	27.6	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.5	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	24	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.6	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.5	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.6	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	27.7	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	26.8	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.1	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.2	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	28.1	n/a	sulphate	Claypool et al. (1980)
Souris River Fm	Devonian	n/a	n/a	WCSB (Sask.)	25.5	n/a	sulphate	Claypool et al. (1980)
N/A	Devonian	n/a	n/a	US+Europ e	27.6	n/a	sulphate	Kampschulte and Strauss (2004)
N/A	Devonian	n/a	n/a	US+Europ e	27.6	n/a	sulphate	Kampschulte and Strauss (2004)
N/A	Devonian	n/a	n/a	US+Europ e	26	n/a	sulphate	Kampschulte and Strauss (2004)
N/A	Devonian	n/a	n/a	US+Europ e	23.4	n/a	sulphate	Kampschulte and Strauss (2004)
N/A	Devonian	n/a	n/a	US+Europ e	20.3	n/a	sulphate	Kampschulte and Strauss (2004)

N/A	Devonian	n/a	n/a	US+Europ e	20	n/a	sulphate	Kampschulte and Strauss (2004)
N/A	Devonian	n/a	n/a	US+Europ e	20	n/a	sulphate	Kampschulte and Strauss (2004)
N/A	Devonian	n/a	n/a	US+Europ e	21.3	n/a	sulphate	Kampschulte and Strauss (2004)
N/A	Devonian	n/a	n/a	US+Europ e	19.7	n/a	sulphate	Kampschulte and Strauss (2004)
N/A	Devonian	n/a	n/a	US+Europ e	20.5	n/a	sulphate	Kampschulte and Strauss (2004)
N/A	Devonian	n/a	n/a	US+Europ e	28.2	n/a	sulphate	Kampschulte and Strauss (2004)
N/A	Devonian	n/a	n/a	US+Europ e	25.5	n/a	sulphate	Kampschulte and Strauss (2004)
Charlie Lake	Triassic	n/a	n/a	WCSB	14.3	n/a	sulphate	Claypool et al. (1980)
Charlie Lake	Triassic	n/a	n/a	WCSB	14.8	n/a	sulphate	Claypool et al. (1980)
Charlie Lake	Triassic	n/a	n/a	WCSB	14.3	n/a	sulphate	Claypool et al. (1980)
Charlie Lake	Triassic	n/a	n/a	WCSB	13.7	n/a	sulphate	Claypool et al. (1980)
Charlie Lake	Triassic	n/a	n/a	WCSB	13.4	n/a	sulphate	Claypool et al. (1980)
Charlie Lake	Triassic	n/a	n/a	WCSB	14	n/a	sulphate	Claypool et al. (1980)
Charlie Lake	Triassic	n/a	n/a	WCSB	13.7	n/a	sulphate	Claypool et al. (1980)
Charlie Lake	Triassic	n/a	n/a	WCSB	13.7	n/a	sulphate	Claypool et al. (1980)
Charlie Lake	Triassic	n/a	n/a	WCSB	15.7	n/a	sulphate	Claypool et al. (1980)
n/a	Triassic	n/a	n/a	Israel	15.7	n/a	sulphate	Claypool et al. (1980)
n/a	Triassic	n/a	n/a	Israel	17.2	n/a	sulphate	Claypool et al. (1980)
n/a	Triassic	n/a	n/a	Israel	17.8	n/a	sulphate	Claypool et al. (1980)

n/a	Triassic	n/a	n/a	Israel	17.4	n/a	sulphate	Claypool et al. (1980)
n/a	Triassic	n/a	n/a	Israel	16	n/a	sulphate	Claypool et al. (1980)
n/a	Triassic	n/a	n/a	Israel	16.5	n/a	sulphate	Claypool et al. (1980)
n/a	Triassic	n/a	n/a	Israel	17.2	n/a	sulphate	Claypool et al. (1980)
n/a	Triassic	n/a	n/a	Israel	15.7	n/a	sulphate	Claypool et al. (1980)
n/a	Triassic	n/a	n/a	Utah USA	28.2	n/a	sulphate	Claypool et al. (1980)
n/a	Triassic	n/a	n/a	Utah USA	28.3	n/a	sulphate	Claypool et al. (1980)
n/a	Triassic	n/a	n/a	Europe	13.4	n/a	sulphate	Kampschulte and Strauss (2004)
n/a	Triassic	n/a	n/a	Europe	13.4	n/a	sulphate	Kampschulte and Strauss (2004)
n/a	Triassic	n/a	n/a	Europe	14.7	n/a	sulphate	Kampschulte and Strauss (2004)
n/a	Triassic	n/a	n/a	Europe	16.4	n/a	sulphate	Kampschulte and Strauss (2004)
n/a	Triassic	n/a	n/a	Europe	16.4	n/a	sulphate	Kampschulte and Strauss (2004)
n/a	Triassic	n/a	n/a	Europe	16.4	n/a	sulphate	Kampschulte and Strauss (2004)
n/a	Triassic	n/a	n/a	Europe	16.4	n/a	sulphate	Kampschulte and Strauss (2004)
n/a	Triassic	n/a	n/a	Europe	23.3	n/a	sulphate	Kampschulte and Strauss (2004)
n/a	Triassic	n/a	n/a	Europe	25.8	n/a	sulphate	Kampschulte and Strauss (2004)
n/a	Triassic	n/a	n/a	Europe	18.8	n/a	sulphate	Kampschulte and Strauss (2004)
-----	----------	-----	-----	--------	------	------	----------	--------------------------------------
n/a	Triassic	n/a	n/a	Europe	18.8	n/a	sulphate	Kampschulte and Strauss (2004)
n/a	Triassic	n/a	n/a	Italy	15.1	10.3	sulphate	Boschetti et al. (2011)
n/a	Triassic	n/a	n/a	Italy	15.9	11.2	sulphate	Boschetti et al. (2011)
n/a	Triassic	n/a	n/a	Italy	15.5	12.6	sulphate	Boschetti et al. (2011)
n/a	Triassic	n/a	n/a	Italy	15.7	11.4	sulphate	Boschetti et al. (2011)
n/a	Triassic	n/a	n/a	Italy	15.4	9.1	sulphate	Boschetti et al. (2011)
n/a	Triassic	n/a	n/a	Italy	17	12.9	sulphate	Boschetti et al. (2011)
n/a	Triassic	n/a	n/a	Italy	16	10.7	sulphate	Boschetti et al. (2011)
n/a	Triassic	n/a	n/a	Italy	15.1	10.4	sulphate	Boschetti et al. (2011)
n/a	Triassic	n/a	n/a	Italy	15.1	11	sulphate	Boschetti et al. (2011)

UWID	δ34S (VCDT)	Sample Depth (m; TVD)	Formation or Zone	Latitude	Logitude	Data Source
202/b-090-J 094-B-16/00	11.3	1474.0	Baldonnel	56.98368	-122.24734	This Study
200/a-079-F 094-G-01/00	15	1501.8	Baldonnel	57.14176	-122.35711	This Study
200/b-059-K 094-G-01/00	13.9	1391.2	Baldonnel	57.2098	-122.36378	This Study
200/b-037-F 094-G-01/00	14.4	1367.3	Baldonnel	57.11088	-122.33573	This Study
200/a-083-L 094-G-01/00	14.3	1838.5	Baldonnel	57.23389	-122.40684	This Study
200/a-004-D 094-G-08/00	15.2	1452.6	Baldonnel	57.25405	-122.41927	This Study
100/06-29-085-19W6/00	4.4	1372.5	Charlie Lake	56.39722	-120.97029	This Study
203/b-069-A 094-B-16/00	14.1	1697.4	Charlie Lake	56.80208	-122.10801	This Study
200/c-026-B 094-G-08/00	11.1	1542	Charlie Lake	57.2741	-122.19942	This Study
200/b-002-F 094-G-08/00	13.8	1900.5	Charlie Lake/Baldonnel	57.33417	-122.27313	This Study
200/c-064-C 094-G-08/00	13.4	1895.0	Charlie Lake/Baldonnel	57.30543	-122.30086	This Study
200/c-035-F 094-G-08/00	14.3	1684.5	Charlie Lake/Baldonnel	57.36422	-122.30901	This Study
200/d-032-E 094-G-08/00	12.4	1941.5	Charlie Lake/Baldonnel	57.36416	-122.3934	This Study
200/B-018-G 094-G-08/00	14.3	1451.7	Charlie Lake/Baldonnel	57.34403	-122.22437	This Study
202/c-084-B 094-G-08/00	13.4	1394.5	Charlie Lake/Baldonnel	57.32219	-122.17462	This Study
200/c-030-A 094-G-08/00	17.6	1544.5	Halfway	57.27391	-122.12338	This Study
200/d-095-B 094-G-08/00	17.7	1525.9	Halfway	57.33187	-122.17901	This Study
200/d-015-A 094-B-09/00	20.17	1599.5	Halfway	56.51629	-122.05164	This Study
200/a-061-C 094-G-01/00	14.6	1607.0	Halfway	57.05154	-122.25391	This Study
100/01-29-082-19W6/02	17.4	1794.5	Montney (Upper)	56.13250	-120.929690	This Study
100/01-29-082-19W6/02	16.9	1794.5	Montney (Upper)	56.13250	-120.929690	This Study
200/a-064-h 094-b-08/00	12.4	2127.6	Montney (Upper)	56.38534	-122.042120	This Study
200/a-064-h 094-b-08/00	12.5	2127.6	Montney (Upper)	56.38534	-122.042120	This Study
203/d-010-G 094-G-08/00	12.2	1707.8	Montney (Upper)	57.33831	-122.242510	This Study

Appendix B: Sulphur Isotopic Ratio for Hydrogen Sulphide Gas in Formations of WCSB.

202/с-050-В 094-G-08/00	11.4	1777.5	Montney (Upper)	57.29098	-122.250180	This Study
202/с-070-В 094-G-01/00	12.6	1827.6	Montney (Upper)	57.05420	-122.248120	This Study
200/c-089-C 094-G-01/00	14.1	1942.7	Montney (Upper)	57.07321	-122.360750	This Study
200/c-057-C 094-G-01/00	13.3	1919.1	Montney (Upper)	57.04778	-122.333910	This Study
202/b-100-К 094-G-07/00	14.7	1858.0	Montney (Upper)	57.49365	-122.875210	This Study
202/c-069-C 094-G-08/00	14.0	1794.8	Montney (Upper)	57.30685	-122.361710	This Study
100/14-05-080-17W6/00	14.7	2183.0	Montney (Upper)	55.91107	-120.623690	This Study
105/16-04-080-17W6/00	15.8	2167.5	Montney (Upper)	55.91047	-120.589920	This Study
102/04-15-072-09W6/00	14.4	2598.6	Montney (Upper)	55.23079	-119.305230	This Study
100/16-34-071-08W6/00	12.3	2442.8	Montney (Upper)	55.19846	-119.130820	This Study
100/16-34-071-08W6/00	12.6	2442.8	Montney (Upper)	55.19846	-119.130820	This Study
102/16-25-071-09W6/00	15.8	2507.7	Montney (Upper)	55.18300	-119.236910	This Study
100/02-15-072-09W6/00	14.8	2644.5	Montney (Upper)	55.23162	-119.294740	This Study
100/12-25-071-09W6/00	15.7	2570.8	Montney (Upper)	55.17811	-119.252130	This Study
102/04-15-072-09W6/00	14.4	2622.1	Montney (Upper)	55.23079	-119.305230	This Study
100/16-34-071-08W6/00	12.3	2442.8	Montney (Upper)	55.19846	-119.130820	This Study
102/16-34-071-08W6/00	12.6	2442.8	Montney (Upper)	55.19846	-119.130820	This Study
102/16-25-071-09W6/00	15.8	2507.7	Montney (Upper)	55.18300	-119.236910	This Study
100/08-03-071-08W6/00	14.8	2473.6	Montney (Upper)	55.11631	-119.131420	This Study
100/05-24-068-05W6/02	14.9	2353.9	Montney (Upper)	54.89891	-118.630140	This Study
100/05-24-068-05W6/02	15.2	2353.9	Montney (Upper)	54.89891	-118.630140	This Study
100/05-24-068-05W6/02	16.3	2353.9	Montney (Upper)	54.89891	-118.630140	This Study

202/a-091-D 094-H-05/00	16.7	1469.4	Montney (Upper)	57.32852	-121.846040	This Study
202/a-091-D 094-H-05/00	16.9	1469.4	Montney (Upper)	57.32852	-121.846040	This Study
200/a-054-H 094-B-08/00	20.9	2336.0	Montney (Middle)	56.37771	-122.041560	This Study
200/d-100-J 094-B-16/00	9.3	2042.5	Montney (Middle)	56.99588	-122.244410	This Study
100/08-03-071-08W6/00	14.8	2473.6	Montney (Middle)	55.11631	-119.131420	This Study
200/b-056-C 094-H-05/00	16.1	1555.4	Montney (Middle)	57.29443	-121.845010	This Study
200/b-056-C 094-H-05/00	17.2	1555.4	Montney (Middle)	57.29443	-121.845010	This Study
100/06-15-063-07W6/02	17.1	3807.1	Montney (Lower)	54.44887	-118.971560	This Study
100/13-23-080-17W6/02	13.2	2261.1	Montney (Lower)	55.95472	-120.553150	This Study
100/16-11-080-17W6/00	14.7	2324.9	Montney (Lower)	55.92461	-120.534820	This Study
100/10-30-079-17W6/00	15.4	2523.5	Montney (Lower)	55.87857	-120.647020	This Study
104/16-09-080-17W6/00	11.9	2357.4	Montney (Lower)	55.92495	-120.589830	This Study
102/09-26-079-17W6/00	15.8	2417.0	Montney (Lower)	55.87733	-120.535080	This Study
106/09-10-080-17W6/00	11.9	2314.6	Montney (Lower)	55.92219	-120.534080	This Study
100/07-30-079-17W6/00	12.9	2528.1	Montney (Lower)	55.87510	-120.600820	This Study
200/b-018-K 094-A-12/00	14.2	2037.8	Debolt	56.67705	-121.84799	This Study
202/c-060-K 094-A-12/00	14.5	2116.0	Debolt	56.71399	-121.8704	This Study
200/d-061-L 094-A-12/00	15.8	2098.9	Debolt	56.72258	-121.88058	This Study
200/d-086-D 094-A-13/00	15.9	2193.0	Debolt	56.82258	-121.9433	This Study
200/d-086-G 094-G-07/00	14.7	2008.5	Debolt	57.4074	-122.68933	This Study
200/d-086-B 094-G-10/00	16.8	1883.0	Debolt	57.57173	-122.69513	This Study
200/d-006-J 094-G-07/00	19.3	3350.8	Slave Point	57.42378	-122.68979	This Study
200/a-047-A 094-G-08/00	10.9	3235.5	Slave Point	57.28506	-122.07858	This Study
100/05-24-068-05W 6/02	15.2	n/a	Montney (undef.)	54.90731	-118.65807	Liseroudi et al. (2021)
100/05-24-068-05W 6/02	16.3	n/a	Montney (undef.)	54.90731	-118.65807	Liseroudi et al. (2021)

100/05-24-068-05W 6/02	14.9	n/a	Montney (undef.)	54.90731	-118.65807	Liseroudi et al. (2021)
100/06-15-063-07W6/02	17.1	n/a	Montney (undef.)	54.4335	-118.97201	Liseroudi et al. (2021)
100/12-25-071-09W6/00	15.7	n/a	Montney (undef.)	55.20054	-119.28031	Liseroudi et al. (2021)
100/02-15-072-09W6/00	14.8	n/a	Montney (undef.)	55.21331	-119.26439	Liseroudi et al. (2021)
102/04-15-072-09W6/00	14.4	n/a	Montney (undef.)	55.21331	-119.264	Liseroudi et al. (2021)
100/16-34-071-08W6/00	12.3	n/a	Montney (undef.)	55.2005	-119.18673	Liseroudi et al. (2021)
102/16-34-071-08W6/00	12.6	n/a	Montney (undef.)	55.2005	-119.18673	Liseroudi et al. (2021)
102/16-25-071-09W6/00	15.8	n/a	Montney (undef.)	55.20054	-119.28028	Liseroudi et al. (2021)
100/08-03-071-08W6/00	14.8	n/a	Montney (undef.)	55.1352	-119.16368	Liseroudi et al. (2021)
100/15-20-073-06W6/00	13.2	n/a	Montney (undef.)	55.34187	-118.8787	Liseroudi et al. (2021)
100/02-32-073-06W6/00	14.1	n/a	Montney (undef.)	55.36319	-118.88057	Liseroudi et al. (2021)
100/08-28-074-07W6/00	13.2	n/a	Montney (undef.)	55.43678	-119.00573	Liseroudi et al. (2021)
100/14-13-074-07W6/00	13.3	n/a	Montney (undef.)	55.41437	-118.93673	Liseroudi et al. (2021)
100/06-16-072-04W6/00	14.6	n/a	Montney (undef.)	55.23446	-118.55222	Liseroudi et al. (2021)
10007-22-073-04W6/00	14.7	n/a	Montney (undef.)	55.3351	-118.52421	Liseroudi et al. (2021)
100/13-14-074-11W6/00	14	n/a	Montney (undef.)	55.41509	-119.58353	Liseroudi et al. (2021)
100/09-33-074-11W6/00	14	n/a	Montney (undef.)	55.45718	-119.6207	Liseroudi et al. (2021)
100/13-23-080-17W6/02	13.2	n/a	Montney (undef.)	55.9409	-120.51626	Liseroudi et al. (2021)
100/09-11-080-17W6/00	14.7	n/a	Montney (undef.)	55.94274	-120.56966	Liseroudi et al. (2021)
104/16-09-080-17W6/00	11.9	n/a	Montney (undef.)	55.90477	-120.55158	Liseroudi et al. (2021)
100/07-30-079-17W6/00	12.9	n/a	Montney (undef.)	55.85505	-120.60082	Liseroudi et al. (2021)

100/10-30-079-17W6/00	15.4	n/a	Montney (undef.)	55.85505	-120.60066	Liseroudi et al. (2021)
102/09-26-079-17W6/00	15.8	n/a	Montney (undef.)	55.90036	-120.55626	Liseroudi et al. (2021)
100/08-02-080-17W6/00	11.9	n/a	Montney (undef.)	55.9046	-120.53496	Liseroudi et al. (2021)
105/16-04-080-17W6/00	15.8	n/a	Montney (undef.)	55.89995	-120.55503	Liseroudi et al. (2021)
100/14-05-080-17W6/00	14.7	n/a	Montney (undef.)	55.89664	-120.57978	Liseroudi et al. (2021)
100/06-34-072-08W6/00	9.7	2131	Doig	55.27909	-119.14206	Desrocher (1997)
100/16-34-072-08W6/00	9.5	2110	Doig	55.28366	-119.12926	Desrocher (1997)
100/06-14-074-12W6/00	22.8	2426.5	Doig	55.40783	-119.73476	Desrocher (1997)
100/08-27-073-12W6/00	22.9	2537	Doig	55.35224	-119.7495	Desrocher (1997)
100/10-22-073-12W6/00	21.7	2535.5	Doig	55.33833	-119.75085	Desrocher (1997)
100/06-29-073-08W6/00	8.1	2025.9	Halfway	55.34949	-119.19719	Desrocher (1997)
100/08-23-073-09W6/00	6.2	2151.3	Halfway	55.33724	-119.26219	Desrocher (1997)
100/14-14-073-09W6/00	6.9	2179.6	Halfway	55.32736	-119.27024	Desrocher (1997)
100/06-13-073-09W6/00	6.5	2166.4	Halfway	55.31973	-119.24997	Desrocher (1997)
100/06-13-073-05W6/00	7.9	1723	Halfway	55.32158	-118.63137	Desrocher (1997)
100/15-31-074-13W6/00	21	2501	Halfway	55.46086	-119.98273	Desrocher (1997)
100/12-20-074-12W6/00	23.6	2428	Halfway	55.42856	-119.81907	Desrocher (1997)
100/11-34-076-10W6/00	20.6	1937.8	Halfway	55.63221	-119.46754	Desrocher (1997)
100/06-15-072-05W6/00	12.2	1858.2	Halfway	55.23288	-118.6853	Desrocher (1997)
100/15-20-073-06W6/00	13.2	2094.5	Montney (undef.)	55.34187	-118.8787	Desrocher (1997)
100/02-32-073-06W6/00	14.1	2068.8	Montney (undef.)	55.3619	-118.88057	Desrocher (1997)
100/08-28-074-07W6/00	13.2	2135.2	Montney (undef.)	55.43678	-119.00573	Desrocher (1997)

100/14-13-074-07W6/00	13.3	2071.6	Montney (undef.)	55.41437	-118.93673	Desrocher (1997)
100/06-16-072-04W6/00	14.6	1984	Montney (undef.)	55.23446	-118.55222	Desrocher (1997)
100/07-22-073-04W6/00	14.7	1718	Montney (undef.)	55.3351	-118.52421	Desrocher (1997)
100/13-14-074-11W6/00	14	n/a	Montney (undef.)	55.41492	-119.58376	Desrocher (1997)
100/09-33-074-11W6/00	14	2551	Montney (undef.)	55.45718	-119.6207	Desrocher (1997)

# Appendix C: Detailed methodology of the kinetic model for kerogen conversion of the Doig Formation



# Hydrocarbon-Generation Kinetics of the Doig Formation, Northeastern British Columbia and West-Central Alberta

P.L. Silva<sup>1</sup>, The University of British Columbia, Vancouver, British Columbia, pablols@alumni.ube.ca R.M. Bustin, The University of British Columbia, Vancouver, British Columbia

Silva, P.L. and Bustin, R.M. (2020): Hydrocarbon-generation kinetics of the Doig Formation, northeastern British Columbia and westcentral Alberta; *in* Geoscience BC Summary of Activities 2019: Energy and Water, Geoscience BC, Report 2020-02, p. 65–76.

### Introduction

Reliable petroleum-system models require kinetic parameters of the reaction induced by thermal decomposition of kerogen into hydrocarbons to be calibrated to the source rock (Peters et al., 2018). Formation-specific kinetic parameters for the Doig Formation are not in the public domain; therefore, any previous attempt to model the hydrocarbon generation history would have required kinetic analyses to be undertaken or reliance on analogue data, both of which may produce erroneous results.

The Lower to Middle Triassic Doig Formation of the Western Canada Sedimentary Basin (WCSB) extends continuously across northeastern British Columbia (BC) and westcentral Alberta. Historically, the Doig and the underlying Montney formations were viewed as source rocks for other conventional reservoirs in the basin, mainly in other Triassic and Cretaceous strata (Du Rouchet, 1985; Creaney and Allan, 1990; Riediger et al., 1990; Edwards et al., 1994). With the industry shifting the focus of development to unconventional reservoirs, the Doig Formation has been recognized as an important resource of gas and natural-gas liquids. The Gas Technology Institute (Faraj et al., 2002) estimated the total gas-in-place in the Doig Formation at 4 trillion m<sup>3</sup> (140 tcf), whereas Walsh et al. (2006) estimated the total gas-in-place as ranging from 1.1 to 5.7 trillion m<sup>3</sup> (40-200 tcf). A more recent study by the United States Energy Information Administration (2013) estimated 2.8 trillion m<sup>3</sup> (100 tcf) of gas-in-place for the Doig Phosphate Zone alone.

This paper presents the results of the reaction kinetics parameter modelling for immature rocks of the Doig Formation source rock. The Doig kinetic parameters are compared with those published for other North American shale plays and the variability of activation energies is explained. This study is part of a broader research project on the Doig Formation petroleum system and the results of the reaction kinetics presented here provide the inputs required to proceed with the subsequent steps in modelling thermogenic hydrocarbon generation across the basin.

### **Geological Framework**

The Doig was deposited in the Middle Triassic, between the Anisian and Ladinian, and is part of the Diaber Group along with the underlying Montney Formation (Figure 1). The sedimentation in the Triassic of the WCSB is marked by a transition from earbonate-dominated intracratonic and passive-margin conditions, predominant during the Paleozoic, to a siliciclastic-dominated, active embryonic foreland basin. The Triassic succession was deposited in a series of three major third- or fourth-order transgressive-regressive cycles (Gibson and Barclay, 1989; Edwards et al., 1994). The interval from the Doig through the Halfway and Charlie Lake formations corresponds to the second cycle and the phosphatic interval at the base of the Doig represents a condensed section formed during the initial transgression of the second cycle (Gibson and Barclay, 1989).

The main elements that influenced the distribution of the Triassic interval were the underlying Devonian Leduc and Swan Hills reefs, and the Mesozoic reactivation of the Mississippian Dawson Creek graben complex (DCGC), which includes the Fort St. John graben and the Hines Creek graben. The DCGC formed in response to localized differential subsidence in the Peace River Embayment. The DCGC faults continued to be active during the Triassic, imposing significant controls on the distribution of sediments (Marshall et al., 1987; Barclay et al., 1990; Davies, 1997; Eaton et al., 1999). The Devonian reefs exerted a topographic influence on Triassic sedimentation by controlling facies changes (Davies, 1997), and may also have influence subsidence rates and, hence, thickness variation.

The Doig Formation consists of mudstone, siltstone and subordinate sandstone, bioclastic packstone and grainstone, deposited under marine conditions in environments ranging from shoreface through offshore (Evoy and Moslow, 1995). The Doig can be informally subdivided into three units, as proposed by Chalmers and Bustin

<sup>&</sup>lt;sup>1</sup>The lead author is a 2019 Geoscience BC Scholarship recipient. This publication is also available, free of charge, as colour digital files in Adobe Acrobat<sup>®</sup> PDF format from the Geoscience BC website: http://www.geosciencebc.com/updates/summary-ofactivities/.





Figure 1. Stratigraphic chart of the Triassic, in the subsurface of the Peace River area, northeastern British Columbia and adjacent areas (after Gibson and Barclay, 1989; Golding et al., 2015). Eustatic level based on Hardenbol et al. (1998). Abbreviations: Fm., Formation; Gp., Group.

(2012): the basal unit, Doig A, corresponding to the also informal but widely referred to 'Doig Phosphate Zone' (DPZ), composed of organic-rich radioactive dark mudstone with common phosphate granules and nodules (the DPZ is generally readily distinguishable in well logs by its high gamma-ray signature); the intermediate Doig B, primarily composed of medium to dark grey argillaceous siltstone and mudstone intercalated with localized sandstone; and the upper Doig C, composed of relatively organic-lean siltstone and argillaceous fine-grained sandstone. The DPZ is considered a good to excellent hydrocarbon source rock and an important source for many conventionally hosted hydrocarbons in the basin, including Triassic strata, such as Halfway, Charlie Lake and Doig sands. Previous studies found type II oil and gas-prone kerogen with total organic carbon content ranging from 1.8 to 11 wt. % (Riediger et al., 1990; Faraj et al., 2002; Ibrahimbas and Riediger, 2004).

### **Material and Methods**

Twenty-three samples were selected for reaction-kinetics analysis through multiple heating-ramp open-system pyrolysis. These samples cover a significant portion of the Doig Formation subcrop area and a wide range of maturitics (Figure 2), as well as all its stratigraphic subdivisions (Figure 3). The samples were chosen from among more than 440 analyses carried out on cuttings and whole-rock core using the Rock-Eval pyrolysis method (Espitalié et al., 1977), based on sharpness and intensity of the kerogen conversion peak, and a wide range of hydrogen index (HI) and oxygen index (OI) values to capture all of the pseudo-van Krevelen kerogen types identified (Figure 4). Samples were classified in discrete kerogen-type categories based on the pseudo-van Krevelen crossplot. Approximately 70 mg of powdered bulk rock (i.e., not concentrated kerogen) of each sample was pyrolyzed, using a HAWK® instrument from Wildcat Technologies, at 5°C, 25°C and 45°C per minute to 600-700°C, following an isothermal plateau of up to 260-310°C to purge free hydrocarbons. The pyrolysis curves were trimmed in the time domain and the flame-ionization detector signal was baseline corrected, smoothed, integrated and processed using the commercially sourced Kinetics2015 software (GeoIsoChem Corporation, 2019). Reaction-activation energies and pre-exponential factors were modelled through a distributedreactivity method (Braun and Burnham, 1987; Ungerer and Pelet, 1987) with a fixed activation energy (E) spacing of 1 kcal/mol, and an isoconversional method (Friedman, 1964; Vyazovkin and Lesnikovich, 1988), assuming a scries of parallel first-order reactions in 0.01 conversionfraction increments, to determine the variation of activation energy as a function of conversion.

## **Results and Discussion**

Approximately half of the samples analyzed are of kerogen type II, as determined by hydrogen- and oxygen-index evo-





Figure 2. Location of wells from which samples were selected for reaction kinetics analysis in northeastern British Columbia and adjacent area, against a backdrop of the Doig Formation thermal-maturity map (after Silva and Bustin, 2018) and main structural elements that influenced the Triassic deposition (after Davies, 1997). Cross-sections shown in Figure 3 indicated by A–A' and B–B'. Abbreviation: Prec., Precambrian.

Geoscience BC Report 2020-02



Geoscience BC





Geoscience BC Report 2020-02



lution paths, whereas one third is of type III. The remaining are classified as type II/III, due to either kerogen mixing, contamination or high maturity causing points to plot too close to the origin. The median value of the activation energy of all Doig samples analyzed ranges from 51 to 67 kcal/mol with a pre-exponential factor that varies from  $5.3 \times 10^{13}$  to  $2.7 \times 10^{18}$  (Figure 5). The correlation between the median activation-energy and frequency factor is log linear, with an r<sup>2</sup> of 0.98. The activation-energy distribution of kerogen type II samples is noticeably narrower than that of type III, with median values ranging from 53 to 63 kcal/ mol. The precision of the global kinetic parameters was determined by repeated analyses of a standard sample. The 95% confidence interval (i.e., two standard deviations divided by the median) is  $\pm 1.2$  kcal/mol around the median activation-energy value of 55 kcal/mol, and within a factor of 2 for the average frequency factor of  $2 \times 10^{15}$ .

There is a clear thermal-maturity influence on the activation-energy distributions, despite a scatter of up to 5 kcal/ mol for a given temperature of maximum rate of hydrocarbon-generation ( $T_{max}$ ) value (Figure 6). The correlation is obscured due to variations in activation energies introduced by mixture of kerogen types during deposition, and possibly to cross-contamination between cuttings samples of different depths containing different kerogen types. Nonetheless, it is possible to distinguish two different trends and generate linear regressions for kerogen types II (blue dashed line in Figure 6) and III (black dashed line in Figure 6), with  $r^2$  values of 0.49 and 0.22, respectively. The lowest maturity samples analyzed in this study, for which kerogen type can be determined with reasonable confidence, fall between 438 and 439°C. By comparing the extrapolated trends for kerogens type II and type III to thermally immature samples (i.e., lower than 430°C) from the literature, there appears to be an inflection point in the decreasing activation energy, with decreasing maturity levelling off at approximately 435°C.

Due to a shift toward higher activation energies as thermal maturation progresses, the standard deviation of the activation-energy distributions for each sample also has a positive correlation with  $T_{max}$  values. Similarly to the regression of median activation energies, a distinct trend can be generated for kerogen type II (Figure 7) and a less well-defined trend for type III (Figure 7), with  $r^2$  values of 0.54 and 0.25, respectively.

Based on the regression of median and standard deviation values for different maturities, the median activation energies ( $\tilde{E}$ ) and standard deviation ( $\sigma_E$ ) of lower maturity type II (equations 1 and 2) and III (equations 3 and 4) kerogens of the Doig Formation can be determined as a function of  $T_{max}$  according to the following equations:

- $\bar{E}_{typeII} = -108.98 + (0.37 \times T_{max})$  (1)
- $\sigma_{E \text{ type II}} = -38.53 + (0.0930 \times T_{\text{max}})$ (2)
- $\bar{E}_{typeIII} = -137.34 + (0.44 \times T_{max})$  (3)
- $\sigma_{E \text{ type III}} = -27.14 + (0.0687 \times T_{\text{max}})$ (4)

Based on the 435°C inflection point in the decreasing trend of the median activation energy with decreasing maturity, median values of activation-energy distributions are deter-



Figure 5. Pre-exponential factor versus median activation-energy crossplot of all samples, and frequency distribution of all activation energies classified by kerogen type.



Geoscience BC

Figure 6. Crossplot of median activation energy versus Rock-Eval pyrolysis T<sub>max</sub> of the Doig Formation samples from the study area in northeastern BC and west-central Alberta, and select samples from other kerogen-rich rocks from literature for comparison (Tegelaar and Noble, 1994; Burrus et al., 1996; Schenk and Dieckmann, 2006; Dieckmann, 2005; Hill et al., 2007; Nordeng, 2012), showing the trend of decreasing activation energies toward lower maturity samples. Data points from the study area samples are plotted as the median value of the distribution, thin the 80%; shape as verticed has the median value of the distribution. Burant et al. (1996; Schenk and Dieckmann, 2006; Bull et al., 2007; Vorteng, 2012), and parter as the reading value of the distribution. Burant et al. (1997) and Petersen (2003).

Geoscience BC Report 2020-02

71





Figure 7. Crossplot of the standard deviation of the activation-energy distributions versus Rock-Eval pyrolysis  $T_{max}$  of the Doig Formation samples from the study area in northeastern BC and west-central Alberta, showing the trend of decreasing standard deviations toward lower maturity samples. Blue and black dashed lines represent the linear regression for type II and type III kerogens, respectively. Boundaries between generation windows for different kerogen types are after Dow (1977) and Petersen (2003).

mined to be 52 and 54.1 kcal/mol for immature kerogen of types II and III, respectively. Conversely, the standard deviations for immature type II and type III are determined to be 1.93 and 2.75 kcal/mol, respectively. Based on these statistical parameters, synthetic activation-energy Gaussian distributions were created for kerogen types II and III of the Doig Formation (Figure 8).

The wider activation-energy distributions of kerogen type III are not only evident on the discrete activation-energy distribution histograms but can also be observed in the reaction profile generated by the isoconversional kinetic modelling. The isoconversional results are plotted as a single activation energy for conversion rates from 10 to 90% (Figure 9), since the first and last 10% values are often unreliable due to analytical noise in the data (Burnham, 2017). This profile shows that for lower present-day maturity samples, predominant activation energies range from 40 to 58 kcal/mol at 10% conversion. These lower activation energies are associated with samples predominantly of kerogen type III and are likely the product of the breaking of C-O bonds, and possibly C-S bonds. Activation energies at 10% conversion for most lower present-day maturity kerogen type II samples are higher than 50 kcal/mol. At 50% conversion, lower maturity samples have activation energies in the 48 to 60 kcal/mol range. Within this conversion range, bitumen decomposition is probably the cause of the narrower spread and large overlap between activation

energies of kerogen types II and III. At 90% conversion, the high end of activation-energy distributions of type III kerogen causes the spread of dominant activation energies to increase again, ranging from 52 to 90 kcal/mol for low present-day maturities. The results of this study suggest that mixing between kerogen types II and III in the Doig Formation translates into an early hydrocarbon-generation window due to the low activation energies of type III. Furthermore, the kerogen mixing extends the generation process over a broader temperature range due to the combined effect of the lower end of type II activation energies and upper end of those of type III.

### **Ongoing Work**

The work presented here will serve as foundation for a reconstruction of the Doig Formation thermal history through basin modelling. The modelled kerogen activation-energy distributions for different types of kerogen will be used as reaction-kinetics input for the model thermalmaturation simulation, providing reliable source-rock-calibrated parameters, thus decreasing the uncertainty related to timing and type of hydrocarbons generated across the basin.





Figure 8. Histograms of modelled activation-energy distributions of the Doig Formation, northeastern British Columbia and west-central Alberta, based on samples of varying degrees of maturity: Top, immature kerogen type II; Bottom, immature kerogen type III.

## Acknowledgments

The authors acknowledge financial support from Geoscience BC, Canadian Natural Resources Limited, Chevron Canada Limited, Devon Energy Corporation, EnCana Corporation, geoLOGIC systems ltd., Husky Energy Inc. and AGAT Laboratorics. The donation of software by geoLOGIC systems ltd. and Paradigm Geophysical Canada Limited was also instrumental in handling the well and core data, and greatly appreciated. The authors would also like to acknowledge the time and effort dedicated to the thorough review of the manuscript by G. Chalmers, research associate at The University of British Columbia.

Geoscience BC Report 2020-02





Figure 9. Kerogen conversion profile, showing reaction progress generated by the isoconversional method.

### References

- Barclay, J.E., Krause, F.F., Campbell, R.I. and Utting, J. (1990): Dynamic casting of the Dawson Creek Graben Complex: Carboniferous–Permian Peace River Embayment, western Canada; Bulletin of Canadian Petroleum Geology, v. 38(A), p. 115–145.
- Braun, R.L. and Burnham, A.K. (1987): Analysis of chemical reaction kinetics using a distribution of activation energies and simpler models; Energy and Fuels, v. 1, no. 2, p. 153–161.
- Burnham, A.K. (2017): Global Chemical Kinetics of Fossil Fuels: How to Model Maturation and Pyrolysis (1<sup>st</sup> edition); Springer-Verlag, 315 p.
- Burrus, J., Wolf, S., Osadetz, K. and Visser, K. (1996): Physical and numerical modelling constraints on oil expulsion and accumulation in the Bakken and Lodgepole petroleum systems of the Williston Basin (Canada-USA); Bulletin of Canadian Petroleum Geology, v. 44, no. 3, p. 429–445.
- Chalmers, G.R.L. and Bustin, R.M. (2012): Geological evaluation of Halfway–Doig–Montney hybrid gas shale-tight gas reservoir, northeastern British Columbia; Marine and Petroleum Geology, v. 38, no. 1, p. 53–72.
- Creancy, S. and Allan, J. (1990): Hydrocarbon generation and migration in the Western Canada sedimentary basin; *in* Classic Petroleum Provinces, J. Brooks (ed.), Geological Society of London, Geological Society Special Publications, v. 50, p. 189–202.
- Davies, G.R. (1997): The Triassic of the Western Canada Sedimentary Basin: tectonic and stratigraphic framework, paleogeography, paleoclimate and biota; Bulletin of Canadian Petroleum Geology, v. 45, no. 4, p. 434–460.

- Dieckmann, V. (2005): Modelling petroleum formation from heterogeneous source rocks: the influence of frequency factors on activation energy distribution and geological prediction; Marine and Petroleum Geology, v. 22, no. 3, p. 375–390.
- Dow, W. (1977): Kerogen studies and geological interpretations; Journal of Geochemical Exploration, v. 7, p. 79–99.
- Du Rouchet, J. (1985): The origin and migration paths of hydrocarbons accumulated in the Lower Cretaceous sandstone 'giant' tar accumulations of Alberta – Part II; Journal of Petroleum Geology, v. 8, no. 1, p. 101–114.
- Eaton, D.W., Ross, G.M. and Hope, J. (1999): The rise and fall of a cratonic arch: a regional seismic perspective on the Peace River Arch, Alberta; Bulletin of Canadian Petroleum Geology, v. 47, no. 4, p. 346–361.
- Edwards, D.E., Barclay, J.E., Gibson, D.W., Kvill, G.E. and Halton, E. (1994): Triassic strata of the Western Canada Sedimentary Basin; Chapter 16 in Geological Atlas of the Western Canada Sedimentary Basin, G.D. Mossop and I. Shetsen (comp.), Canadian Society of Petroleum Geologists and Alberta Research Council, Edmonton, Alberta, p. 257–275, URL <a href="https://ags.aer.ca/publications/chapter-16-triassic-strata">https://ags.aer.ca/publications/chapter-16-triassic-strata</a>[October 2018].
- Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J. and Boutefeu, A. (1977): Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution; Revue de l'Institut Français du Pétrole, v. 32, no. 1, p. 23–42.
- Evoy, R.W. and Moslow, T.F. (1995): Lithofacies associations and depositional environments in the Middle Triassic Doig Formation, Buick Creek Field, northeastern British Columbia; Bulletin of Canadian Petroleum Geology, v. 43, no. 4, p. 461–475.



- Faraj, B., Harold, W., Addison, G., McKinstry, B., Donaleshen, R., Sloan, G., Lee, J., Anderson, T., Leal, R., Anderson, C., Lafleur, C. and Ahlstrom, A. (2002): Shale gas potential of selected Upper Cretaceous, Jurassic, Triassic and Devonian shale formations in the WCSB of Western Canada: implications for shale gas production; Gas Technology Institute, Report GRI-02/0233, 258 p.
- Friedman, H.L. (1964): Kinetics of thermal degradation of charforming plastics from thermogravimetry: Application to a phenolic plastic; Journal of Polymer Science, v. 6, no. 1, p. 183–195.
- GeoIsoChem Corporation (2019): Kinetics2015: chemical reaction kinetics analysis and applications; GUI-based computer program for Windows, URL <a href="http://www.geoisochem.com/software/kinetics2015/index.html">http://www.geoisochem.com/ software/kinetics2015/index.html</a> [November 2019].
- Gibson, D.W. and Barclay, J.E. (1989): Middle Absaroka sequence – the Triassic stable craton; *in* Western Canada Sedimentary Basin – A Case History, B.D. Ricketts, (ed.), Canadian Society of Petroleum Geologists, Calgary, Special Publication, p. 219–232.
- Golding, M.L., Orchard, M.J., Zonneveld, J.P. and Wilson, N.S.F. (2015): Determining the age and depositional model of the Doig phosphate zone in northeastern British Columbia using conodont biostratigraphy; Bulletin of Canadian Petroleum Geology, v. 63, no. 2, p. 143–170.
- Hardenbol, J., Thierry, J., Farley, M.B., Jacquin, T., De Graciansky, P.-C. and Vail, P.R. (1998): Cenozoic sequence chronostratigraphy; *in* Mesozoic and Cenozoic Sequence Chronostratigraphic Framework of European Basins, P.C. De Graciansky, J. Hardenbol, T. Jacqui and P.R. Vail (ed.), Society for Sedimentary Geology, SEPM Special Publication 60, p. 3–13.
- Hill, R.J., Zhang, E., Katz, B.J. and Tang, Y. (2007): Modeling of gas generation from the Barnett Shale, Fort Worth Basin, Texas; American Association of Petroleum Geologists Bulletin, v. 91, no. 4, p. 501–521.
- Ibrahimbas, A. and Riediger, C. (2004): Hydrocarbon source rock potential as determined by Rock-Eval 6/TOC pyrolysis, northeast British Columbia and northwest Alberta; *in* Summary of Activities 2004, British Columbia Ministry of Energy, Mines and Petroleum Resources, Resource Development and Geoscience Branch, p. 7–18.
- Marshall, G.M., Noble, I.A.R. and Tang, C.W. (1987): Triassic/Jurassic fields; Chapter 7 in Geophysical Atlas of Western Canadian Hydrocarbon Pools, N.L. Anderson, L.V. Hills and D.A. Cederwall (ed.), Canadian Society of Exploration Geophysicists and Canadian Society of Petroleum Geologists, Calgary, Alberta, p. 187–215, URL <a href="https://cseg.ca/assets/files/atlas/L\_Chapter\_7.pdf">https://cseg.ca/assets/files/atlas/L\_Chapter\_7.pdf</a> [October 2018].
- Nordeng, S.H. (2012): Determination of activation energy and frequency factor for samples of the Bakken Formation (Miss.-

Dev.): Williston Basin, ND; North Dakota Geological Survey, Geological Investigations No. 163, 15 p.

- Peters, K.E., Burnham, A.K., Walters, C.C. and Schenk, O. (2018): Guidelines for kinetic input to petroleum system models from open-system pyrolysis; Marine and Petroleum Geology, v. 92, p. 979–986.
- Petersen, H.I. (2003): A reconsideration of the 'oil window' for humic coal and kerogen type III source rocks; Journal of Petroleum Geology, v. 25, no. 4, p. 407–432.
- Riediger, C.L., Fowler, M.G., Brooks, P.W. and Snowdon, L.R. (1990): Triassic oils and potential Mesozoic source rocks, Peace River Arch area, Western Canada Basin; Organic Geochemistry, v. 16, no. 1–3, p. 295–305.
- Schenk, H.J. and Dieckmann, V. (2004): Prediction of petroleum formation: The influence of laboratory heating rates on kinetic parameters and geological extrapolations; Marine and Petroleum Geology, v. 21, no. 1, p. 79–95.
- Silva, P.L. and Bustin, R.M. (2018): Preliminary liquid hydrocarbon potential assessment of the Doig Formation, northeastern British Columbia and west-central Alberta, based on thickness, organic richness and maturity; *in* Geoscience BC Summary of Activities 2017: Energy, Geoscience BC, Report 2018-04, p. 39–50, URL <a href="http://www.geoscience">http://www.geoscience</a> bc.com/i/pdt/SummaryofActivities2017/Energy/ SoA2017\_E\_Silva.pdf> [October 2019].
- Tegelaar, E.W. and Noble, R.A. (1994): Kinetics of hydrocarbon generation as a function of the molecular structure of kerogen as revealed by pyrolysis-gas chromatography; Organic Geochemistry, v. 22, no. 3–5, p. 543–574.
- Ungerer, P. and Pelet, R. (1987): Extrapolation of kinetics of oil and gas formation from laboratory experiments to sedimentary basins; Nature, v. 327, p. 52–54.
- United States Energy Information Administration (2013): Technically recoverable shale oil and shale gas resources: an assessment of 131 shale formations in 41 countries outside the United States; United States Department of Energy, 76 p., URL <https://www.eia.gov/analysis/studies/worldshale gas/pdf/overview.pdf> [October 2018].
- Vyazovkin, S.V. and Lesnikovich, A.I. (1988): Estimation of the pre-exponential factor in the isoconversional calculation of effective kinetic parameters; Thermochimica Acta, v. 128, p. 297–300.
- Walsh, W., Adams, C., Kerr, B. and Korol, J. (2006): Regional "shale gas" potential of the Triassic Doig and Montney formations, northeastern British Columbia; BC Ministry of Energy Mines and Petroleum Resources, Oil and Gas Division, Resource Development and Geoscience Branch, Open File 2006-0, 19 p., URL <a href="https://www2.gov.bc.ca/assets/gov/farming-natural-resources-and-industry/natural-gas-oil/petroleum-geoscience/petroleum-open-files/pgof200">https://www2.gov.bc.ca/assets/gov/farming-natural-resources-and-industry/natural-gas-oil/ petroleum-geoscience/petroleum-open-files/pgof200</a> 62.pdf [October 2018].

Geoscience BC Report 2020-02