RESEARCH ARTICLE

Origin and significance of barium, boron and lithium in Montney formation flowback water, Western Canada

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ABSTRACT

The Ba, B and Li concentrations in produced water (formation water) and flowback water following hydraulic fracturing of 24 Montney formation horizontal wells in Northeast British Columbia (BC) were investigated. The wells were drilled and completed in the upper, middle or lower Montney formation utilizing mainly freshwater or blended freshwater and recycled flowback water. The concentration of Ba, B and Li are more regionally variable than the major ion chemistry in the flowback water. The Ba concentrations in the flowback waters, range from below the detection limit (<1 mg/L) up to 467 mg/L. There is generally an increase in Ba concentration in the flowback water over the flowback period for each of the study wells, although considerable variability exists between different sites and there is no consistent variation in Ba content in flowback waters between wells completed in the upper, middle or lower members. Regionally, Ba concentrations in the flowback water generally show a decreasing trend from the Northwestern to the Southeastern sites, a distance of about 350 km. Longer shut-in periods also correlates with a higher Ba concentration in the initial flowback water samples (R^2=0.37) due to greater opportunity for mixing of formation water and fracturing fluid. There is a negative correlation between Ba and SO_4 concentrations for the flowback water reflecting the importance of SO_4 reduction on the concentrations of these ions; SO_4 reduction increases barite solubility due to the removal of SO_4 ions from solution. However, saturation calculations indicate that both barite dissolution and/or precipitation is occurring in different wells and for some wells, at different flowback times. The increasing Ba concentrations in flowback water thus is likely a product of both barite dissolution and the increasing proportion of formation water with time, while the SO_4 concentrations are impacted by a combination of pyrite oxidation, bacterial SO_4 reductionand barite precipitation/dissolution.

The B concentrations in the flowback waters range from 3.1 mg/L to 38 mg/L and increase in parallel with increasing TDS over the flowback period for most wells. For a given site, the B concentration varies between flowback waters from the different Montney members, but the trend is not consistent between sites. The B concentrations in the Montney formation flowback water increases regionally across the study area from the Northwestern sites to the Southeastern site.

Li concentrations in the flowback water are <20 mg/L for most sites and are less variable between wells than either the concentration of Ba or B. B and Li are strongly, although variably, linearly correlated at the different study sites. Overall, there is a trend from the Northwestern region of high Li and low B to the Southeastern region with low Li and high B. No B or Li containing minerals are close to saturation in any of the produced or flowback waters. The increasing B and Li concentration with increasing TDS indicates that the concentration of both ions mainly reflects the relative amount of formation water contributing to the flowback water. The origin of both B and Li and the variable B/Li ratio in the flowback and formation water is however equivocal. Both B and Li ions are present in organic matter and can be released under high temperatures and although there is moderate correlation (R^2=0.58) between B and reservoir temperature, there is no correlation with Li concentrations (R^2<0.01) and reservoir temperature. Substitution of B and Li ions in smectite illite diagenesis and ion exchange, also at best accounts for minor variation in these ion concentrations as suggested by lack of correlation of either B and Li concentrations with clay content and the overall low clay abundance (<<25%) in the formation.

Keywords: Montney formation; Barium; Boron; Pyrite oxidation; Lithium

INTRODUCTION

Following hydraulic fracturing of unconventional oil and gas wells, the fluid is flowed back to the surface prior to the well-being tied into a production gathering system. The liquid recovered at surface prior to production is referred to as flowback water. The flowback water has elevated Total Dissolved Solids (TDS) due to the high concentrations of the major ions, including Chloride (Cl), Sodium (Na), Calcium (Ca), Potassium (K), Magnesium (Mg) and Strontium (Sr). If the well is hydraulically fractured with a freshwater based fluid, the ion concentration normally increases during the flowback period due to mixing between the injected hydraulic fracturing fluid and the formation connate water. Additionally, the flowback fluid chemistry is more or less impacted by fluid-rock interactions that may include mineral precipitation and dissolution and ion exchange. Previous studies of the inorganic chemistry of flowback water have focused on the major ions. Some studies have also characterized the Naturally Occurring Radioactive Materials (NORM) and trace elements in flowback water, both of which may be important to consider for the storage and recycling of flowback water. The minor ions and most notably Barium (Ba), Boron (B) and Lithium (Li) can occur in significant concentrations and provide insight as to the origin of the flowback water, reservoir dynamics during completion and flowback, fluid-rock interactions and possible contamination. Barium, for example, is often high in flowback water (>100 mg/L) and shows more variability between wells in a particular formation relative to the major cations. Boron (B) and lithium (Li), may be useful in distinguishing the fluid from hydraulically fractured wells from surface water or from water produced from conventional oil and gas wells by examining the B/Cl and Li/Cl ratios and the B and Li isotopic values of the fluids.

To understand fluid rock interactions during hydraulic fracturing and their impact on production and possibly groundwater, we have undertaken a basin wide study of the flowback fluids following hydraulic completions of the lower triassic Montney formation. The Montney formation is the most important unconventional gas and hydrocarbon liquids producing shale in the Western Canadian sedimentary basin and currently accounts for one-third of all the gas produced in Canada. In this study, flowback fluids were sampled from 24 wells located at 9 sites (Figure 1). All the wells samples in

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this study were drilled horizontally and completed in between 14 to 26 isolated stages. All the stages in each well were completed prior to flowing the wells back. The studied wells were drilled and completed in either the upper (13 wells), middle (9 wells) or lower (2 wells) parts of the Montney formation.

The present paper focusses on Ba, B and Li concentrations in flowback water from the Montney formation in Northeast British Columbia (BC) and Northwest Alberta. The three minor ions Ba, B and Li were selected for study as these ions are often elevated (>10 mg/L) in the Montney formation flowback water sampled in our study and show more variability between different regions or between different members of the Montney formation compared to the major ions. High concentrations of these elements are not unique to Montney formation flowback water as they are commonly elevated in flowback water from other hydraulically fractured formations.

Geology

The Montney formation is a Lower triassic section of dominantly dolo-siltstone and fine-grained sandstone, deposited along the Northwestern coast of Pangea in a marine inner to distal shelf environment. The Montney formation uncomfortably overlies the Permian Belloy formation and is in turn overlain by the Doig phosphate zone of the middle Triassic Doig formation. In the eastern part of the study area, the Montney formation is unconformable overlain by a variety of younger units.

Recent stratigraphic studies of the Montney formation divide the formation into lower, middle and upper informal members, each representing a third-order sequence. The division into these three informal members is used in the present study. Flowback water samples for this study were obtained from two lower Montney member wells, eleven middle Montney member wells and eighteen upper Montney member wells. The wells are located on nine well pads across the formation with one to eight wells sampled per pad (Figures 1 and 2).

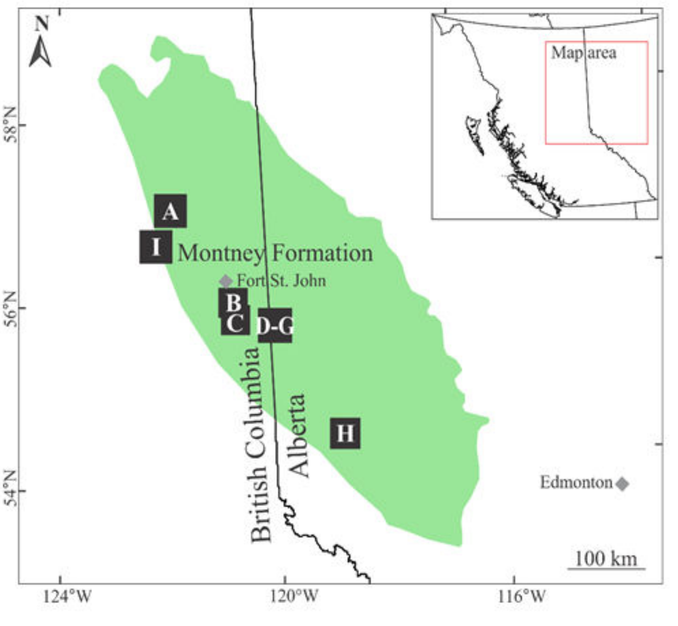

Figure 1: Location of the study sites in northeastern BC and Northwestern Alberta. Fluid samples were collected from 9 sites in the Montney formation. Sites with upper Montney member wells include: Site A: (8 wells); site B: (2 wells); Site C: (5 wells); site D: (2 wells) and site H: (1 well). The sites with middle Montney member wells include site C (2 wells), site D (2 wells), site E (4 wells), site F (2 wells) and site G (1 well). The lower Montney member wells include the two wells at site I.

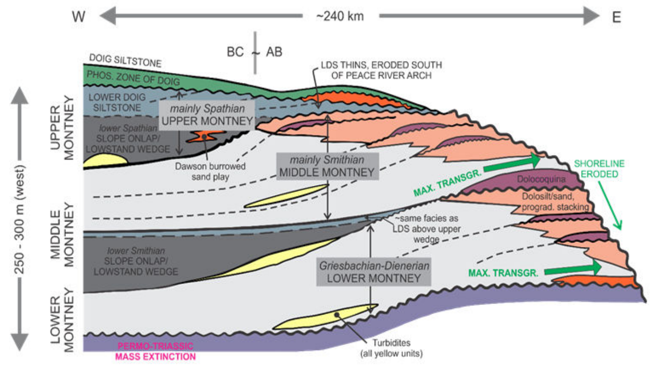

Figure 2: Schematic cross-section of the Montney formation in BC and Alberta. The formation is divided into the lower, middle and upper Montney formation informal members based on three third-order sequences, determined by lithostratigraphy and biostratigraphy. The upper Montney member includes the lower Doig siltstone and underlies the Doig phosphate zone. This member thins to the east and is absent in Eastern locations in Alberta. Overall, the formation becomes coarser grained moving from west to east, towards the paleo-shoreline.

MATERIALS AND METHODS

Fluid chemistry

Hydraulic fracturing fluids, comprised of the base liquid with additives, were collected from all sites, except for site C. For sites A, B, D, E, G and H a separate sample of the fluid used in each of the stages of the fracturing program was collected (14 to 26 samples per well). The overall Ba, B and Li concentrations of the fracturing fluid were calculated by integrating the volume and ion concentrations for all frac stages per well. Only one hydraulic fracturing fluid sample was obtained for the site F wells and each of the site I wells.

Flowback water samples were collected from all sites over the flowback period, which ranged between one day and 33 days. A higher sampling frequency of two to three samples per day was utilized early in the flowback period in order to capture the variation in fluid chemistry when flowback rates are high. After one week of flowback, sampling frequency was reduced to one sample per day. Produced water samples were collected from the site A wells, the site B wells and a well approximately 20 km away from site I. No produced water samples were available from wells at other sites. Hence, for these wells, produced water results were compiled from public data for wells completed in the Montney formation within approximately 20 km of the study wells in order to provide an estimate of the produced water chemistry. However, the public data are generally limited to the major cations and only rarely include Ba concentrations and never B or Li.

All samples were stored at 4°C following collection and prior to analysis. As filtering and sample preservation was not conducted at the time of sampling at the well site, the flowback and produced water samples were heated in Teflon® containers in a hot water bath back to reservoir temperature (75°C-80°C) prior to analysis. This step was conducted to approximate reservoir temperatures to re-dissolve any precipitate that had formed during sample transportation and storage. The hydraulic fracturing fluids were not heated. All samples were filtered and subsampled for the separate analyses: a) anions; b) pH, electrical conductivity and alkalinity; and c) dissolved metals. The anion samples were analyzed by ion chromatography at an external laboratory whereas the remaining analyses were conducted at our laboratory at The University of British Columbia (UBC) in Vancouver. The pH was measured using an OMEGA® PHB21 portable pH meter, the electrical conductivity was measured using a HACH® CDC401 conductivity probe and the alkalinity was determined by titrating the sample with sulfuric acid (H_2SO_4) using a HACH® Model 16900 digital titrator. The dissolved metal samples were preserved with trace metal grade nitric acid (HNO_3) to pH<2. The preserved samples were acid digested with HNO_3 and Hydrochloric acid (HCl) to eliminate interference by the organic molecules in the analysis. The major cations and Ba, B and Li concentrations were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) using a varian 725-ES ICP-OES.

Montney formation mineralogy

The study wells were not cored therefore mineralogy is not available directly from these wells. To obtain an approximation of the mineralogy of the completed zones of the study wells, publicly available X-Ray Diffraction (XRD) data were compiled from nearby wells completed in the same stratigraphic interval of the Montney formation. Gaps in the publicly available data were identified near site A and for the upper Montney member at site C and site D. Thus, samples from wells nearby these sites were obtained from the BC oil and gas commission core research facility in Fort St. John, BC and their mineralogy were determined using the modified smear mount method at UBC using a Bruker D8 focus X-ray powder diffractometer. The results were quantified using the Rietveld method. Select samples were examined with Philips XL30 Scanning Electron Microscope (SEM).

The potential for barite precipitation or dissolution was investigated by calculating the barite Saturation Indices (SI) of the flowback water samples. All Saturation Index (SI) values were calculated using the flowback water chemistry in PHREEQC, version 3.2.0 at a reservoir temperature of 75°C using the Pitzer database due to the high ionic strength of the formation water [1-5].

Major ion chemistry of the Montney formation flowback water

The dominant ions in Montney formation flowback water are Cl, Na, Ca, K, Mg and Sr (Table 1). Wells completed at the same site and within the same member of the Montney formation generally have similar major ion chemistry. Overall, the major ion concentrations are slightly higher in the upper Montney member flowback water for most, but not all study wells. Sr concentrations in the upper Montney member flowback water range from high concentrations in the Northwestern part of the study area to low concentrations in the southeastern region of the study area.

The concentrations of the major ions increase during the flowback period for all of the study wells, which is mainly due to mixing between the injected hydraulic fracturing fluid and the formation water. Mixing has previously been suggested as the source of increasing TDS and ion concentrations in flowback water by others. The injected hydraulic fracturing fluids for the wells in our study were composed of a freshwater based fluid for well A-3, the site C wells, wells D-1 through D-3, well H-1 and the site I wells and a blend of freshwater with recycled flowback water for the remaining site A wells, the site B wells, well D-4 and the sites E, F and G wells. The TDS of the initial flowback water is either close to or higher than the injected hydraulic fracturing fluid TDS for all wells. The chemistry of the injected fluid impacts the initial flowback water chemistry, with higher injected fluid major ion concentrations resulting in higher initial flowback water concentrations for Cl, Ca, Mg and Sr [6,7].

The length of the shut-in period is the dominant determinant of the flowback chemistry; longer shut-in periods correlate to higher initial TDS and major ion concentrations, likely due to a longer time for fluid mixing in the fractures and countercurrent imbibition. The increasing contribution from formation water over the flowback period was calculated for the study wells using Cl and the stable water isotopes ($\delta^{18}O$ and $\delta^{2}H$) as conservative tracers. In general, the proportion of formation water increases to approximately 60% of the flowback water by the end of the flowback period. Mixing between the hydraulic fracturing fluid and the formation water is interpreted to be the dominant influence on Montney formation flowback water chemistry. However, the concentration of divalent ions (Ca, Mg and Sr) is also influenced by ion exchange with Na as evident from their lower concentrations in the early time flowback water relative to the concentrations predicted from conserved element mixing models.

Sulfate (SO_4) concentrations are not elevated in all wells (Table 1) and display no consistent increase in concentration with flowback time as found with other ions. For the study wells, the SO_4 concentrations are interpreted to be the result of pyrite oxidation as well as bacterial SO_4 reduction in response to the introduction of oxygenated fracturing fluid and organic additives. A similar origin for SO_4 in flowback water has been suggested in studies in other areas.

TABLE 1

Summary of the general chemistry and the major ion, Ba, B and Li concentrations for the study wells. The results for wells located on the same site and within the same member of the Montney formation are grouped together.

Montney formation member site		Upper					Middle					lower
		A	B	C	D	H	C	D	E	F	G	I
Parameter	No. of wells	8	2	5	2	1	2	2	4	2	1	2
	n	22	30	52	19	18	20	22	26	12	8	28
pH	Min	7.5	6.3	6.6	2.3	6.1	6.5	6.6	6	3.4	6.8	6.4
	Median	7.8	7	6.9	6.9	6.3	6.8	7.2	7.4	6.3	7.3	7.1
	Max	8.1	7.9	7.4	9.2	8.1	7	9.5	7.8	6.7	7.6	7.7
Conductivity (mS/cm)	Min	60.8	47.6	56.1	50.4	33.8	120	7.12	22.1	29.1	27.9	11.1
	Median	102	123	102	86.4	113	147	36.1	35.7	37.5	64.8	56.1
	Max	131	190	157	107	135	171	74.6	51.8	50.4	95.4	130
Total alkalinity (mg $CaCO_3$ per L)	Min	115	71	95	<10	67	76	135	222	<10	205	172
	Median	195	119	144	104	80	99	236	337	51	228	232
	Max	405	188	190	685	128	123	475	395	91	260	403
TDS (mg/L)	Min	41,358	30,135	34,137	31,522	20,713	82,519	3,609	11,105	18,655	13,972	4,587
	Median	61,220	89,949	70,449	62,520	83,807	1,10,450	21,631	18,672	24,009	38,963	31,998

	Max	92,731	2,28,259	1,47,839	80,944	1,12,226	1,40,538	56,800	32,864	34,139	65,052	90,178
Cl (mg/L)	Min	25,722	18,541	21,344	19,303	12,308	52,570	1,893	6,671	10,295	8,186	2,260
	Median	43,437	55,235	44,439	38,355	49,006	71,218	12,510	12,251	14,455	24,790	17,678
	Max	65,777	1,64,018	1,04,897	50,963	66,998	93,007	34,565	21,611	21,495	41,783	51,038
Na (mg/L)	Min	8,264	9,162	9,932	9,960	6,451	23,802	1,344	2,787	6,849	3,895	1,991
	Median	12,759	25,609	19,779	18,489	28,509	30,960	7,884	5,256	9,066	10,999	12,112
	Max	17,818	51,027	33,212	23,974	37,637	38,460	18,872	9,119	10,575	18,244	33,782
Ca (mg/L)	Min	1,616	1,789	1,359	1,169	629	3,638	13	350	560	174	110
	Median	3,059	5,950	3,088	2,874	2,798	5,310	628	641	702	845	1,032
	Max	5,389	11,705	7,333	4,058	3,677	7,332	2,112	1,126	795	2,229	4,081
K (mg/L)	Min	553	284	569	466	414	1,065	49	187	166	186	105
	Median	796	1,035	1,025	860	1,534	1,461	257	295	196	410	558
	Max	1,239	1,920	1,500	1,171	1,806	1,865	466	474	251	650	1,296
Mg (mg/L)	Min	296	154	191	171	102	441	9.5	62	93	74	32
	Median	547	619	402	418	650	669	79	107	117	273	166
	Max	941	1,369	680	611	808	945	223	220	136	586	524
Sr (mg/L)	Min	298	60	194	123	30	573	3.7	38	33	29	13
	Median	630	404	477	264	141	893	55	72	44	73	206
	Max	1,219	924	916	358	195	1,263	268	161	69	101	1,011
SO_4 (mg/L)	Min	51	<0.1	<0.1	134	575	19.3	98	90	379	1,308	0.7
	Median	91	59	0.6	189	899	21	126	113	560	1,370	19
	Max	234	174	26	645	1,084	24	189	202	824	1,407	48
Ba (mg/L)	Min	1.7	1.9	12	1	<1	142	<1	2.1	0.1	<1	1.9
	Median	13	5.8	52	5.2	1.2	213	3.1	3.9	0.6	<1	46
	Max	20	7.5	202	7.3	1.4	311	4.9	6.4	1.4	<1	467
B (mg/L)	Min	6	3.1	11	12	13	19	3.1	7.2	6	7.4	2.1
	Median	8	10	14	18	33	21	10	11	9	13	8.7
	Max	10	14	20	21	38	24	15	15	12	16	11
Li (mg/L)	Min	15	11	10	8.3	4	34	<1	4	4.5	4.5	1.1
	Median	19	28	16	14	13	43	5	6.5	6.3	12	10
	Max	23	47	31	17	18	49	13	11	7.4	17	22

Minor elements in flowback water

Similarly to the major ions, the concentrations of Ba, B and Li are significantly influenced by mixing between the injected hydraulic fracturing fluid and the formation water and possibly by water rock interactions. The minor ion concentrations are not directly related to the injected hydraulic fracturing fluid chemistry as the concentrations of these ions are generally low (<10 mg/L) and for sites where freshwater is used as the base fluid, the Ba, B and Li concentrations are also low (<3 mg/L) (Table 2). The variability between sites and the potential sources of Ba, B and Li in flowback water are discussed in the following subsections [8-10].

TABLE 2

Summary of the hydraulic fracturing fluid Ba, B and Li concentrations for each of the study wells. These values are derived from the composite fluid samples and are estimates of the overall fluid chemistry based on the volumetric proportion of fluid that was used in each of the hydraulic fracturing stages. Only one hydraulic fracturing fluid sample was collected for the site F wells and for each of the site I wells. No hydraulic fracturing fluids were collected for the site C wells.

Site	Well	Ba (mg/L)	B (mg/L)	Li (mg/L)
A	1	11	2	7.1

	2	8.8	2.3	8.8
	3	<0.2	<0.2	<0.2
	4	27	2.4	10
	5	32	2.6	11
	6	15	2.3	7.8
	7	4.9	<1	2.5
	8	31	2.5	9.8
B	1	4.8	5.1	13
	2	3.1	4.4	10
D	1	1.3	2.2	<1
	2	2	0.4	<1
	3	1.4	0.5	<1
	4	2.1	1.3	<1
E	1	4.7	5	3.2
	2	2.6	2.3	1.5
	3	3	2.5	1.4
	4	4.5	4.3	2.5
F	1, 2	1.4	3	2.9
G	1	4.5	5	2.9
H	1	0.5	0.4	0.01
I	1	1	0.7	<0.2
	2	0.7	0.6	<0.2

Barium

The Ba concentrations in the flowback waters range from below the detection limit (<1 mg/L) up to 467 mg/L (Table 3). Barium concentration generally increases in the flowback water over the flowback period for each of the study wells but there is considerable variability between different sites (Figure 3).

Wells with longer shut-in periods correlate moderately to a higher Ba concentration in the initial flowback water samples (R^2=0.37). This relationship is interpreted to be the result a longer shut in period prior to commencement of flowback providing more time for countercurrent imbibition of fracturing fluid into the reservoir matrix and for geochemical reactions prior to the initiation of flowback from the well.

Regionally, the Ba concentrations 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 extended 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 often reach concentrations >1,000 mg/L after one week of flowback, which is considerably higher than those measured in the Montney formation (Figure 3) [11-13].

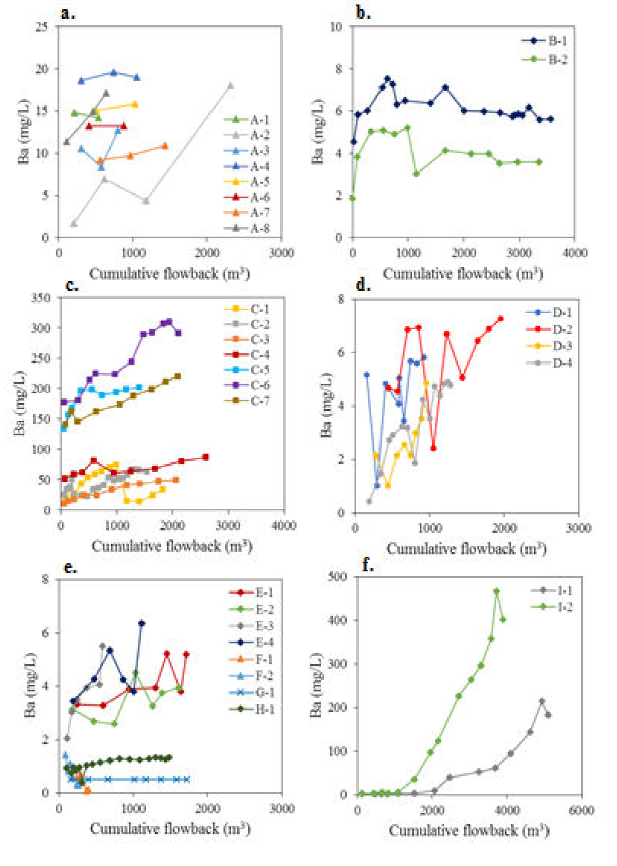

Figure 3: Ba concentrations over the flowback period plotted as cumulative flowback volume for a: Site A wells; b: Site B wells; c: Site C wells; d: Site D wells; e: Site E-H wells; and f: Site I wells. The Ba concentrations increase over the flowback period for the majority of wells. The upper Montney 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.

Ba concentrations in flowback water from the upper and middle members of the Montney formation differ when comparing wells completed at the same site. At site C, the upper Montney member flowback water generally has lower Ba concentrations compared to the middle Montney member flowback water; however, well C-5 is an exception in that the upper Montney member has a similar Ba concentrations to the two middle Montney member wells (Figure 3). The site D wells show the opposite trend in that the higher Ba concentrations occur in the upper member flowback when compared to the middle member flowback water, although there is some overlap in concentrations (Figure 3). The upper Montney member wells at site D also have longer shut-in periods, which likely contribute to the higher Ba concentrations. The two wells completed in the lower Montney member are located at site I. Both of these wells have high Ba concentrations (>100 mg/L) near the end of the flowback period; however, as there are no other wells in this region with comparable cumulative flowback volumes, an evaluation of the relative Ba concentration in flowback water with stratigraphy is not possible.

The regional variability in the flowback water Ba concentrations may be related to spatial variability in Ba concentrations in formation water. The formation water chemistry in this study is approximated by the produced water results (Table 3). The produced water concentrations are expected to approach those of formation water. Ba concentrations are high in the publicly reported produced water results from wells completed within the Montney formation near site C. Ba in the produced water sample near site I analyzed as part of this study (Figure 4) include the wells with the highest flowback water Ba concentration. The Ba concentrations in the hydraulic fracturing fluid are low (<5 mg/L) for the majority of the study wells; however, elevated Ba values (up to 32 mg/L) occur in the fracturing fluids used at site A (Table 2). These higher Ba concentrations could result in higher concentrations in the initial flowback water, although the later stage flowback water is influenced mainly by the formation water chemistry and fluid rock interactions (Table 3).

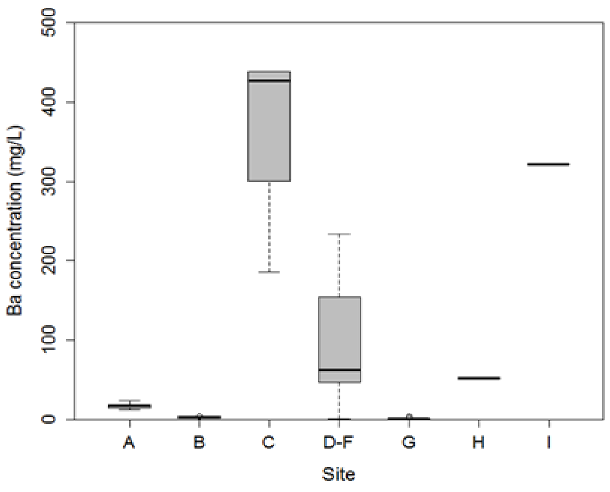

Figure 4: Ba concentrations in produced water samples from wells completed in the Montney formation and located up to 20 km from the study sites. Results for sites A, B and I are for samples collected in the present study, results for sites D-H were compiled from publicly available produced water results. The box portion of the boxplot shows the 25th percentile, the median and the 75th percentile. The whiskers show the Interquartile Range (IQR). Site H and site I appear as a line as only one sample which included Ba results was available for these sites.

TABLE 3

Summary of produced water Ba, B and Li concentrations compiled as part of the study. The results for site A and site B are from produced water samples collected from the study wells. The results for sites C-H are from publically available results, which did not include B and Li concentrations. The concentrations for site I was from a produced water sample obtained from a nearby well. Where multiple samples were analyzed, a median value is given.

Site	Well	n	Ba (mg/L)	B (mg/L)	Li (mg/L)
A	1	2	13	10	28
	2	1	19	10	32
	3	2	18	11	31
	4	2	24	10	31
	5	3	14	11	30
	6	2	14	11	31
	7	7	18	13	39
	8	1	16	11	28

B	1	4	3	11	33
	2	4	2	12	32
C	1-7	5	427	no results	
D-F	All	14	63		
G	1	15	0.6		
H	1	1	52		
I	1, 2	1	321	15	61

The Ba concentrations in both the formation water and the flowback water may be impacted by different geochemical processes acting across the study area. Overall, Ba concentrations in the study wells are negatively correlated with SO_4 concentrations (Figure 5). A negative correlation between Ba and SO_4 has also been observed in previous studies of Marcellus Shale flowback water and was interpreted to be the result of bacterial SO_4 reduction. The lower salinity environment resulting from the injection of the hydraulic fracturing fluid into the formation creates a more favorable environment for SO_4 reducing bacteria. Removal of SO_4 by bacterial sulphate reduction would increase the barite solubility in the formation, thereby increasing the Ba concentrations [14-18].

Barite dissolution has previously been suggested as a source of Ba in flowback water in which case Ba concentrations in the flowback water would be positively correlated to the amount of barite in the formation. Significant barite does not occur in the Montney formation and is rarely detected by XRD analysis; however, small (<0.5 cm) barite crystals occur in core examined with a scanning electron microscope from near site A (Figure 6). The higher barite solubility in the formation in comparison to the solubility in freshwater at surface may also be due to the high ionic strength of the water involved in the water rock interactions during hydraulic fracturing combined with the reducing conditions in the formation. The elevated temperatures and pressures in the formation and the presence of organic matter may also inhibit barite precipitation (Figures 5 and 6).

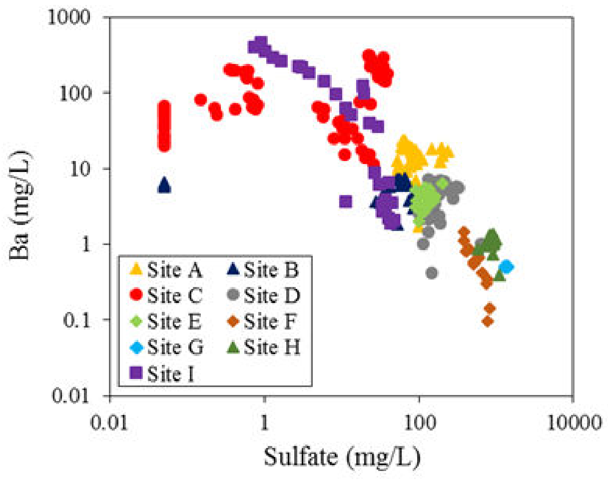

Figure 5: The relationship between Ba and SO_4 concentrations for the sampled wells. Results for individual wells are grouped by site. These parameters are negatively correlated, which is related to SO_4 reduction and barite solubility. Note the logarithmic scale used for both axis due to the large variability in concentrations between wells. **Note:** ▲: Upper Montney member wells; ●: Upper and middle Montney member; ◆: Middle Montney member wells; ■: Lower Montney member wells.

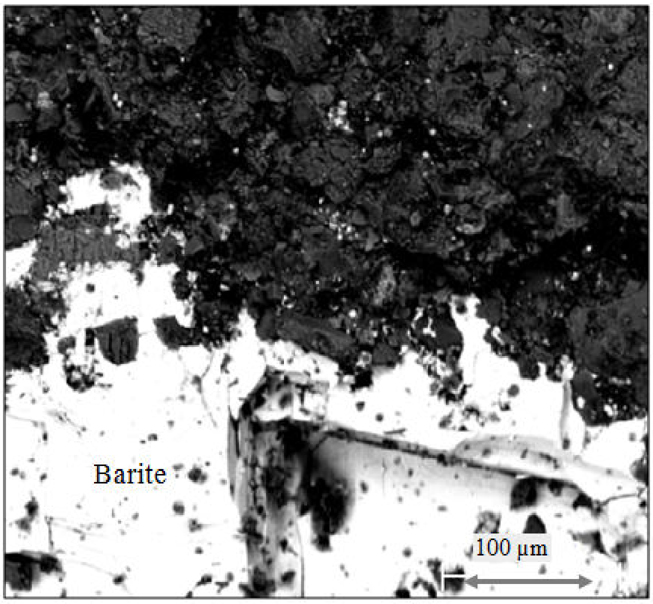

Figure 6: Barite in a core sample from a well located near site A. SEM photomicrography in back scattering mode.

The results of the study do not directly support barite dissolution as a dominant geochemical process impacting the Ba concentrations given that the Ba and SO_4 concentrations in flowback water do not increase in parallel as would be expected if only barite dissolution was occurring. The SI for barite in the flowback water remains 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. The flowback water from the wells at sites A and D mainly have increasing Ba concentrations, but stable SO_4 concentrations over time. The increase in Ba may be due primarily to mixing with formation water as the SI values do not show an increasing trend, which would indicate barite dissolution. Site B is notable in that it has relatively consistent (well B-1) or decreasing (well B-2) Ba concentrations over the flowback period, in contrast to increasing Ba concentrations observed in the flowback water from the majority of the other wells. The flowback water from the site B wells also show stable or decreasing SO_4 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_4 concentrations at well B-2, along with the decreasing barite SI values, which decrease from -0.1 to -1.0, support barite precipitation in this well [19-24].

The site C wells have high Ba in flowback water, reaching concentrations >20 mg/L by the middle of the flowback period and corresponding low (<30 mg/L) SO_4 concentrations. As these wells were shut-in for 21 to 30 days prior to the start of flowback, bacterial SO_4 reduction along with barite dissolution may have taken place in the reservoir during the shut-in time. These two processes would in combination explain the low SO_4 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_4 reduction was occurring at a faster rate than barite dissolution, in this scenario, the flowback water could still remain under saturated 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_4 reduction is occurring at a slower rate for these wells [25,26].

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 oversaturated, but saturation declines through the flowback period. The decreasing SI indicates barite precipitation. The decreasing SO_4 concentrations in the flowback water from these wells may be due to Ba precipitation rather than SO_4 reduction, while the increasing Ba concentrations may be due to mixing with formation water with higher Ba concentrations and not Ba dissolution. Well E-3 has barite SI values that increase over the flowback period from 0.2 to 0.4 and also shows a more rapid increase in Ba concentrations relative to the other site E well (Figure 3). The increasing SI, along with the increase in Ba and SO_4 concentrations supports barite dissolution in this well. SO_4 reduction may be occurring, but at a slower rate relative to SO_4 production by barite dissolution.

The site F wells have increasing SO_4 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 until under saturated (-0.4; well F-1). The decreasing trend for SI is indicative of barite precipitation, which is further confirmed by the decreasing Ba concentrations over the flowback period. The site F flowback waters show increasing SO_4 concentrations; however, this is likely a result of the chemical reaction that occurs due to the addition of Sodium Hypochlorite (NaOCl) to treat Hydrogen Sulfide (H_2S) in the flowback water at surface. SO_4 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 [27-30].

The site G and site H wells have high SO_4 (>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_4 is likely related to pyrite oxidation, which has been suggested as a source of SO_4 in both formation water and in flowback water due to pyrite oxidation from the injection of oxic hydraulic fracturing fluid into the formation. There is no indication that SO_4 reduction is a dominant process in these wells as the SO_4 concentrations remain high and relatively stable suggesting SO_4 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_4 .

The flowback water from the two site I wells have the highest Ba concentrations of the wells in our study with values up to 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_4 concentrations are measured during this period of flowback, (Figure 7) which is likely due to pyrite oxidation caused by the injection of the hydraulic fracturing fluid. 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 Ba concentrations increase and the SO4 concentrations decrease, which may be related to barite dissolution with SO_4 reduction. The SI of barite initially increases (up to 0.6 and 0.8, for well I-1 and well I-2, respectively), supporting the occurrence of barite dissolution, 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 through the flowback period (Figure 7). Although decreasing SI values suggest barite precipitation (Figure 7), the continually increasing Ba concentrations (Figure 7) do not support precipitation and hence suggest the source of the high Ba in these wells is from formation water with high Ba concentrations [31-35].

The variable behavior of Ba and SO_4 concentrations in the study wells shows that these ions are influenced by both barite precipitation and dissolution, as well as SO_4 reduction and mixing with formation water, depending on the well and, in the case of the site I wells, the time during flowback.

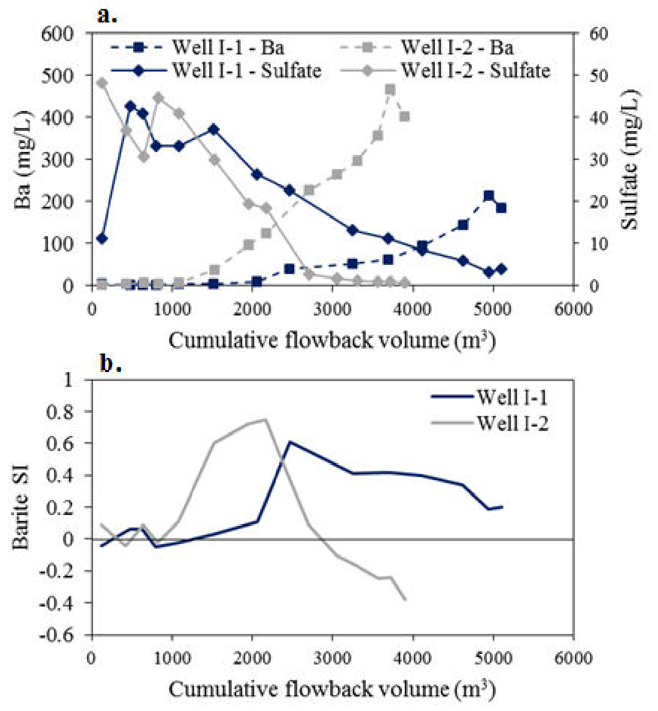

Figure7: a) Ba and SO_4 concentrations for well I-1 and well I-2. Ba concentrations are initially low in the flowback water from both wells. As the Ba concentrations begin to increase, the SO_4 concentrations decrease; b) The Saturation Indices (SI) for barite for well I-1 and well I-2. The flowback water is initially close to equilibrium with barite. The increasing SI supports barite dissolution, while the decreasing SI supports barite precipitation. Both barite dissolution and mixing with high Ba formation water are interpreted to contribute to the Ba concentrations, while bacterial SO_4 reduction and barite precipitation contribute to the removal of SO_4 from the water.

RESULTS

An additional process that has been suggested as a possible source of Ba in flowback water in previous studies is cation exchange with clay. In sequential extraction experiments on Marcellus Shale samples, the majority of the Ba ions were found in the exchangeable fraction providing support for the release of Ba ions through cation exchange. The Cation Exchange Capacity (CEC) measured on 15 samples of varying clay content from the Montney formation is low (<25 cmol(+)/kg) and does not correlate with the percentage of clay in the rock (R^2<0.05). Consequently cation exchange may not be as important in the Montney formation compared to other hydraulically fractured formations. Additionally, geochemical modelling with the major ions in our study indicate that ion exchange would produce a decrease in the concentrations of the divalent ions rather than an increase, due to the divalent ions displacing Na ions on the exchange sites when the relatively low TDS hydraulic fracturing fluid is injected into the formation [36-40].

Boron

Boron concentrations increase with TDS over the flowback period in most wells. Several of the site C wells (wells 1, 5, 6 and 7) and well D-2 are exceptions and have B concentrations that remain relatively stable over the course of the flowback period (Figure 8). The B concentrations are typically similar between wells from the same site and which are completed in the same member of the Montney formation (Figure 8). In the upper Montney member flowback water, the B concentrations are lower for the site A and site B wells (3.1 mg/L to 14 mg/L), moderate for site C and site D wells (11 mg/L to 21 mg/L) and highest at well H-1 (13 to 38 mg/L). The middle Montney member wells can be divided into sites D-G with lower B (3.1 mg/L to 16 mg/L) and site C with higher B (19 mg/L to 24 mg/L). The lower Montney member wells have similar or slightly lower B values relative to the upper and middle Montney member flowback water with maximum values of approximately 11 mg/L. No minerals containing B are at equilibrium or saturated in the flowback water. The B concentrations in the Montney formation flowback water are comparable to or slightly higher than the concentrations in flowback water from other hydraulically fractured formations, including the Marcellus Shale where B typically reaches concentration in the flowback water of approximately 20 mg/L. The high B concentrations in the flowback water in this study are not related to the hydraulic fracturing fluid chemistry as B concentrations are low in this fluid (≤ 5.1 mg/L) (Table 2). The early flowback water B concentrations in the study wells show some correlation with the length of the shut-in period (R^2=0.37).

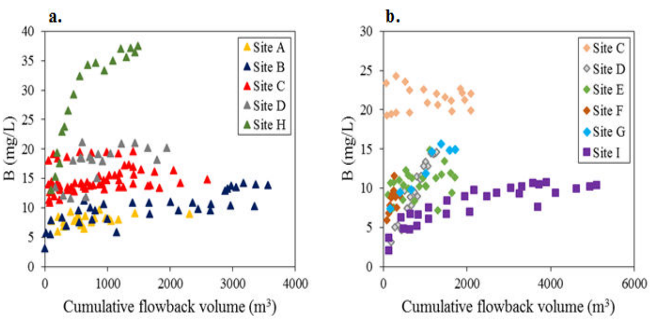

Figure 8: Boron concentrations over the flowback period, plotted as cumulative flowback volume. a) Upper Montney member wells. The produced water samples from sites A and B are not included; b) Middle and lower Montney member wells. Individual wells are grouped by site. **Note: ▲**: Upper Montney member wells; ◆: Middle Montney member wells; ■: Lower Montney member wells.

The B concentrations of Montney formation produced waters are expected to approach the B concentrations in formation water. There is low variability in the B concentrations in the produced water from these wells; values range from 9.3 mg/L to 15 mg/L. Such results are anticipated since the flowback waters from these three sites all are low (<15 mg/L) and have similar B concentrations. Further sampling of produced waters is required to determine if the B variability in formation water between the different regions is related to differences in formation water chemistry [41].

A potential source of B in formation water is kerogen decomposition. The B content in kerogen is high and can be released under high temperature conditions. The current temperature of the Montney formation is 75°C-80°C; however, the maximum paleo temperature is estimated at 175°C. There is a moderate correlation (R^2=0.58) (Figure 9) between the completion depth and the maximum flowback water B concentration from the study wells. The formation temperature for the Montney formation for all the study wells is about 75°C and hence the trend with depth more likely reflects the paleo temperature across the formation rather than the current temperature. The B concentrations in flowback water across the study area mirrors the B concentration of produced water; higher B concentration occurring at greater depths and hence increases from the northwest to the southeast (Figures 9 and 10).

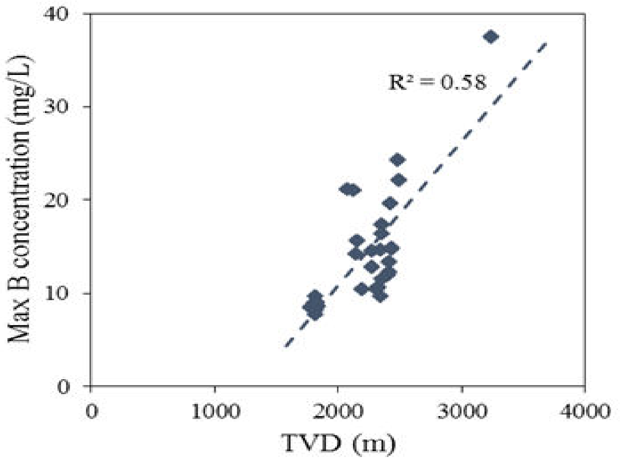

Figure 9: Correlation between the maximum B concentration in flowback water for each of the wells and the Total Vertical Depth (TVD) of the well. There is some correlation with increasing B concentrations and increasing depth; however, this relationship could also be impacted by the percentage of illite due to substitution of B in illite during diagenesis.

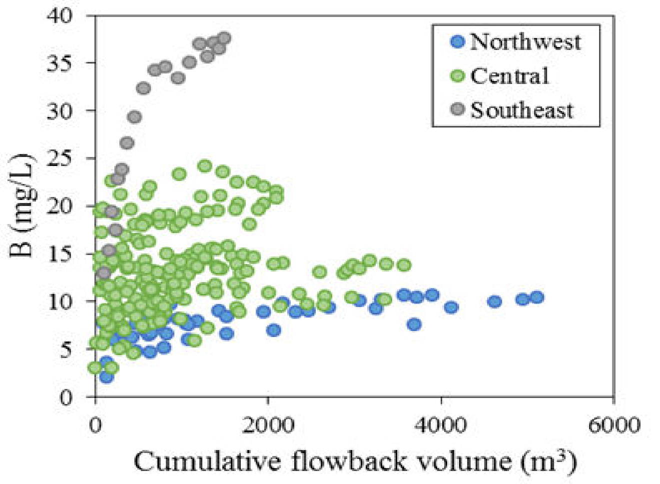

Figure 10: Boron concentrations across the formation plotted as cumulative flowback volume. The highest concentrations are observed in the well to the southeast, while the lowest concentrations are observed in the wells to the Northwest, although there is some overlap with some of the central wells. The produced water samples from site A, site B and nearby to site I are not included in this plot.

In areas where the temperature of the formation is lower (<150°C), B can be removed from formation water during smectite-illite diagenesis by substitution of Si with B in the tetrahedral sites [42]. This process applies to longer timescales for water rock interactions rather than occurring on the timescale of the hydraulic fracturing and flowback process. In the Montney formation there is a decrease in clay content from the Northwest to the Southeast. The mineralogy results compiled in the regions near the study wells indicate that the clays present include illite, kaolinite and chlorite, with illite making up the majority of the clay (Table 4). A negative correlation would be anticipated between the percentage of illite and B if the B was removed in part from the formation water by illitization during diagenesis. However, in our samples, there is only a weak negative correlation ($R^2=0.12$) between B concentrations and median weight percent illite. In the regions near site A, site C, site D (upper Montney member wells,) and site H the completed Montney intervals all have relatively low clay (<10%, by weight), although the flowback water from these wells have B concentrations spanning from low (<10 mg/L) to high (>30 mg/L). Such results may indicate further substitution and leaching of the B from the clay over time, which would minimize the correlation between illite and B in the water [43].

Table 4 Median mineralogy of the Montney formation by member.

Mineral	**Upper Montney member**				
(wt. %)	**Site A (n=14)**	**Site B (n=75)**	**Site C (n=40)**	**Site D (n=32)**	**Site H (n=21)**
Carbonates	34.9	29.5	30.3	30.9	19.3
Ankerite	Trace	12.9	trace	trace	-
Calcite	16.5	6.9	9.7	12.2	-
Dolomite[a]	18	20.7	17.1	16.8	19.3
Siderite	trace	-	0.8	0.9	-
Clays	6.9	16.5	5.1	7.7	6.8
Chlorite	trace	3.4 10	1.2	trace	2.7
Illite and mica	6.4		4	5.6	2.6
Kaolinite	-	2.7	1	-	-
Feldspar	22.3	19.4	23.1	14.6	24.4
K-Feldspar	10.1	5.5	11.8	7.1	11.4
Plagioclase	11.5	8.7	11.1	7.7	12
Other					
Quartz	34.1	32.3	37	40.6	45.1
Fluorapatite	-	-	0.3	1.4	-
Pyrite	2.1	1.5	1.6	2.4	1.2

Mineral	**Middle Montney member**					**Lower Montney member**
(wt. %)	**Site C (n=31)**	**Site D (n=19)**	**Site E (n=17)**	**Site F (n=22)**	**Site G (n=10)**	**Site I (n=29)**
Carbonates	28.5	18.8	18.8	18	17.7	15
Ankerite	2.6	-	-	-	-	-
Calcite	7.2	5	5	4	2	7
Dolomitea	18.3	13	13	14	14.8	8
Siderite	trace	-	-	-	-	-
Clays	9.9	16.2	16.2	16.3	17.3	25
Chlorite	1	-	-	-	4.7	3
Illite and mica	7.3	14	13.5	15.5	12.3	19.5
Kaolinite	1	2	2	2		2.1
Feldspar	16	21	21	20.2	26.2	12
K-Feldspar	7.6	7.7	7.7	7.4	14.6	4
Plagioclase	8.2	11.5	11.5	11	12.2	7
Other						
Quartz	41.7	39.6	39.6	40.3	35.4	44
Fluor apatite	0.3	trace	trace	trace	-	-
Pyrite	1.8	2.2	2	2.7	1.5	3

Note: [a]Includes ferrodolomite

In addition to the impact of the formation water B concentrations on the flowback water chemistry through mixing; there is the potential for ion exchange during the hydraulic fracturing process resulting in B that had been adsorbed onto the clay surface, being released due to the injection of the relatively low salinity hydraulic fracturing fluid. Overall; however, the CEC of the Montney formation is low and therefore cation exchange is likely not a significant source of B ions in flowback water.

Lithium

Lithium concentrations increase slightly over the flowback period for most wells. The majority of the flowback water samples from upper and middle Montney member wells have Li concentrations <20 mg/L; with the site B wells and wells C-5, C-6 and C-7 reaching slightly higher concentrations (>30 mg/L) (Table 1). Li concentrations in lower Montney member flowback water remain low for well I-1 with a maximum concentration of 15 mg/L and moderate for well I-2 with a maximum of 22 mg/L. For site I wells maximum Li concentration occur at the end of the flowback period. The produced water samples collected from Montney formation wells as part of the present study have Li concentrations between 27 and 41 mg/L for the site A and site B wells and 61 mg/L for the well nearby site I. No minerals containing Li ions were found to be close to saturation in the flowback water [44].

The Montney formation flowback water Li concentrations are low compared to the Marcellus Shale where the Li concentrations in flowback water are often >50 mg/L within the first week and >90 mg/L within the first 30 days of the flowback period. The dominant control on the increasing Li concentrations in flowback water in the Marcellus shale is likely a result of mixing progressively higher amounts of formation water with injected fluid through the flowback period.

Mixing of variable proportions of fracturing fluid and formation water during flowback also accounts for the increasing Li concentrations observed over the flowback period in our study. The hydraulic fracturing fluids used in the Montney wells have low Li concentrations (≤ 11 mg/L). The Li concentrations in the initial flowback water samples have a moderate positive correlation (R^2=0.43) with the length of shut-in period prior to flowback suggesting the greater shut-in time enables greater mixing of formation water with completion fluid and greater opportunity for fluid-rock interactions. In sequential extraction experiments on shale samples is the greatest proportion of Li in the rock was found in the silicate mineral fraction, most of which is likely in clays, although the oxidizable fraction, including organic matter, could account for up to 20% of the total Li. The organic matter is a potential source of Li in formation water, as Li can be released from organic matter under high temperatures. A regional increase in Li concentrations in formation water with increasing depth of burial and temperature has been shown is other studies. In this study we find no correlation (R^2<0.01) between the between the maximum Li concentration in the flowback water or produced water and the completion depth. However, the basin has been uplifted significantly and there is substantial areal variation in heat flow in the basin, thus the role of temperature in determining Li concentration cannot be discounted.

The concentration of Li in formation water may also be affected by smectite to illite diagenesis or ion exchange. During diagenesis, Li ions can substitute for the cations in the octahedral layers of the clay. The incorporation of Li into illite during diagenesis would be expected to produce a negative correlation between illite and Li concentrations in formation water. However, the results from the present study only show a weak negative correlation (R^2=0.14) between the maximum Li concentration in formation water (or flowback water with a high proportion of formation water) and the median percent illite for the corresponding well suggesting clay diagenesis has not played a significant role in the concentration of Li in the flowback water. Another potential source of Li in flowback water is ion exchange occurring during hydraulic fracturing, through the same process as described here for B ions. However, a sequential extraction study conducted on Marcellus shale samples found only a minor amount of Li (<2%) on the exchangeable sites. The ion exchange capacity of the Montney formation is less than the shale due to the low clay content of the Montney formation. Consequently ion exchange is not expected to be a dominant contributor to Li concentrations in Montney formation flowback water.

Boron and lithium

Due to the potential impact of formation temperature and smectite-illite diagenesis on both Li and B concentrations, the areal variability of these two ions was examined. B and Li are variably positively correlated in all wells. The correlation between B and Li is consistent between wells from the same site. When all data are considered; however, three Li-B data trends can be defined from linear cross-plots of the B-Li concentration of the flowback water (Figure 11) that generally correlate with geographic location of the wells. Samples that have relatively high Li and relatively low B values are from sites A and B and later flowback samples from site I, which are from the Northwest part of the study area. Wells in the central part of the study area at sites C through G and early samples from site I have moderate low Li and B whereas wells C-5, C-6 and C-7, have high Li and moderate B values. The third population includes site H wells, which have low Li and relatively high B values. The origin of the regional trends in B and Li is unknown; the trends might be related to currently unresolved paleo burial temperature and abundance and type of organic matter since B and Li are released from organic matter at different temperatures.

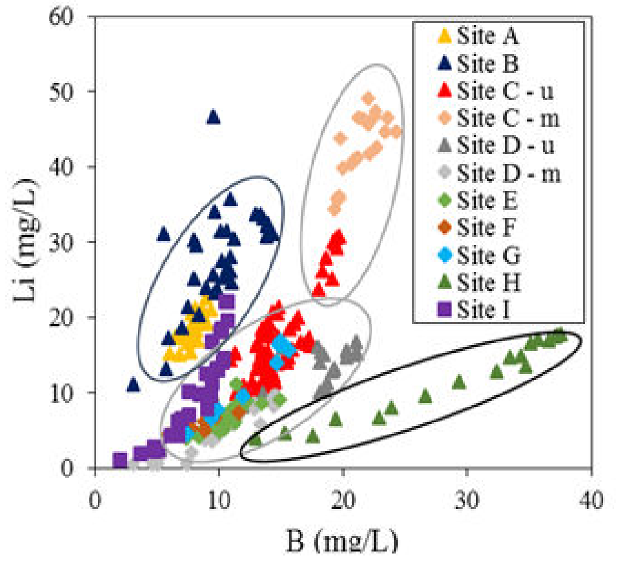

Figure 11: Li-B plot showing the three regions where the sampled wells plot. Wells from the same site consistently fall within the same region. ▲ : Upper (u) Montney member wells; ◆: Middle (m) Montney member wells; ▬ : Lower Montney member wells.

DISCUSSION

The concentration of the minor ions, Ba, B and Li in Montney flowback water show greater areal variability across the study area than the major ions. Ba, B and Li concentrations increase concurrently with an increase TDS over the flowback period in most wells, but not however in a consistent ratio. The variability in the minor ions in formation connate water between regions is likely a contributing factor to the differences in the concentrations of Ba, B and Li in flowback water as mixing between the hydraulic fracturing fluid and the formation water is an important geochemical process as shown by analyses of conserved tracers. In addition to mixing, the concentrations of Ba, B and Li show some evidence of other geochemical processes.

The Ba concentrations in the flowback waters range from below the detection limit (<1 mg/L) up to 467 mg/L. 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. There is no constant variation in Ba content in flowback waters between wells completed in the upper, middle or lower members of the Montney formation; however, regionally Ba concentrations in flowback water generally show a decreasing trend from the Northwestern (sites A and I) to the Southeastern sites (site H). Longer shut-in periods also correlates with a higher Ba concentration in the initial flowback water samples (R^2=0.37) due to greater opportunity for mixing of formation water and fracturing fluid. The negative correlation observed between Ba and SO_4 concentrations for the flowback water supports the influence of SO_4 reduction on the concentrations of these ions, as has been suggested for flowback waters from the Marcellus formation. SO_4 reduction would in turn increase the barite solubility due to the removal of SO_4 ions from solution. If only barite dissolution were occurring, a positive correlation would be expected between Ba and SO_4 concentrations for all wells. The saturation calculations indicate; however, that both barite dissolution and/or precipitation may be occurring in different wells and for some wells, at different flowback times. The increasing Ba concentrations in flowback water, thus is likely a product of both barite dissolution and the increasing proportion of formation water with time, while the SO_4 concentrations are impacted by a combination of pyrite oxidation, bacterial SO_4 reduction and barite precipitation/ dissolution [45].

The B concentrations in the flowback waters range from 3.1 mg/L to 38 mg/L and increase in parallel with increasing TDS over the flowback period for most wells. The exceptions are some site C wells and well D-2 where B concentrations are near constant. For a given site, the B concentration varies between flowback waters from Montney members, but the trend is not consistent between sites. The B concentrations in the Montney formation flowback waters increase regionally across the study area from the Northwestern sites to the Southeastern site.

CONCLUSION

Li concentrations in the Montney formation flowback water are mainly <20 mg/L for most sites and are less variable between wells than either the concentrations of Ba or B. Higher Li concentrations >30 mg/L were measured in the flowback water from the site B wells and wells C-5, C-6 and C-7. B and Li are strongly, although variably, linearly correlated at the different study sites. Overall, there is a trend from the Northwestern region (high Li, low B) to the Southeastern region (low Li, high B), except for site B in the central region, which has B/Li ratios closer to those in the flowback water from the Northwestern region wells. No B or Li containing minerals are close to saturation in any of the flowback waters. The increasing B and Li concentrations with increasing TDS indicate that the concentration of both ions mainly reflects the relative amount of formation water contributing to the flowback water. The origin of both B and Li and the variable B/Li ratio in the flowback and formation water is however equivocal. Both B and Li ions are present in organic matter and can be released from the organic matter into the formation water under high temperatures. There is a moderate correlation (R^2=0.58) between B concentration and completed depth and current reservoir temperature of the Montney; however, there is no correlation with Li concentrations (R^2<0.01). It might be fortuitous that the B correlates with current reservoir temperature and Li does not and rather other processes are responsible for the concentration of one or both these ions. Substitution of B and Li ions in smectite illite diagenesis and ion exchange during hydraulic fracturing are not considered important in the Montney formation due to lack of correlation of either B or Li with clay content and the overall low clay content of the formation.

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CONFLICT OF INTEREST

The authors declare they have no conflict of interest.

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