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Florian Osselin, S. Saad, M. Nightingale, G. Hearn, M. Desaulty, et al.. 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*, 2019, 687, pp.1389-1400. 10.1016/j.scitotenv.2019.07.066 . insu-02270202

HAL Id: insu-02270202

<https://insu.hal.science/insu-02270202v1>

Submitted on 1 Apr 2020

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Geochemical and sulfate isotopic evolution of flowback and produced waters reveals water-rock interactions following hydraulic fracturing of a tight hydrocarbon reservoir

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Abstract

Although multistage hydraulic fracturing is routinely performed for the extraction of hydrocarbon resources from low permeability reservoirs, the downhole geochemical processes linked to the interaction of fracturing fluids with formation brine and reservoir mineralogy remain poorly understood. We present a geochemical dataset of flowback and produced water samples from a hydraulically fractured reservoir in the Montney Formation, Canada, analyzed for major and trace elements and stable isotopes. The dataset consists in 25 samples of flowback and produced waters from a single well, as well as produced water samples from 16 other different producing wells collected in the same field. Additionally, persulfate breaker samples as well as anhydrite and pyrite from cores were also analyzed. The objectives of this study were to understand the geochemical interactions between formation and fracturing fluids and their consequences in the context of tight gas exploitation. The analysis of this dataset allowed for a comprehensive understanding of the coupled downhole geochemical processes, linked in particular to the action of the oxidative breaker. Flowback fluid chemistries were determined to be the result of mixing of formation brine with the hydraulic fracturing fluids as well as coupled geochemical reactions with the reservoir rock such as dissolution of anhydrite and dolomite; pyrite and organic matter oxidation; and calcite, barite, celestite, iron oxides and possibly calcium sulfate scaling. In particular, excess sulfate in the collected samples was found to be mainly derived from anhydrite dissolution, and not from persulfate breaker or pyrite oxidation. The release of heavy metals from the oxidation activity of the breaker was detectable but concentrations of heavy metals in produced fluids remained below the World Health Organization guidelines for drinking water and are therefore of no concern. This is due in part to the co-precipitation of heavy metals with iron oxides and possibly sulfate minerals.

Keywords: Tight gas, hydraulic fracturing, flowback geochemistry, persulfate breaker, heavy metals, stable isotopes

1. Introduction

Oil and gas production from unconventional hydrocarbon resources is now more important than ever in the global geopolitical and energy landscape. In 2018, the United States produced a total of 30 Tcf (trillion cubic feet) of natural gas with two-thirds of it coming from tight unconventional plays (~20 Tcf) [1] and the production of natural gas from unconventional plays is expected to reach 90% of the total production

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6 by 2050. In Canada, 34% of the total production of natural gas originated from the unconventional Mont-
7 ney formation, with almost 2 Tcf produced in 2017 [2]. Other large Canadian tight gas plays such as the
8 Duvernay formation or the Horn River basin in northwestern Alberta and northeastern British Columbia
9 produced another 0.2 Tcf in 2018 [2]. The development and rapid expansion of these low permeability
10 hydrocarbon resources is closely linked to the development of horizontal drilling and multistage hydraulic
11 fracturing over the past 20 years. Hydraulic fracturing techniques involve injecting a fluid (usually water
12 based) at very high pressure in order to fracture the reservoir and open paths for the hydrocarbons to flow
13 to the casing of the horizontal portion of the well. However, there are concerns about increasing freshwater
14 usage especially in zones where the water supply is already under stress [3, 4, 5]. After the hydraulic frac-
15 turing operations, the well usually produces variable quantities of saline water along with the produced
16 gas [6]. This water is characterized by high TDS contents (Total Dissolved Solids) [7, 8, 9] and is consid-
17 ered to be the result of mixing of low salinity injected fracturing fluids with high salinity formation brine
18 [10, 11]. Additionally, the flowback fluids are often characterized by a strong signature of water rock in-
19 teractions, principally through the action of the hydraulic fracturing fluids and their additives [12, 13, 14]
20 on the host rock. Reactions highlighted in the literature include pyrite oxidation by either dissolved oxy-
21 gen [15, 16, 17] or the oxidative action of the commonly used persulfate breakers; carbonate dissolution
22 [18]; and the precipitation of different sulfate-bearing minerals such as barite, gypsum or anhydrite [19].
23 Other interactions such as cation exchange with clay minerals [20], ion diffusion [21] and osmosis may also
24 contribute to changes in flowback and produced water geochemistry. The understanding of the causes of
25 changes in flowback and produced water compositions are of key importance in the design of more opti-
26 mized and more environmental friendly hydraulic fracturing fluid recipes, while improving the potential
27 of reuse and recycling of such waters, helping to reduce the stress on freshwater resources.

28 In this study, we present the analysis of a dataset based on 24 flowback water samples taken from
29 one well from a tight gas play in Alberta, Canada during the first week after hydraulic fracturing, and
30 one produced water sample taken from the same well after 14.5 months. These samples were analyzed
31 for concentrations of major ions and traces elements, as well as various stable isotopic compositions. The
32 results were then compared to those of water samples from an additional 16 producing wells sampled
33 112 days to 3.7 years after commencement of production to determine if similar geochemical processes
34 are occurring in other reservoir portions across the field. These 16 produced water samples were obtained
35 from wells representing a wide spatial area and different stratigraphic intervals within the same target
36 formation to demonstrate that the identified processes were not constrained to one location or interval in
37 the investigated tight unconventional natural gas play.

38 A portion of this dataset has been previously described in [22] and the mixing behavior between forma-
39 tion water and hydraulic fracturing fluids was demonstrated through the study of conservative species such
40 as Cl and oxygen and hydrogen isotopes of water. The objective of this second article is to build upon the
41 conclusions of the previous study and to develop a semi-quantitative model of the complex downhole geo-
42 chemical interactions between formation water, injected fracturing fluids, and reservoir rocks. Chemical
43 and isotopic parameters, including the isotopic composition of sulfate, were used to elucidate the sources
44 of flowback and produced water constituents and to understand the interplay between hydraulic fracturing
45 fluids, formation brine and reservoir minerals such as dolomite, pyrite and anhydrite.

46 2. Study site, well completions and sampling

47 Tight gas wells drilled in the Montney Formation in the provinces of Alberta and British Columbia
48 (Figure 1) remain among the top producers in Canada, with ~570 wells drilled in 2018. The Montney For-
49 mation is a dark dolomitic siltstone interbedded with shale of lower Triassic age. This siltstone is composed
50 primarily of quartz, illite, dolomite and K-feldspar with a high pyrite contents (varying from <1.0% up to
51 4.0%) [23, 24]. Petrophysical properties associated with this formation are: 3% porosity, permeability of 10
52 μD [25] and water saturation of 31% [26, 27]. The Montney Formation is overlain by the Doig Formation of
53 Middle Triassic age, characterized by a phosphatic black shale unit; and is lying unconformably above the
54 Permian Belloy Formation [28]. The diagenetic history of the Montney Formation involves strong dolomi-
55 tization of the calcite and reduction of the initial dissolved sulfate content to sulfide that was subsequently

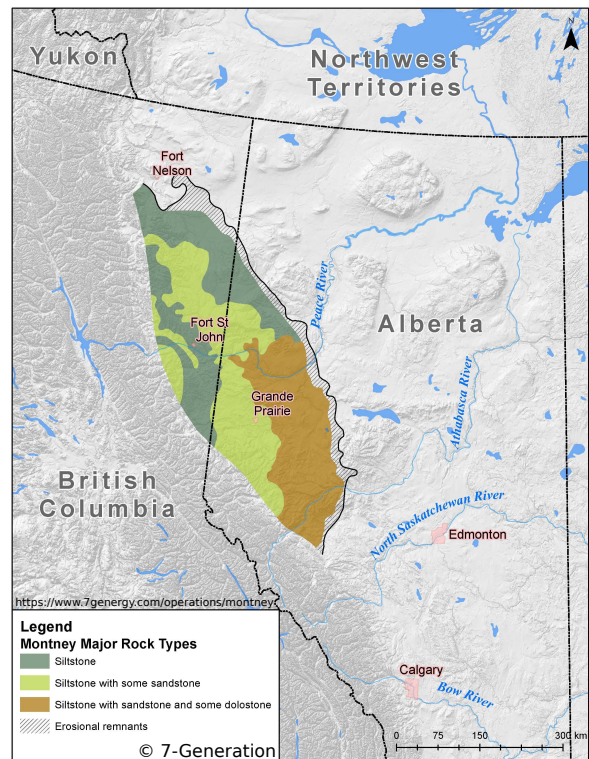


Figure 1: Location of the Montney formation straddling Alberta and British Columbia.

56 converted to pyrite [29]. The Montney Formation also contains minor amounts (usually <1.0%, sometimes
57 up to several %) of early and late diagenetic anhydrite [30].

58 Previously, formation waters from tight gas reservoirs were not considered in the hydrogeological and
59 geochemical studies of the area. However, in the Western Canadian Sedimentary Basin, formation waters
60 are generally believed to originate from the evaporation of seawater past the point of halite saturation that
61 were later diluted by various extents of less concentrated saline fluids, or even meteoric waters [31, 32]. In
62 particular, it is believed that some high TDS formation waters in Alberta are sourced from residual brines
63 from the evaporite rich Charlie Lake Formation [28].

64 2.1. *High-frequency sampling from a hydraulically fractured well*

65 A well targeting the Middle Montney Formation was drilled to a true vertical depth of 3300 m before
66 deviating to the 3000 m long horizontal section. The horizontal wellbore was completed using 28 fracture
67 stages separated by approximately 106 m. Fracturing was conducted with a mixture of nitrogen (135,000
68 m³ under standard conditions per stage) and water (280 m³ per stage) at a pressure of around 9000 psi.
69 Samples were collected once every 20 m³ until 100 m³ of flowback and once every 100 m³ until 1600 m³ of
70 flowback. The last two samples were obtained at 2000 m³ of flowback (after 7 days) and 14.5 months after
71 the hydraulic fracturing, corresponding to a total of 18,000 m³ of produced water.

72 Following the literature consensus, the term *flowback water* will be used in the following to characterize
73 the 24 samples collected in the first week after commencement of production while *produced water* will be
74 used to characterize the other samples collected months or years after hydraulic fracturing occurred.

75 2.2. *Produced waters from multiple wells across the field*

76 In addition, 16 samples of produced water were collected from 16 horizontal wells on four pads through-
77 out the same tight unconventional natural gas play in northwestern Alberta. The total vertical depths of
78 the wells ranged from 2874 to 3212 m (mean 3030 m) and the horizontal sections were between 1508 m
79 and 3184 m long (mean 2438 m). The majority of the wells were fractured using slickwater, whereas five
80 wells were hydraulically fractured using a nitrogen foam approach. The number of fracture stages ranged
81 from 19 to 60, with an average of 30 stages. The samples were collected from the separator between 3.7 and
82 45.3 months after the "on production" date. Producing zones represented in these produced water samples
83 include the entire Montney Formation succession (i.e. Upper, Middle and Lower Montney).

84 2.3. *Pyrite, anhydrite and persulfate samples*

85 In addition to the flowback and produced water samples, a total of 12 core plugs were collected from
86 a 222 m core extending from the base of the Doig Formation down to the Lower Montney Formation.
87 Three samples from the Upper Montney, four from the Middle Montney and five from the Lower Montney
88 Formation were collected for mineralogical, chemical and isotopic analyses. All plugs were preserved with
89 three layers of protective wrapping.

90 Four persulfate breaker samples representing chemicals typically used in hydraulic fracturing oper-
91 ations were obtained from three service companies for geochemical and isotopic analyses. The samples
92 represent potassium and sodium persulfate and were encapsulated with a water-resistant coating.

93 Finally, some additional core plugs were obtained from several wells within the area that penetrated the
94 Montney Formation and were used for determining the isotope composition of anhydrite.

95 3. Analytical Methods

96 3.1. *Flowback and produced water samples*

97 Flowback water and produced water samples were collected on site while minimizing exposure to oxy-
98 gen and stored in 1 L plastic bottles. Bottles were then shipped within a few days to the University of
99 Calgary (Calgary, Alberta, Canada) for chemical and isotopic analyses.

100 3.1.1. *Major ion analysis*

101 Upon arrival at the laboratory, flowback and produced water samples were filtered through a 0.45 μ m
102 nitrocellulose filter before acidifying cation samples to pH < 2, while samples for anion analysis were
103 not acidified. Cation concentrations were determined by ICP-OES (Inductively Coupled Plasma - Optical
104 Emission Spectrophotometer) on a Varian 725-ES, while anion concentrations were measured by ion chro-
105 matography (Dionex ICS 2000). Electric conductivity and pH were obtained with Orion Star instruments
106 and bicarbonate alkalinity was measured using an Orion 960 Titrator. The Total Dissolved Solid value was
107 calculated by adding all the measured concentrations of major ions. Consistency of the results was con-
108 firmed by checking that the ionic balance is <5% for each sample. Analytical precision and accuracy for
109 anion and cation analysis is typically $\pm 5\%$.

110 3.1.2. *Trace elements*

111 Trace element concentrations on the flowback water samples were measured at the French Geological
112 Survey (BRGM, France) on a Thermo Scientific XSERIES 2 ICP-MS (Inductively Coupled Plasma - Mass
113 Spectrometry). Analytical quality was controlled by internal standard addition (In and Re) and regular
114 international geo-standard (i.e. SLRS4) measurements. The precision for trace element concentrations is
115 generally better than 5%.

116 3.1.3. *Stable isotope compositions of dissolved sulfate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$)*

117 Sulfur and oxygen isotope ratios of dissolved sulfate were measured on all flowback and produced
118 water samples by first converting dissolved sulfate to pure BaSO₄, which was subsequently thermally de-
119 composed in an elemental analyzer yielding SO₂ and a pyrolysis reactor yielding CO for isotope ratio mass
120 spectrometry. Results of the isotope ratio analyses are reported in the delta notation (δ) with V-SMOW
121 (Standard Mean Ocean Water) as the reference for oxygen isotopes of sulfate, and V-CDT (Vienna Canyon
122 Diablo Troilite) for sulfur isotope ratios. Analytical uncertainties are $\pm 0.3\text{‰}$ and $\pm 0.5\text{‰}$ for $\delta^{34}\text{S}$ and
123 $\delta^{18}\text{O}$ values of sulfate, respectively.

124 3.2. *Sulfur in core samples*

125 Based on XRD, sulfur in the core samples occurred predominantly as pyrite (FeS₂). Total sulfur contents
126 ranges from 0.45% in the Upper Montney to 1.59% in the Lower Montney, with an average of 0.9 % across
127 the entire Montney Formation. The $\delta^{34}\text{S}$ values of total sulfur, representing predominantly pyrite, were
128 determined on powdered core samples that were thermally decomposed in an elemental analyzer followed
129 by isotope ratio mass spectrometry in continuous flow mode. For anhydrite sulfur isotope ratio, small
130 powdered aliquots of the core samples were reacted with HCl and then filtered to separate the sulfate
131 (dissolved anhydrite) from the sulfide (pyrite). Barium chloride (BaCl₂) was then added to the solution and
132 the sample was heated for approximately 30 minutes to allow for the barium sulfate (BaSO₄) to precipitate.
133 The BaSO₄ samples were then placed into silver cups and the $\delta^{34}\text{S}$ value was measured using Continuous
134 Flow-Isotope Mass Spectrometry. Results are expressed relative to V-CDT with a measurement uncertainty
135 of $\pm 0.5\text{‰}$.

136 3.3. *S and O isotope ratios of persulfate breakers*

137 The isotopic composition of sulfate from the decomposition of the four persulfate breaker samples was
138 also determined by thermal decomposition in an elemental analyzer yielding SO₂ and a pyrolysis reactor
139 yielding CO for isotope ratio mass spectrometry with measurement uncertainties of $\pm 0.3\text{‰}$ and $\pm 0.5\text{‰}$
140 for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of sulfate, respectively.

141 **4. Results**

142 4.1. *Methodology*

143 Similar to most previous flowback studies (e.g. [7, 8, 10]), the TDS of the flowback samples in this study
144 increased quickly as the result of the mixing of low salinity hydraulic fracturing fluids with high salinity

145 formation water [22]. In order to separate the contributions from water-rock interactions, from the simple
146 mixing between formation water and fracturing fluids, the different species of interest are plotted against Cl
147 concentrations. In the absence of halite dissolution, chloride can be considered as conservative [13, 33]. As
148 such, the Cl concentrations are representative of the relative proportions of fracturing fluids and formation
149 water in the samples as described in [22]: $\frac{V_{inj}}{V_{inj}+V_{form}} = \frac{[Cl]_{spl}-[Cl]_{\infty}}{[Cl]_0-[Cl]_{\infty}}$ with V_{inj} the volume of injected water
150 in the sample and V_{form} the volume of formation water in the sample, while $V_{form} + V_{inj} = V_{spl}$; $[Cl]_{spl}$
151 is the chloride concentration in the sample while $[Cl]_0$ and $[Cl]_{\infty}$ are respectively the concentrations of
152 chloride in the hydraulic fracturing fluid and in the formation water. Another option for a conservative
153 tracer would be bromide but the dataset did not include this element. The conservative behavior of Cl was
154 also confirmed in [22] using stable isotopes of water.

155 The advantage of plotting the different water constituents against Cl is that it allows the identification of
156 conservative and non-conservative species. Indeed, if a species is conservative, it will correlate exactly with
157 Cl and the data points should plot on a line connecting the hydraulic fracturing fluid composition to the
158 formation water composition (red lines on the different figures). Any species plotting above or below the
159 line reveals a non-conservative behavior with more or less of the species than conservative mixing would
160 predict and thus, a source or sink of this species is required. This behavior is likely the result of water-rock
161 interactions.

162 A complete results table can be found in Supplementary Materials.

163 4.2. Chemical and isotopic composition of flowback samples

164 The mixing of fracturing fluids with formation water as well as water-rock interactions caused the TDS
165 contents of the flowback samples to increase rapidly and steadily from 396 mg/l in the fracturing fluid to
166 96,000 mg/l after 7 days of flowback, and up to 204,000 mg/l for the produced water sample obtained after
167 14.5 months (Figure 2 and table SI-1).

168 Figures 3a-d and table SI-1 show the evolution of Ca (a), Mg (b), Ba (c) and Sr (d) concentrations in
169 flowback and produced water samples versus Cl concentrations. In Figures 3a and 3b, Ca and Mg con-
170 centrations increased from 71 and 18 mg/l in the fracturing fluids to 4,200 and 800 mg/l after 7 days of
171 flowback, and further to 7,900 and 1,200 mg/l respectively after 14.5 months of production. Figures 3a and
172 3b reveal that the Ca and Mg concentrations in flowback waters obtained between days 2 and 7 plot above
173 the conservative mixing line between fracturing fluids and formation water, hence indicating an additional
174 source of Ca and Mg.

175 Ba and Sr concentrations increased from 0.16 mg/l and 0.52 mg/l in the fracturing fluids to 2.2 and 170
176 mg/l after 7 days, and further to 8.3 and 640 mg/l, respectively, after 14.5 months of production. Figures
177 3c and 3d reveal that the Ba and Sr concentrations of flowback waters obtained after the beginning of day
178 2 for Ba and day 1 for Sr plot below the conservative mixing line between fracturing fluids and formation
179 water, indicating some removal of Ba and Sr from the flowback fluids.

180 Figure 4 and table SI-1 show the evolution of sulfate concentrations in flowback fluids versus chloride
181 concentrations in all collected samples. Sulfate concentrations increased from 61 mg/l in the hydraulic
182 fracturing fluid to 780 mg/l in the flowback sample taken only a couple of hours later and then remained
183 rather constant (varying only between 690 and 880 mg/l) in samples obtained between the end of day 1 and
184 day 7. After 14.5 months, the sulfate concentration had decreased to 210 mg/l. The cross-plot of sulfate
185 versus chloride concentrations indicates a highly non-conservative behavior of sulfate.

186 To elucidate additional sources of sulfate in flowback waters, $\delta^{34}S$ values of sulfate in the flowback
187 and produced water samples were determined and plotted versus sulfate and chloride concentrations in
188 Figures 5a and 5b, respectively. $\delta^{34}S$ values of sulfate increased from +6.4‰ in the hydraulic fracturing
189 fluid exponentially to $\approx +23\%$ after 7 days and further to +26.4‰ after 14.5 months. A cross-plot of
190 $\delta^{34}S$ values versus $\delta^{18}O$ values of sulfate is shown in Figure 5c. Oxygen isotope ratios of sulfate increase
191 similarly from 0‰ to 12.6‰ after the first week of flowback. Unfortunately, the last sample obtained after
192 14.5 months was not analyzed for oxygen isotope ratios of sulfate.

193 Analysis of the concentrations of traces metals revealed that As, Ni, Pb, Ti, Th and Zn are characterized
194 by a distinctive pattern (table SI-1): while both the hydraulic fracturing fluid and the last sample obtained

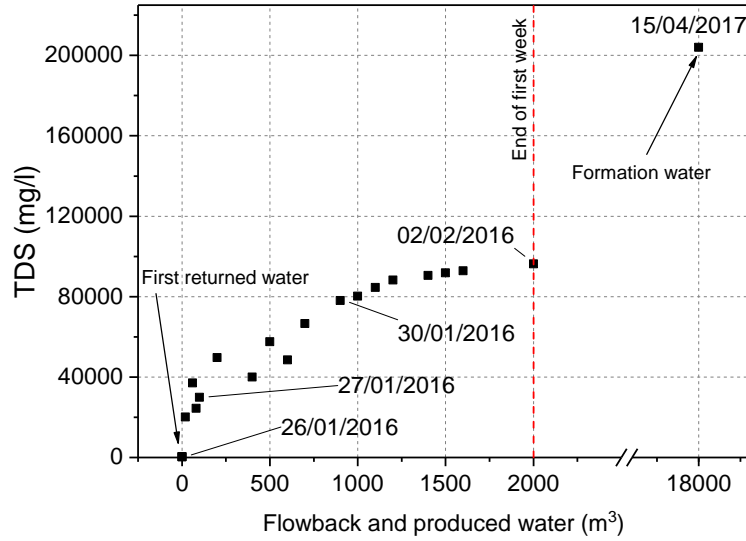


Figure 2: Evolution of TDS in samples versus volume of flowback and produced water.

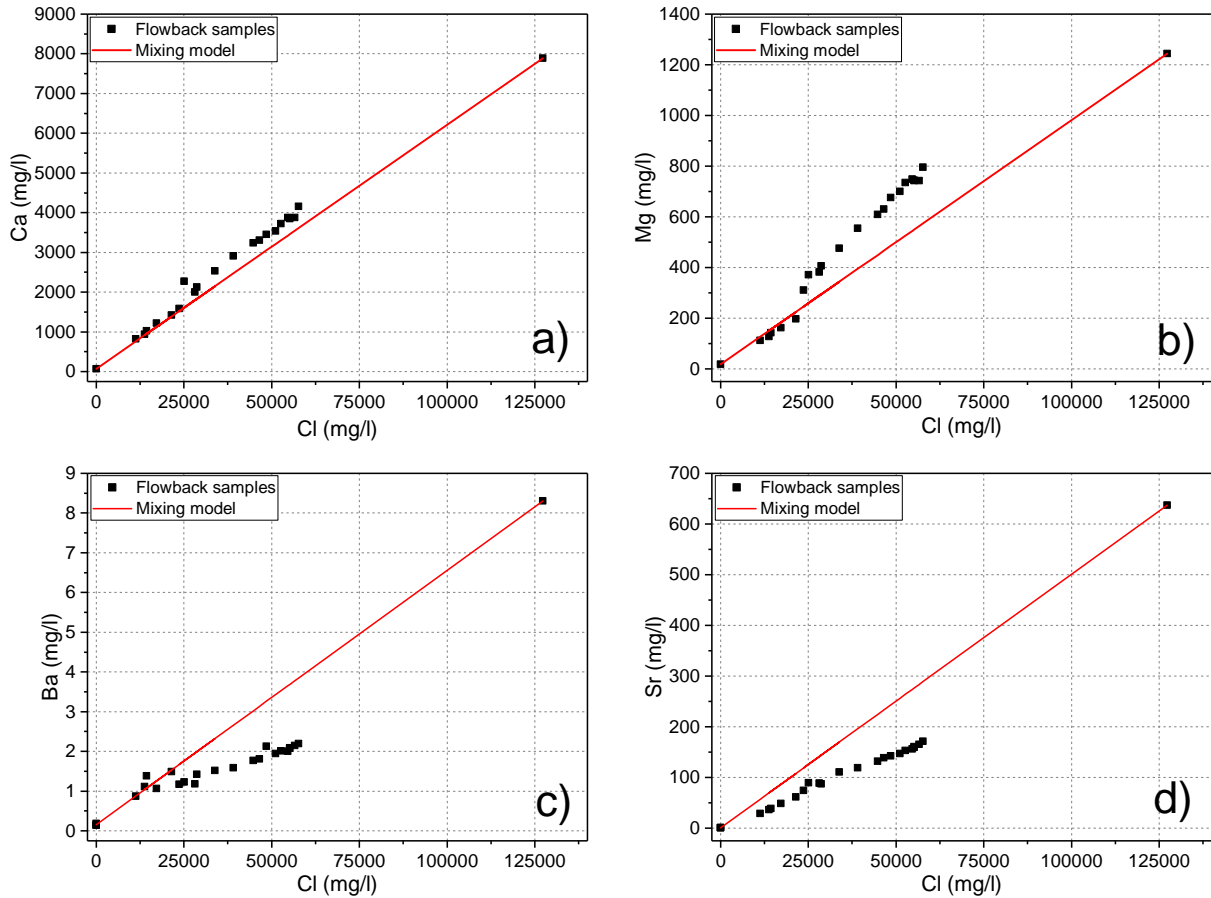


Figure 3: Evolution of calcium (a), magnesium (b), barium (c) and strontium (d) concentrations plotted versus chloride concentrations in flowback and produced water samples and the corresponding conservative mixing lines between fracturing fluids and formation water based on the conservative parameter Cl^- .

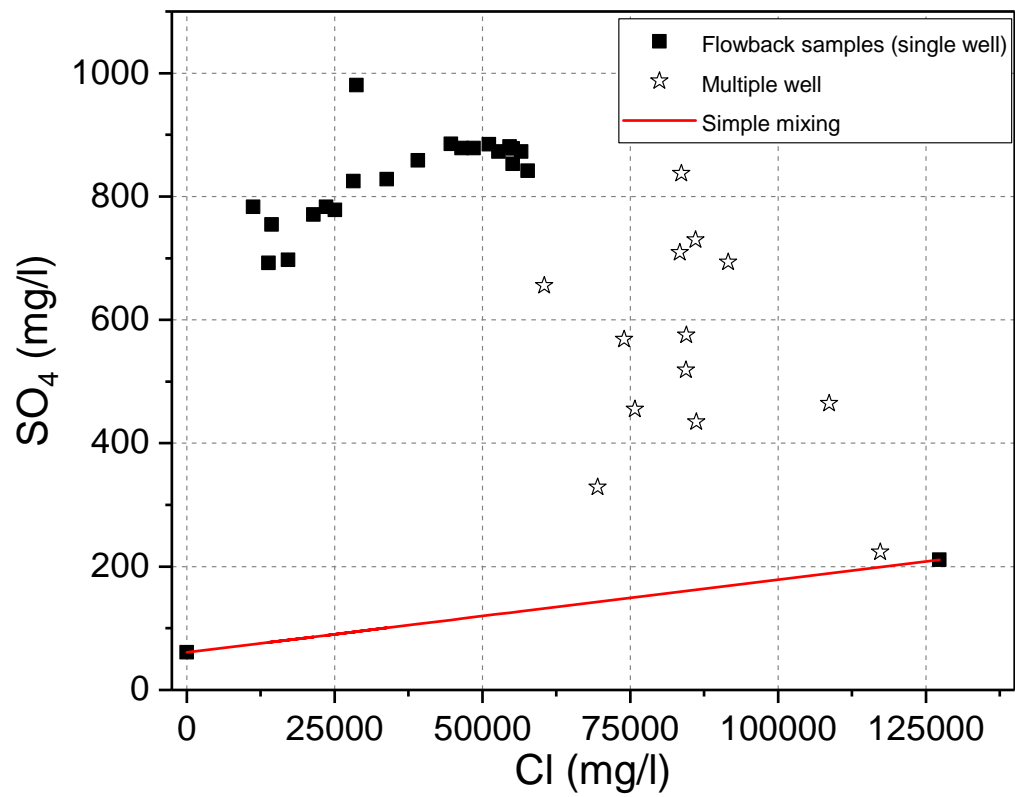


Figure 4: Evolution of sulfate concentration in flowback and produced water versus chloride concentrations.

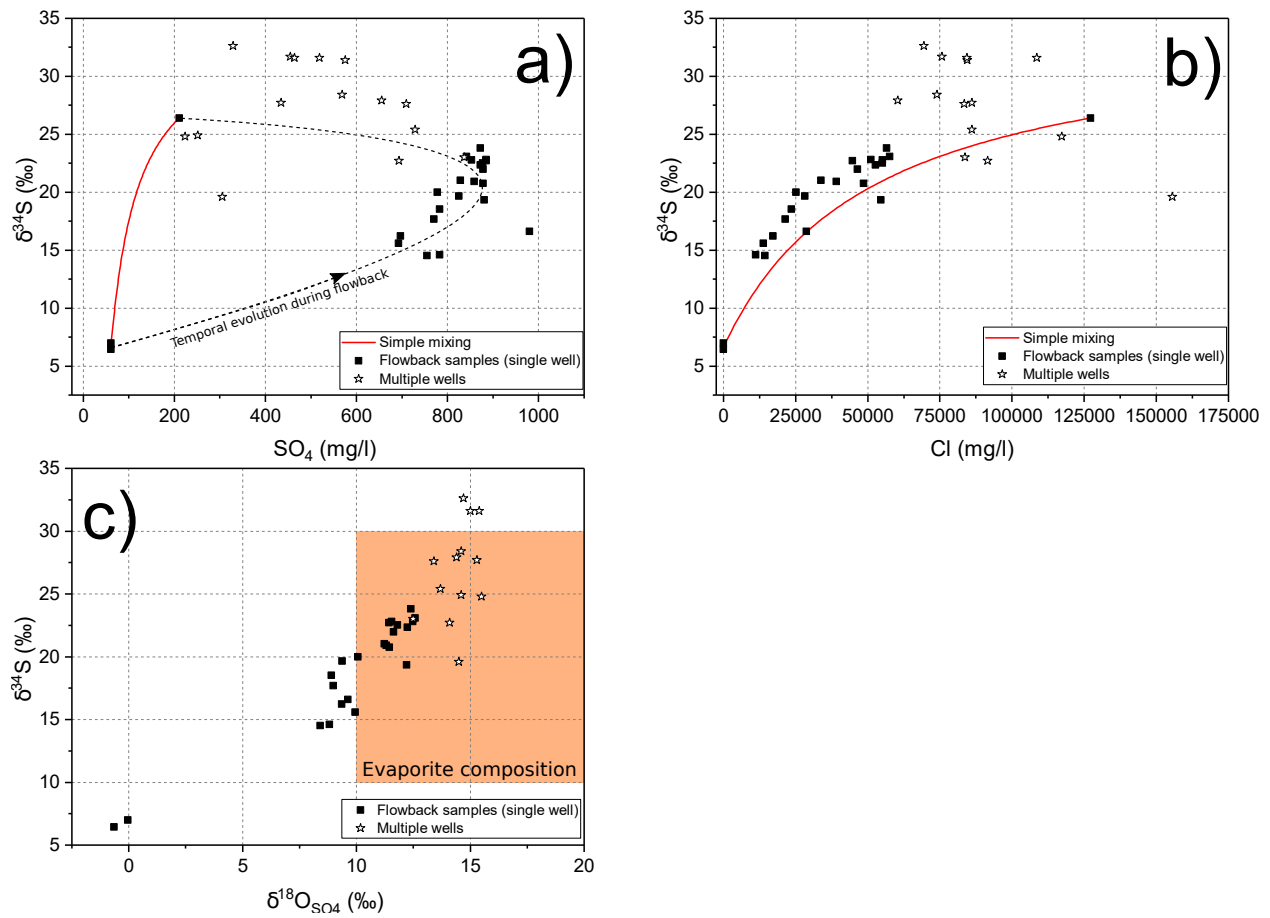


Figure 5: Evolution of $\delta^{34}\text{S}$ values of dissolved sulfate plotted versus dissolved sulfate (a) and chloride (b) concentrations, and crossplot of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of dissolved sulfate (c).

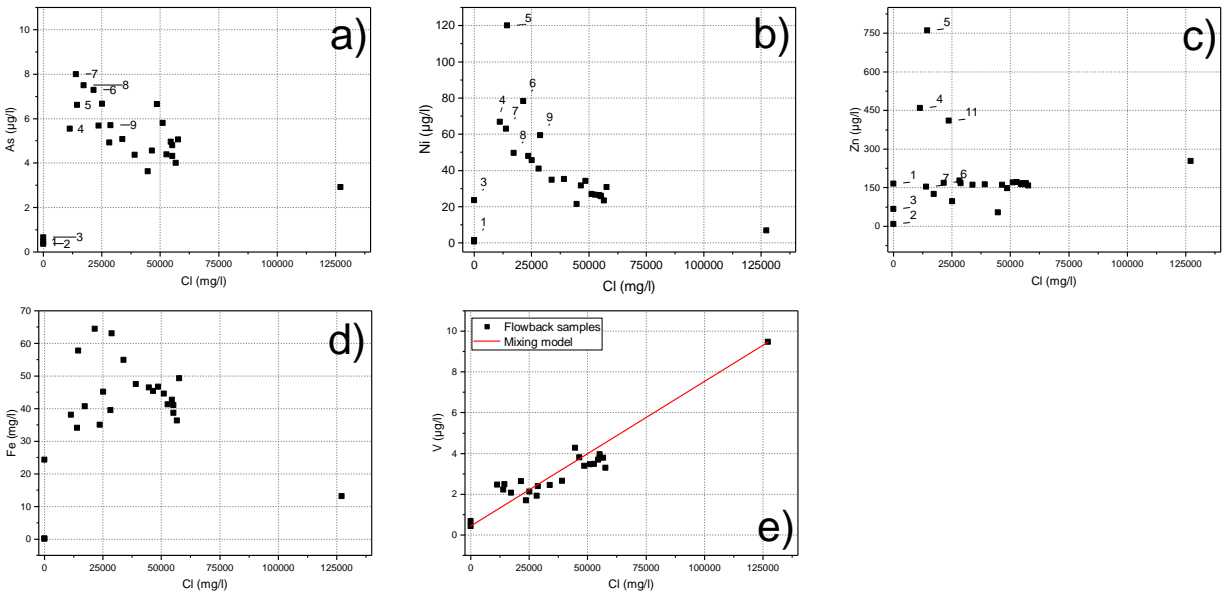


Figure 6: Evolution of arsenic (a), nickel (b), zinc (c), iron (d) and vanadium (e) concentrations in flowback samples plotted versus chloride concentrations – the labels correspond to the sequence of samples

195 after 14.5 months of production have low concentrations, shortly after the beginning of the flowback, the
 196 concentrations of these elements spiked as shown in Figures 6a-c for As, Ni and Zn respectively. The
 197 concentrations follow then a quick decrease toward the composition of the formation water. For Pb, the
 198 peak concentration occurred slightly later than the other trace elements at a Cl concentration of 14000 mg/l
 199 (i.e. at 4 hours of flowback), while most of the trace elements displayed a peak concentration as early as Cl
 200 concentration of 11000 mg/l (i.e. 1.5 hours after the beginning of flowback). The decrease in these trace
 201 metal concentrations after the peak is different for each element with the sharpest decrease for Zn, and the
 202 slowest decrease for As. Fe concentrations shown in Figure 6d display a similar pattern to the other trace
 203 elements with a sharp increase in the early flowback from 0.22 mg/l to 64.5 mg/l after 9 hours and a very
 204 slow decrease to 36 mg/l after a week. The sample collected after 14.5 months had an Fe concentration
 205 which had further decreased to 13 mg/l. Finally, Figure 6e presents the evolution of the concentration of
 206 vanadium relative to the concentrations of Cl in flowback and produced water samples. Contrary to the
 207 other trace metals V (and Be) exhibit a steady increase in respective concentrations. The concentration of
 208 Be rose from 0.006 µg/l in the fracturing fluid to approximately 0.07 µg/l in the sample after one week
 209 of flowback and after 14.5 months the concentration had doubled to 0.14 µg/l. The concentration of V
 210 increased from 0.43 µg/l in the hydraulic fracturing water to about 4 µg/l after one week of flowback and
 211 9.5 µg/l after 14.5 months.

212 4.3. Chemical and isotopic compositions of produced water samples from multiple wells

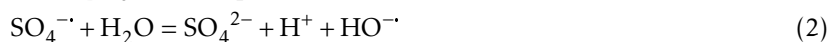
213 The TDS concentrations of the produced waters from the 16 wells sampled in the vicinity of the above
 214 described well ranged from 102,000 mg/l in the well sampled after 118 days to 252,000 mg/l in the well
 215 sampled after 1202 days after commencement of production (mean 151,000 mg/l). TDS concentrations in
 216 produced waters increased with increasing number of days after production commenced. Sulfate concen-
 217 trations in produced waters ranged from 220 mg/l in the well sampled after 1202 days to 840 mg/l in the
 218 well that was sampled after 301 days (mean 530 mg/l) (Figure 4). In contrast to TDS, sulfate concentra-
 219 tions in produced waters were highest (> 600 mg/l) in wells that were sampled within 200 to 600 days after
 220 commencement of production and which target the Upper Montney Formation. The lowest sulfate concen-
 221 trations (< 300 mg/l) were associated with produced waters from wells that were sampled more than 800
 222 days after commencement of production, from the same pad. Figure 4 reveals that sulfate concentrations

223 of produced waters from the 16 wells display a trend of decreasing sulfate with increasing chloride concen-
224 trations and plot between the flowback samples (first week) from the single well and the produced water
225 sample taken 14.5 months later.

226 Sulfur isotope ratios of the dissolved sulfate in produced waters ranged from 19.6‰ to 36.2‰ while
227 oxygen isotope ratios of sulfate in produced waters ranged from 12.5‰ to 15.4‰. Figures 5a and b reveals
228 that data for produced waters from the 16 wells plot between the first samples from the single well and the
229 last sample taken after 14.5 months, similarly to Figure 4. On Figure 5c, the data for sulfate from the 16
230 wells extent the trend of sulfate isotope compositions from the flowback fluids of the single well.

231 4.4. Potential sources of additional sulfate and their isotopic fingerprints

232 The highly non-conservative behavior of sulfate concentrations in flowback fluids shown in Figure 4
233 suggests the existence of additional sulfate sources (on top of the sulfate derived from mixing with forma-
234 tion water) that appear to contribute in variable quantities to flowback fluids and produced waters as a
235 function of time. These sources of additional sulfate include a) sulfate sourced from the decomposition of
236 the ammonium persulfate breaker ($(\text{NH}_4^+)_2 \cdot \text{S}_2\text{O}_8^{2-}$), b) sulfate derived from pyrite (FeS_2) oxidation, and
237 c) sulfate derived from anhydrite dissolution (CaSO_4). Ammonium persulfate is a strong oxidant ($E^\circ = 2.6$
238 V [34]) used for breaking the guar gum in order to reduce the viscosity of the fluid upon flowback [35],
239 reacting as follows:



240 The four persulfate breaker samples were found to have $\delta^{34}\text{S}$ values of +5.5, +3.7, -1.5 and -5.0‰
241 yielding a mean $\delta^{34}\text{S}$ value of 0.7 ± 4.8 ‰. This average $\delta^{34}\text{S}$ value is considered representative for persulfate
242 breakers used in the industry.

243 $\delta^{34}\text{S}$ values of total sulfur in the core samples, that is predominantly represented by pyrite, varied
244 considerably from -20 to +15‰. Using concentration and $\delta^{34}\text{S}$ values an amount-weighted average $\delta^{34}\text{S}$
245 value for pyrite of -1.1‰ for the entire Montney section, and an amount-weighted average $\delta^{34}\text{S}$ value of
246 1.6‰ for the pyrite in Middle Montney Formation was determined. As a consequence, a $\delta^{34}\text{S}$ value of 0‰
247 for pyrite, and for sulfate derived from pyrite oxidation was used for this study.

248 And finally, a $\delta^{34}\text{S}$ value of anhydrite was measured for small amounts of sulfate leached from the
249 Montney Formation core samples. Results ranged from +16 to +22‰ while [36] reported $\delta^{34}\text{S}$ values as
250 high as +28.8‰ for anhydrite extracted from the Montney Formation. In addition, anhydrite at the inter-
251 face of the Upper Montney and the overlying Doig Formation was found to have $\delta^{34}\text{S}$ values ranging from
252 +24 to +26‰ [29]. Therefore, sulfate derived from anhydrite dissolution is expected to have $\delta^{34}\text{S}$ values
253 as high as $+25 \pm 3$ ‰, whereas sulfate from pyrite oxidation or persulfate breakers would be characterized
254 by $\delta^{34}\text{S}$ near 0‰, with the latter two sources being indistinguishable based on sulfur isotope fingerprints.

255 Another phenomenon which could impact the sulfur isotope systematics is bacterial sulfate reduction
256 (BSR), which reduces sulfate to sulfide and is known to be accompanied by strong isotope fractionation
257 (~ 30 ‰ - [37, 38]) for both sulfur and oxygen affecting the remaining sulfate. Figure 5c, shows that the
258 oxygen isotopes of dissolved sulfate in produced water are around +15‰. $\delta^{18}\text{O}$ values of dissolved sulfate
259 in the flowback samples plot between the value of the hydraulic fracturing fluid and that of sulfate in the
260 produced waters. Considering that typical $\delta^{18}\text{O}$ values of sulfate in natural evaporites plot between +10
261 and +20‰ and +10 and +30‰ for $\delta^{34}\text{S}$ [39, 40], it is unlikely that extensive bacterial sulfate reduction is
262 occurring during the flowback as such a process would result in oxygen and sulfur isotope ratio of sulfate
263 much higher than the ones recorded. The high salinity of the flowback samples [41] may explain the limited
264 extent of BSR in the flowback and produced fluids from the investigated well.

265 5. Discussion

266 5.1. Elucidating sources of sulfate

267 Chemical and isotopic data were used in a semi-quantitative model to reveal the sources of sulfate and
 268 its dependence on flowback volume and time. The model considers that each sample contains sulfate from
 269 both the hydraulic fracturing fluid and the formation water, as well as sulfate from the breaker decom-
 270 position and additional sulfate potentially being derived from the water-rock interactions as expressed in
 271 equation (4).

$$[\text{SO}_4]_{spl} = [\text{SO}_4]_0 f + [\text{SO}_4]_\infty (1 - f) + [\text{SO}_4]_\chi \quad (4)$$

272 where $[\text{SO}_4]_{spl}$ is the sulfate concentration in the sample, $[\text{SO}_4]_0$ the sulfate concentration in the injected
 273 water, $[\text{SO}_4]_\infty$ the sulfate concentration in the formation water and $[\text{SO}_4]_\chi$ the concentration of sulfate
 274 from additional sources (i.e. water-rock interactions and persulfate decomposition). The mixing ratio f is
 275 defined as $f = \frac{V_{inj}}{V_{inj} + V_{form}} = \frac{[\text{Cl}]_{spl} - [\text{Cl}]_\infty}{[\text{Cl}]_0 - [\text{Cl}]_\infty}$ with chloride considered as conservative.

276 Similarly S isotope ratios of sulfate in the sample can be expressed as follow (e.g. [42]):

$$\delta_{spl} = \frac{\delta_0 [\text{SO}_4]_0 f + \delta_\infty [\text{SO}_4]_\infty (1 - f) + \delta_\chi [\text{SO}_4]_\chi}{[\text{SO}_4]_{spl}} \quad (5)$$

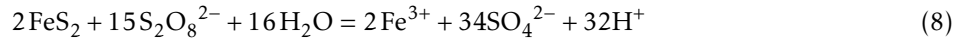
277 Decomposing the S isotopic ratio according to the three identified additional sources (anhydrite, pyrite
 278 oxidation and persulfate decomposition), equation (5) can be written as:

$$\delta_\chi = \frac{[\text{SO}_4]_{an} \delta_{an} + [\text{SO}_4]_{per} \delta_{per} + [\text{SO}_4]_{pyr} \delta_{pyr}}{[\text{SO}_4]_\chi} \quad (6)$$

279 with the subscripts *an*, *per* and *pyr* meaning sulfate sourced respectively from anhydrite dissolution, per-
 280 sulfite decomposition and pyrite oxidation. Since $[\text{SO}_4]_\chi = [\text{SO}_4]_{an} + [\text{SO}_4]_{per} + [\text{SO}_4]_{pyr}$, equation (6) can
 281 be rewritten as follows:

$$\delta_\chi = \delta_{an} + \frac{[\text{SO}_4]_{per}}{[\text{SO}_4]_\chi} (\delta_{per} - \delta_{an}) + \frac{[\text{SO}_4]_{pyr}}{[\text{SO}_4]_\chi} (\delta_{pyr} - \delta_{an}) \quad (7)$$

282 Pyrite oxidation in the hydraulically fractured reservoir can be stimulated by the remaining dissolved
 283 oxygen in the hydraulic fracturing water, or from the attack of persulfate. The injected water was submit-
 284 ted to an oxygen removal stage before injection and hence it was assumed that the oxidation of pyrite is
 285 predominantly caused by persulfate. The reaction can be summarized by the following equation:



286 Equation (8) reveals that 15 moles of persulfate are required to oxidize 2 moles of pyrite, producing
 287 34 moles of sulfate, 30 of which come from the persulfate decomposition and 4 of which come from the
 288 pyrite. As a result, we can write that $[\text{SO}_4]_{pyr} = \frac{4}{15} \alpha [per]$ with α representing the proportion of persulfate
 289 oxidizing the pyrite and $[per]$ the quantity of persulfate which reacted in the sample. Since the primary
 290 purpose of persulfate is to breakdown the guar gum, it can be assumed that α is small.

291 The initial quantity of persulfate added to the injected water in this well was $[per]_0 \approx 200$ mg/l (0.2
 292 kg/m³). One mole of persulfate will, upon reacting with pyrite or guar gum, produce 2 moles of sulfate
 293 according to the mechanism of equations (1) and (2). The quantity of sulfate coming from persulfate
 294 decomposition in a sample will then be:

$$[\text{SO}_4]_{per} = f \left[2([\text{per}]_0 - [\text{per}]_{unreacted}) - [\text{SO}_4]_{per}^{precipitated} \right] \quad (9)$$

$$[\text{SO}_4]_{per} = 2\beta [\text{per}]_0 \quad \text{with} \quad \beta = f \left(1 - \frac{[\text{per}]_{unreacted} + 1/2 [\text{SO}_4]_{per}^{precipitated}}{[\text{per}]_0} \right) \quad (10)$$

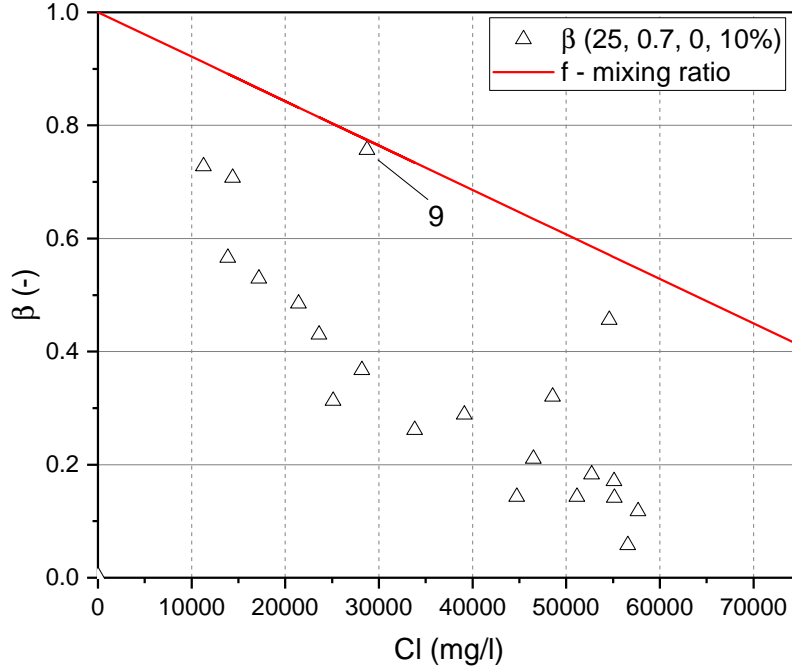


Figure 7: Evolution of parameter β with Cl concentration using $\delta^{34}\text{S}$ values from the sulfate sources

295 where $[\text{per}]_{\text{unreacted}}$ is the quantity of persulfate which did not yet decompose (i.e. still present in per-
 296 sulfate form), and $[\text{SO}_4]_{\text{per}}^{\text{precipitated}}$ is the quantity of sulfate from the decomposition of persulfate which
 297 precipitated as sulfate mineral. Parameter β characterizes the departure between an ideal case with no
 298 precipitation and instantaneous persulfate reaction (i.e. $\beta = f$), and reality (i.e. $\beta < f$, $[\text{per}]_{\text{unreacted}}$ and/or
 299 $[\text{SO}_4]_{\text{per}}^{\text{precipitated}} \neq 0$).

300 Combining the previous considerations, we can rewrite (7) as:

$$\delta_{\chi} = \delta_{an} + \frac{\beta[\text{per}]_0}{[\text{SO}_4]_{\chi}} \left[2(\delta_{\text{per}} - \delta_{an}) + \frac{4}{15}\alpha(\delta_{\text{pyr}} - \delta_{an}) \right] \quad (11)$$

301 If we combine equations (5) and (11), we can express the β parameter:

$$\beta = \frac{\delta_{\text{spl}}[\text{SO}_4]_{\text{spl}} - \delta_0[\text{SO}_4]_0 f - \delta_{\infty}[\text{SO}_4]_{\infty}(1-f) - \delta_{an}[\text{SO}_4]_{\chi}}{[\text{per}]_0 \left[2(\delta_{\text{per}} - \delta_{an}) + \frac{4}{15}\alpha(\delta_{\text{pyr}} - \delta_{an}) \right]} \quad (12)$$

302 Figure 7 displays the evolution of the β parameter using the measured $\delta^{34}\text{S}$ values from all possible
 303 sources: $\delta_{an} = 25\text{‰}$, $\delta_{\text{pyr}} = 0\text{‰}$, $\delta_{\text{per}} = 0.7\text{‰}$ and $\alpha = 10\%$. Even if these parameters are not completely
 304 constrained (no direct measurement, or in the case of α , no literature data or modeling), the system does
 305 not allow for much variation: first of all, because of α and the factor $4/15$, the contribution from pyrite
 306 oxidation toward dissolved sulfate in flowback is negligible and thus its sulfur isotope ratio does not impact
 307 the results. Secondly, the persulfate $\delta^{34}\text{S}$ value is bounded by the relation $\beta < f$, since in the absence of
 308 precipitation and in case of instantaneous decomposition we have $\beta = f$. This leads to a condition of
 309 $\delta_{\text{per}} < 1\text{‰}$ for $\delta_{an} = +25\text{‰}$, calculated on sample #9 (at Cl concentration of 28720 mg/l), which is consistent
 310 with the measurements on persulfate breaker samples and cores.

311 As expected, β plots below the red curve corresponding to the mixing parameter f . This suggests that
 312 the decomposition of persulfate is not instantaneous, and that precipitation of sulfate bearing minerals is
 313 likely to occur at some point in time.

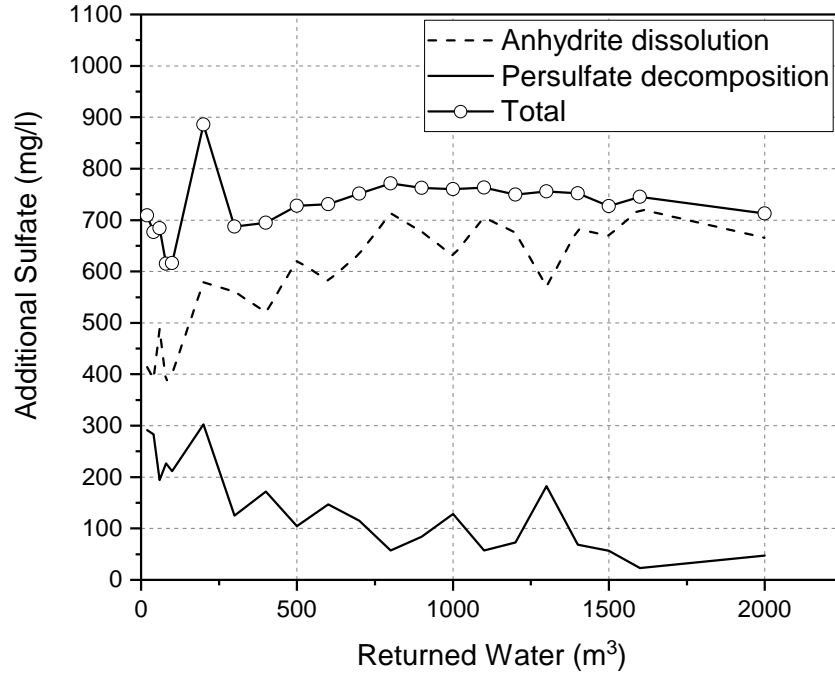


Figure 8: Sources of extra sulfate compared to simple mixing of sulfate in fracturing fluid and sulfate in formation water in the flowback samples as calculated from sulfur isotope ratios of sulfate.

314 Calculation of the different sulfate contributions from anhydrite, persulfate and pyrite oxidation in each
 315 sample is then possible knowing β . Using equation (4) we can write:

$$[\text{SO}_4]_{an} = [\text{SO}_4]_{spl} - [\text{SO}_4]_of + [\text{SO}_4]_{\infty}(1 - f) - \beta[\text{per}]_0 \left(2 + \frac{4}{15} \alpha \right) \quad (13)$$

316 It is evident from Figures 4 and 5 that the rapid increase in sulfate concentrations after hydraulic frac-
 317 turing is accompanied by an increase in $\delta^{34}\text{S}$ values of sulfate from $\approx 6\text{‰}$ to values $>+14\text{‰}$. If the majority
 318 of the additional sulfate was derived from sulfate-containing breakers or from pyrite oxidation, a decrease
 319 of $\delta^{34}\text{S}$ values of sulfate would have been expected. This is not what was observed. The increase in $\delta^{34}\text{S}$
 320 values of sulfate clearly revealed that the majority of the additional sulfate was derived from dissolution of
 321 anhydrite with a $\delta^{34}\text{S}$ of $\approx +25\text{‰}$ consistent with the measurements on rock core samples.

322 Results from the model described above quantify the sources of additional sulfate compared to simple
 323 mixing of sulfate in fracturing fluid and sulfate in formation water, in the flowback and produced water
 324 with respect to time as represented in Figure 8. In the samples from the initial phases of flowback, between
 325 200 and 300 mg/l of sulfate were derived from the persulfate breaker and 500 mg/l from anhydrite dis-
 326 solution. In samples from the next 6 days, the sulfate contribution from persulfate and associated pyrite
 327 oxidation progressively decreased to about 50 mg/l, whereas the contribution from anhydrite dissolution
 328 increased to about 700 mg/l, further supported by a progressive increase in $\delta^{34}\text{S}$ values towards $+24\text{‰}$.
 329 Sulfate derived from pyrite oxidation was found to be negligible with a maximum of 4 mg/l (hence not
 330 shown in Figure 8). This reveals that more than 90% of the extra sulfate in flowback waters one week
 331 after hydraulic fracturing was derived from anhydrite dissolution. Figure 5 further shows that anhydrite
 332 dissolution remains the predominant source of excess sulfate in produced waters 3 to 45 months after
 333 hydraulic fracturing, although it appears that this sulfate source is limited leading to decreasing sulfate
 334 concentrations with time through dilution by formation water and potentially some limited BSR.

335 5.2. *Precipitation of calcite and sulfate bearing minerals*

336 In Figure 7, parameter β plots below the mixing parameter f , revealing that there is less sulfate from
337 persulfate in the flowback samples than simple mixing would suggest. This can be either explained by the
338 delay in persulfate decomposition, or by precipitation of sulfate bearing minerals. Persulfate decomposi-
339 tion and its reaction with guar gum is very fast [43], as most processes involving radicals are. As a result,
340 it can be assumed that after a few hours, all persulfate is completely decomposed into sulfate. Therefore,
341 the only explanation of the discrepancy between β and f is the precipitation of sulfate bearing minerals.
342 There are several candidates for this precipitation, such as re-precipitation of anhydrite (or gypsum), pre-
343 cipitation of barite (BaSO_4) or celestite (SrSO_4). Figures 9a and b show the saturation indices for barite
344 and celestite at three different temperatures, 5°C (average surface temperature for this specific location),
345 95°C (average downhole temperature for this well) and 25°C, calculated with PHREEQC and the Pitzer
346 database [44], from the composition of the different flowback samples. Barite is always supersaturated
347 while celestite is undersaturated at the early stage of flowback and reaches equilibrium in the second half
348 of the first week, suggesting precipitation of barite and celestite (or a solid solution of both minerals). This
349 is further supported by Figures 3c,d revealing that both barium and strontium concentrations plot below
350 the conservative mixing line. Interestingly, barite is still supersaturated (or at equilibrium at 95°C), 14.5
351 months after hydraulic fracturing occurred. Similarly, celestite is also at saturation for all three tempera-
352 tures for the last datapoint, suggesting that precipitation could still be occurring even after 14.5 months
353 of flowback and well production. The sustained supersaturation of barite over the 14.5 months may also
354 be explained by the use of scale inhibitors, as they destabilize and prevent precipitation but only up to a
355 certain threshold of supersaturation. This would suggest that the supersaturation of barium reached values
356 high enough to overcome the effect of scale inhibitors.

357 While Figure 8 reveals that dissolution of anhydrite is the predominant source of excess sulfate in
358 flowback and produced water samples, it is possible that anhydrite or gypsum also reprecipitate in the
359 casing while flowback water flows upward to the surface if temperatures and saturation conditions change
360 from those downhole. The PHREEQC calculation (Figures 9c and d) shows that gypsum is undersaturated
361 at every stage of the flowback while anhydrite reaches saturation (and thus potentially precipitation) after
362 Cl concentrations reach 30,000 mg/l at reservoir temperature, approximatively at the same time as celestite.

363 Anhydrite dissolution and persulfate decomposition/pyrite oxidation have a strong secondary impact
364 on the other minerals and dissolved species present. In particular, the Montney siltstone is composed of
365 16% (w/w) dolomite which can dissolve through the acidification of the solution by the H^+ ions released
366 during pyrite oxidation (equation (8)) and persulfate attack on guar gum (equation (2)). Figure 3, shows
367 that magnesium and calcium concentrations plot above their respective pure mixing lines, which is com-
368 patible with dolomite dissolution.

369 Finally, Figure 9e shows that calcite is supersaturated for every temperature and significant precipita-
370 tion of calcite can then be expected at every stage of flowback. This precipitation is due to the common ion
371 effect, with anhydrite dissolution releasing large amounts of Ca, which then precipitate with the available
372 dissolved inorganic carbon [45].

373 5.3. *Mobilization of trace elements*

374 Another consequence of the oxidating power of the hydraulic fracturing fluids is the potential release of
375 trace metals, which are included in the pyrite matrix and organic matter. Pyrite is known to co-precipitate
376 with numerous heavy metal traces such as nickel, arsenic and lead among others [46], while organic matter
377 can be linked to elements such as uranium, mercury, copper etc. [47, 48]. A combination of the oxidation
378 of pyrite and organic matter by the persulfate breaker has the potential to release these heavy metals in
379 solution which will increase the potential toxicity of the flowback waters and complicate their recycling
380 [49, 50, 51]. The marked increase of the concentrations of the elements represented in Figure 6 is most
381 likely the result of pyrite and organic matter oxidation, releasing those elements into the flowback wa-
382 ter (with the exception of Ti, which is likely a by-product of the Ti-based cross-linker). Once oxidation
383 ceases, formation brine, lower in heavy metals than the initial flowback, will tend to "dilute" the heavy

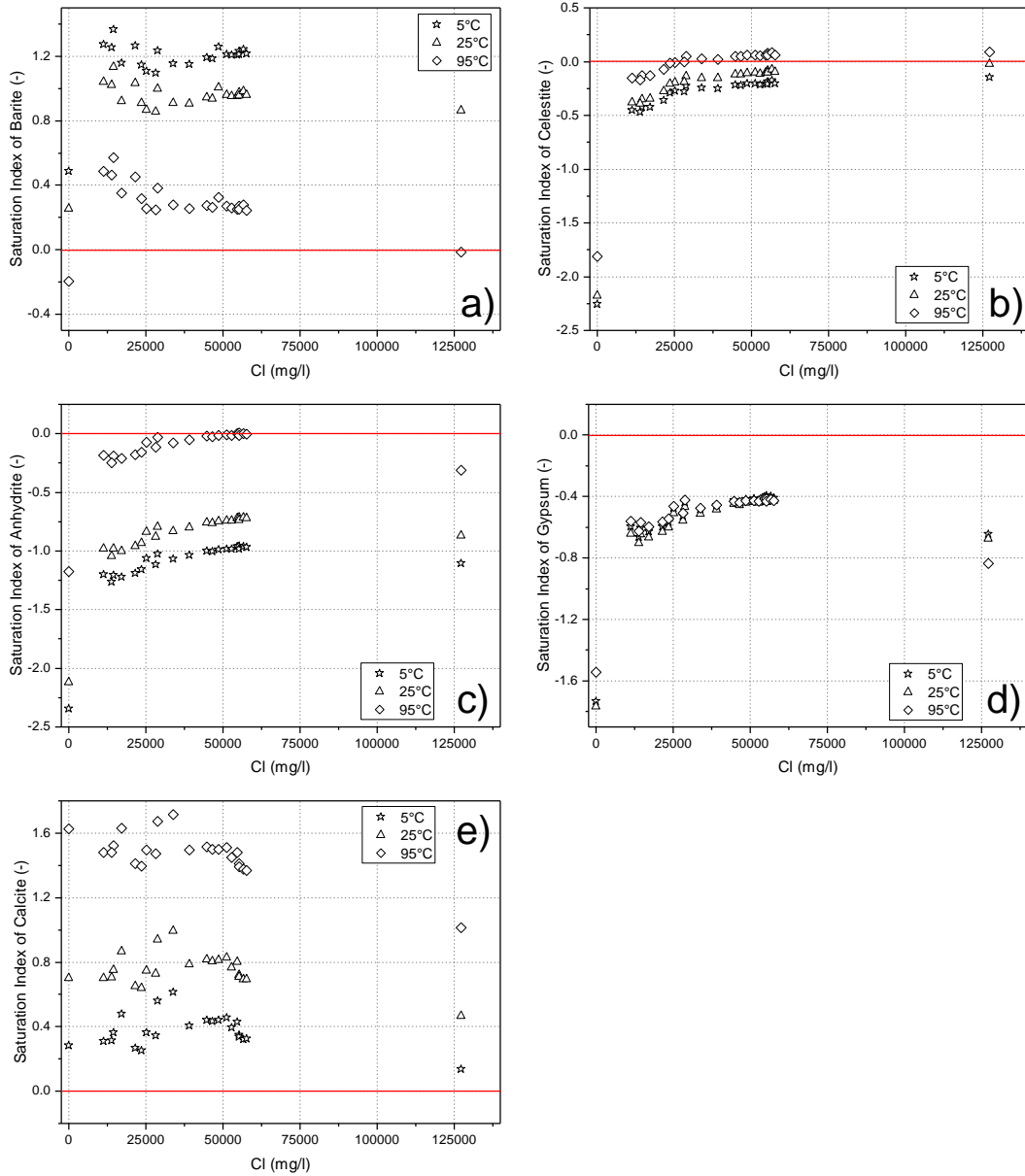


Figure 9: Evolution of the saturation of barite (a), celestite (b), anhydrite (c), gypsum (d) and calcite (e) in the flowback and produced water samples

384 metal concentrations. However, the decrease in concentration is faster than just pure mixing. Some au-
385 thors [18, 52] have previously highlighted this behavior and have linked it to the capture of heavy metals
386 during precipitation of iron oxides which is likely to follow pyrite oxidation [53]. This is supported by
387 the non-conservative behavior of iron in Figure 6d, which appears roughly similar to the behavior of the
388 trace metals and by PHREEQC simulations showing oversaturation for all iron oxi-hydroxides ($\text{Fe}(\text{OH})_2$,
389 $\text{Fe}(\text{OH})_3$, goethite and hematite).

390 Finally some trace elements Be and V (shown in Figure 6e) do not seem to be linked to a particular
391 oxidation behavior and follow a simple mixing behavior. The most likely explanation for this behavior is
392 that as Be and V are incompatible elements (i.e. these elements do not easily get incorporated into minerals)
393 [54, 55]. It is then possible that none of the minerals involved in water-rock interactions contain relevant
394 quantities of these elements, while the precipitation of sulfate-bearing minerals and iron oxi-hydroxides
395 do not impact strongly their concentrations, leading to a somewhat conservative mixing behavior between
396 a V- and Be-poor hydraulic fracturing fluid and a more concentrated formation water.

397 5.4. Field implications and conclusion

398 The evolution of the different elements in the flowback and produced water samples suggests the fol-
399 lowing scenarios for the downhole geochemical reactions in the considered well, following hydraulic frac-
400 turing. First, within a few hours after injection, a small portion of the oxidative breaker reacts with the
401 host rock pyrite and the organic matter, releasing some sulfate and trace metals. The first returned water
402 has brackish salinity, and slightly elevated contents of sulfate and heavy metals. The release of H^+ ions
403 by the oxidation reaction triggers the dissolution of dolomite which releases calcium, magnesium and dis-
404 solved organic carbon in solution. In the meantime, anhydrite in the formation dissolves while the highly
405 saline formation water flows from the formation toward the hydraulic fractures. The barium and strontium
406 contained in the formation water react with the sulfate released predominantly by anhydrite dissolution
407 and minor persulfate decomposition, and precipitate as barite and celestite (and potentially a solid solu-
408 tion of both), despite the use of scale inhibitors. This precipitation along with the precipitation of iron
409 oxide/hydroxide scavenges the heavy metals released by the oxidative attack of the persulfate limiting
410 their concentration in the flowback samples. Meanwhile, the extra calcium released by both dolomite and
411 anhydrite dissolution triggers calcite precipitation.

412 After all the persulfate breaker has either reacted or flowed back to the surface, and after the majority
413 of anhydrite has been dissolved, the process halts and reverts to simple mixing between the formation
414 water and the water present in the hydraulic fractures. Sulfate, iron and heavy metals are diluted to the
415 values of the formation water, while Ca, Mg, Ba and Sr follow a linear evolution with Cl. This dilution of
416 sulfate by the invasion of formation water is further supported by Figures 4 and 5 with the concentrations
417 of constituents in produced waters from the 16 additional wells plotting between the flowback of the first
418 week and the sample 14.5 months later.

419 All the scenarios described here have important implications for field operations. Geochemical pro-
420 cesses such as dissolution, oxidation and scaling may lead to negative consequences on the potential pro-
421 ductivity and longevity of the wells [56]. Mineral dissolution is usually a desirable process since it enhances
422 porosity [57, 52] and increases the permeability: an increase of a few percent of porosity can increase per-
423 meability by several orders of magnitude [58, 59]. This could be of great importance for the optimization of
424 hydraulic fracturing as an increase of permeability means an improvement of the overall production of gas
425 from the fractures. On the other hand, secondary precipitation of minerals such as anhydrite, calcium car-
426 bonate, iron oxides, barite and celestite can have a detrimental effect, by clogging the percolation paths, by
427 decreasing the effective aperture of the hydraulic fractures (proppant grains are very good seeds for mineral
428 precipitation) and by clogging the casing itself. A complete Thermo-Hydro-Chemo-Mechanical (THMC)
429 model seems necessary to grasp all the different processes and for evaluating whether the final outcome of
430 the precipitation/dissolution balance is beneficial or detrimental to the productivity of the well.

431 Additionally, the release of heavy metals by pyrite and organic matter oxidation is problematic for all
432 the recycling and reuse operations of wastewaters [4, 60], especially if these elements include radium. The
433 precipitation of minerals can be a strong asset by trapping the problematic elements downhole. Introducing

434 scale inhibitors early (especially for barite), by forcing the precipitation of colloidal particles of barite are a
435 perfect way to both limit the potential danger of barite scaling and trap radium atoms before they reach the
436 surface [61], as radium easily substitutes to barium in barite. Similarly, the precipitation of iron hydroxides
437 should limit the quantity of heavy metals in the flowback water. The toxicity of flowback and produced
438 waters is mostly linked to the very high TDS [51]. However, it can be of interest to compare the quantities
439 of heavy metals in flowback and produced fluids against drinking water standards. For all heavy metals
440 and trace elements detected in the flowback and produced water samples, only Ni was beyond the World
441 Health Organization guidelines [62] for a short period. The remediation operations should then focus on
442 TDS and organic contaminants [63] as heavy metals do not pose a particular water quality problem.

443 6. Acknowledgements

444 This research was conducted as part of the G-baseline project, co-funded by the French Research Agency
445 (ANR-14-CE05-0050 grant), the Natural Sciences and Engineering Research Council of Canada (NSERC
446 grant n° 463605) and TOTAL.

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