Critical metals in hydraulic fracturing flowback and produced water from the Montney and Duvernay formations, WCSB

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Summary

Critical metals such as lithium (Li) and magnesium (Mg) are either currently (for the former) or will likely be (for the later; Deivanayagam et al., 2019) widely used in making batteries for energy storage—a requirement for the transition to a future low carbon economy. Global Li production primarily comes from brines and a certain amount of Mg is currently being produced from seawater. One source of brine is the produced water from oil and gas wells. Hydraulic fracturing operations in the Devonian Duvernay and the Triassic Montney formations in the Western Canada Sedimentary Basin (WCSB) produce large volumes of high salinity water from most of the stimulated wells during their flowback and production stages. With a total dissolved solids (TDS) content up to 280 g/L, the hydraulic fracturing flowback and produced (HFFP) water was found to contain up to 70 mg/L of Li and as much as 2700 mg/L of Mg although the majority of the dissolved minerals are in the forms of sodium and calcium chlorides. Compared with commercial brines and seawater in terms of their Li and Mg contents and considering its availability and environmental benefit and impact, HFFP water from the Duvernay and Montney unconventional hydrocarbon resources operations in WCSB can be a potential source for these critical metals/minerals with significant economic value if proper extraction technologies are developed and applied.

Method

Forty HFFP water samples from wells completed in the Montney formation and 81 samples from the Duvernay formation were analyzed by ICP-OES for their major metal ions (e.g., Na^+, K^+, Ca^{2+} and Mg^{2+}), ICP-MS for their minor and trace metal ions (e.g., Li^+, Sr^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}), and ion chromatography for anions including Cl^-, SO_4^{2+} and HCO_3^-.

Results

All the analyzed HFFP water samples show high salinity with TDS ranging from 130 to 280 g/L, making them not suitable for reuse in subsequent hydraulic fracturing operations without desalination or dilution (Goss et al., 2015). For temporal HFFP water samples collected from the same wells, their TDS contents generally increase over time during flowback and into early production stage, but then become relatively consistent throughout production. The trend of increasing TDS is also reflected in the concentrations of calcium (Ca), Mg, strontium (Sr) and Li among others during flowback stage (Figs. 1a and 1b). Interestingly, the concentrations of Mg and Sr co-vary with that of Ca (Fig. 1c), suggesting a common source for these metals, likely the pristine formation water and/or dissolution of the rock formations fractured. In addition, the increasing contents of Ca-Mg-Sr of the flowback water is often accompanied by a decrease in the pH values and the contents of anions SO_4^{2-} and HCO_3^- during flowback stage, especially for HFFP water from wells stimulated in the Duvernay formation.

The concentration of Li in the HFFP water is in the range of 28-72 mg/L for samples from the Montney tight gas/light oil reservoir in the Dawson Creek area of BC, 26-54 mg/L for samples collected from the Duvernay shale gas/condensate reservoir in the Fox Creek and Three Hills areas of Alberta (Fig. 1d). These values are in line with the Li contents previously reported for the formation waters or brines from the WCSB (Eccles and Berhane, 2011; Hitchon et al., 1995). While the content of Li in the HFFP water is much lower than in those brines from which Li salts are currently being commercially produced by evaporation techniques (e.g., 230-1500 mg/L; Flexer et al., 2018), the HFFP water is likely a potential source of Li with the application of appropriate extraction technologies for added economic value.

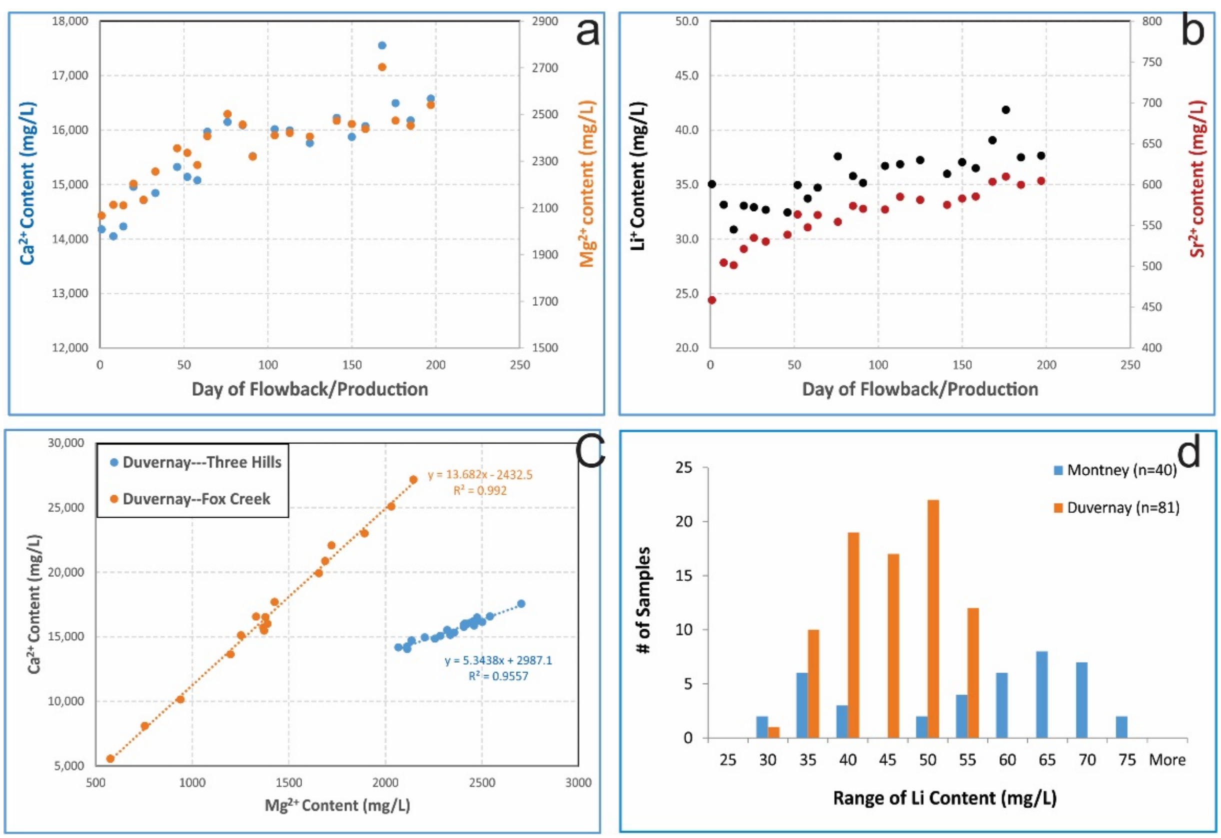

Figure 1. Occurrences of calcium, magnesium, strontium and lithium in hydraulic fracturing flowback water samples: (a) and (b) Ca^{2+}/Mg^{2+} and Li^{+}/Sr^{2+} concentrations in time series water samples collected over the duration of flowback from a Duvernay well in Three Hills area; (b) Cross plot of Mg^{2+} *vs* Ca^{2+} for flowback water samples as in (a) and (b); (d) Histogram showing distribution of lithium contents in Duvernay and Montney flowback water samples in this study.

Further resource valorization of HFFP water from unconventional hydrocarbon resource operations in the WCSB may be realized through the extraction of $Mg(OH)_2$. The concentration of Mg in the Duvernay HFFP water samples ranges from 570 to 2145 mg/L in the Fox Creek area and between 2060 and 2700 mg/L in the Three Hills area (Fig. 1c). In comparison, seawater typically contains about 1260 mg/L of Mg and has been a feedstock for commercial production of $Mg(OH)_2$ via chemical precipitation, even though most Mg in the world is produced from magnesite and dolomite by the Pidgeon process. Moreover, Sr is at the level of 450-1850 mg/L in the Duvernay and 490-1900 mg/L in the Montney HFFP water samples in this study, at much higher level than in seawater, thus making the HFFP water a potential source for the salt or hydroxide of this metal as well via chemical precipitation. As chemical precipitation and direct ion extraction of the related salts or hydroxides from saline water appear to be more environmentally friendly and likely more cost-effective than their extraction and refinery from mined ores, HFFP water from WCSB is believed to be of significant economic potential, rather than a “wastewater” to be managed at significant costs to the industry.

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