Weathering processes, catchment geology and river management impacts on radiogenic and stable strontium isotope compositions of Canadian boreal rivers

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Abstract

Radiogenic ($^{87}Sr/^{86}Sr$) and stable ($\delta^{88/86}Sr$) strontium isotope compositions spanning a calendar year are reported for rivers from across subarctic Canada that drain contrasting lithologies ranging from Precambrian bedrock (Koksoak, Great Whale and La Grande rivers of Northern Quebec) to carbonate and clastic Phanerozoic sedimentary rocks of the Western Interior Platform (Nelson River, of central and western Canada). The $^{87}Sr/^{86}Sr$ isotopic compositions of the rivers reflect the underlying geology, with rivers draining the Precambrian Shield having higher $^{87}Sr/^{86}Sr$ ratios (0.727-0.734) than the Phanerozoic dominated Nelson River (0.713). The stable strontium isotope values ($\delta^{88/86}Sr$) range from 0.26 to 0.39 ‰, with the values for the Nelson River overlapping those of the other three. Rivers that have not been developed for hydroelectric power show a seasonal variation in the $^{87}Sr/^{86}Sr$ ratios, whereas those that have been diverted or dammed show little or no seasonal variation due to increased residence time of their water in hydroelectric reservoirs. The three rivers from Northern Quebec show discrete ranges in their $^{87}Sr/^{86}Sr$ and $\delta^{88/86}Sr$ isotope compositions that correlate with the Ca/Sr and Na/Sr ratios of the river water. These correlations are interpreted to reflect differential chemical weathering of felsic versus mafic source rocks and/or of surficial sediment *vs* bedrock sources.

1. Introduction

The northern boreal rivers of Asia, Europe and North America are important contributors of fresh water and organic carbon to northern seas such as the Arctic Ocean, the Baltic Sea and Hudson Bay (e.g. Moore, 2003; Ingri et al., 2005; Déry et al., 2005; Kritzberg et al. 2014). Many of these boreal rivers are characterized by large accumulations of snow and ice during the winter months that is released as large pulses of spring melt water that ultimately flow into the northern seas and oceans. Trace element and Sr isotope studies of boreal rivers and streams have shown that the injection of melt water leads to a dilution of most trace elements in the river, but can also lead to a change in the source of the elements during the spring flood season (Ingri et al., 2005; Land et al., 2000). This is also true for rivers draining into Hudson Bay where Rosa et al. (2012) have shown that Sr and most major ions and trace elements are diluted by the spring melt water pulse.

Trace element and radiogenic strontium isotope ($^{87}Sr/^{86}Sr$) studies are a proven resource for tracing the transfer of sediment and water from the continents to the oceans. This has been illustrated in a number of studies ranging from the determination of global silicate weathering rates (Millot et al., 2002; Gaillardet et al. 1999) to documenting the flux of major and trace elements to the ocean on a global basis (e.g., Vance et al. 2009). More recently, the stable ($\delta^{88/86}Sr$) isotope ratio of strontium has proven to be a useful proxy for tracing chemical weathering (de Souza et al., 2010; Wei et al., 2013; Pearce et al., 2015; Chao et al., 2015; Andrews et al. 2016; Stevenson et al. 2016). For example; Andrews et al. (2016) and Stevenson et al. (2016) found significant fractionation in the $\delta^{88/86}Sr$ ratio as a result of differential chemical weathering of distinct source rocks. The observed variations in $\delta^{88/86}Sr$ are attributed to a combination of carbonate and silicate weathering, secondary carbonate precipitation, as well as to mixing between river waters and soil/shallow aquifer waters that have been affected by biological (plant) fractionation (Shalev et al., 2013a; Andrews et al., 2016). Wei et al. (2013)

demonstrated that weathering of carbonate rocks led to low stable and radiogenic strontium isotope compositions in the Xijiang River of southeast China and that the isotope compositions increased as a result of increased weathering of silicate rocks in the rainy season. In a study of a river catchment dominated by siliciclastic sedimentary rocks in Taiwan, Chao et al. (2015) observed little or no variation in $\delta^{88/86}$Sr over the course of a year and that the values obtained overlapped with global flux-weighted average of 0.27 ‰ (Krabenhöft et al., 2010). Stevenson et al. (2016) obtained similar results in a study of glacial outflow from the Lemon Creek Glacier in Southeast Alaska that is underlain largely by granitic rocks.

These studies suggest that rivers underlain by calcareous rocks yield the largest fractionation of $\delta^{88/86}$Sr ratios and often portray a correlation between the stable and radiogenic strontium isotope compositions (Krabenhoft et al., 2010; Wei et al., 2013; Pearce et al., 2015). Conversely, rivers draining silicate-dominated terrains show limited variation in the stable strontium isotope composition and no correlation with the radiogenic strontium isotope composition with the exception of rivers that drain volcanic islands (Chao et al., 2015; Pearce et al., 2015; Stevenson et al., 2016). The variable stable Sr-isotope compositions of rivers draining volcanic islands were interpreted to be the result of the formation secondary minerals (Krabenhoft et al., 2010; Pearce et al., 2015).

The above studies have looked at a large number of boreal rivers, but do not include a study of boreal rivers over space and time that would provide insights to the effect of meltwater surges during the spring flood period or to the impact of river management. For example, Déry et al. (2011) documented a shift in the seasonality of Hudson Bay discharge between 1964 and 2008 due to river management. This paper attempts to document seasonal variations in the chemical weathering of silicate vs carbonate dominated catchments, as well as the impact of large hydroelectric reservoirs on Sr-isotope signatures in surbarctic Canada. ^{87}Sr/^{86}Sr and $\delta^{88/86}$Sr isotope data have been collected over a one-year period in the Koksoak, Great Whale and La Grande rivers (northern Quebec), and Nelson River (central and western Canada). These rivers were chosen because they have been previously well studied in terms of trace element data (Rosa et al. 2012) and sub-samples of the Rosa et al. (2012) study were made available for this study. In addition, three of these four rivers (Nelson, La Grande, Koksoak) have either been dammed or diverted in some way, allowing an investigation of the impact of human activity on geochemical fluxes.

2. Materials and Methods

2.1 Geological Setting

The four river catchments sampled in this study drain a combined area of more than 1.5 x 10^6 km^2 in northern and western Canada (Fig. 1). Three of these rivers (the Koksoak, La Grande and Great Whale) drain the Proterozoic granite-greenstone terrains of the Canadian Shield in Northern Quebec, while the fourth (the Nelson River) predominantly drains Paleozoic sediments exposed in the interior of the continent. All of the rivers drain a combination of tundra to boreal and temperate domains, with mean annual temperatures ranging from 4˚C in the Canadian Prairies to -5.7˚C in Kuujjuaq near the outlet of the Koksoak River into Ungava Bay (Déry et al., 2005; Environment Canada, climatic archive database).

The La Grande and Great Whale Rivers principally drain Archean terrains (2.9-2.65 Ga) dominated by intrusive granitoids and metamorphic rocks that discharge into James Bay and Hudson Bay with mean annual discharge rates of 3808 and 632 m^3/s, respectively (Rosa et al., 2012). The Koksoak River has a mean annual discharge rate of 1600 m^3/s (Rosa et al., 2012) and discharges into Ungava Bay. The drainage basin of the Koksoak River differs from the other two Quebec Rivers in that it also flows through extensive areas of Paleoproterozoic intrusive, volcanic (mafic) and sedimentary rocks of the

New Quebec Orogen (Rosa et al., 2012). The Nelson River draws water from melting glaciers in the Rocky Mountains of Western Canada (e.g., Bow River), as well as from a large portion of the interior Western Platform (North and South Saskatchewan Rivers) and the western portion of the Canadian Shield. These diverse waters flow into Lake Winnipeg, thence into the Nelson River and ultimately into Hudson Bay. Unlike the other three rivers of this study, the larger, western portion of the Nelson River drainage basin is predominately underlain by sedimentary rocks ranging from Paleozoic carbonates and evaporites to poorly consolidated Cretaceous clastic sediments and unconsolidated Quaternary sediments mostly deposited during the last glaciation (Klassen, 1989; Stott and Aitken 1993). As a consequence the Nelson River water is significantly more alkaline than the other three rivers (Rosa et al., 2012).

Three of the four rivers have either been dammed or diverted for hydroelectric plants. The Nelson and La Grande Rivers contain one or more dams and their water discharge rates vary as a result of hydroelectricity production. The headwaters of the Koksoak River have been diverted into the Caniapiscau Reservoir that constitutes the head of the La Grande River, but the Koksoak River still captures some of the natural hydro-climatic signals (Rosa et al. 2012) as does the Great Whale River which remains undeveloped.

2.2 Sampling methods

The samples used in this study are a subset of the samples collected between 2007 and 2009 as part of a larger geochemical investigation on rivers feeding into Hudson Bay, James Bay and Ungava Bay. A detailed description of the sampling procedures in that study can be found in Rosa et al. (2012). The samples were taken at different periods of the year in order to monitor chemical and isotopic changes during the summer and snowmelt seasons. In brief, all samples were collected in mid-stream at a depth of about 30 cm below the surface or 50-100 cm below the ice surface in the winter with the exception of the La Grande River that was sampled at a water sampling site at the head of the feed to the turbines of the LG2 hydroelectric dam. The Nelson River was sampled downstream from the Long Spruce Hydroelectric Station in Manitoba. Samples for the Koksoak and Great Whale Rivers were collected a few kilometers upstream from their outlets. The water samples were filtered through a 0.45 μm nylon membrane, acidified to a pH of 2 and stored at ~5˚C until analysis.

2.3 Analytical methods

Radiogenic and stable Sr isotope analyses were conducted at the National Oceanography Centre in Southampton and at the Geotop laboratories at the Université du Québec à Montréal. Both laboratories followed the chemical and analytical procedure described in Pearce et al. (2015): aliquots of the river water samples that contained 1000 ng of Sr were evaporated in Teflon™ beakers, before being re-dissolved and evaporated in concentrated nitric acid to remove any residual organic material and to convert the residues to nitride salts. The salts were then re-dissolved in 2ml of 3N HNO3 acid with half of the solution put aside for radiogenic isotope analysis and the other half spiked with an appropriate amount of a ^{84}Sr–^{87}Sr double spike. The amount of spike was optimized for a 500 ng sample in order to optimize error propagation during the spike deconvolution process (Krabbenhöft et al., 2009; Shalev et al., 2013b; Neymark et al., 2014; Pearce et al., 2015). The Sr in each fraction was then separated using Eichrom Sr-Spec™ resin using the elution sequence described in Pearce et al. (2015).

The purified Sr fractions were loaded onto a single zone-refined Re filament using the 'Parafilm dam' technique described by Charlier et al. (2006), prior to being analyzed on a Triton™ Thermal Ionisation Mass Spectrometer in both Southampton and Montreal via static analysis. The samples were analyzed at an intensity of 8 V for 54 cycles with 10 ratios in each cycle using a 16 second integration time. A detailed description of the analytical routine can be found in Stevenson et al. (2014). The analyses for the radiogenic aliquots were normalized to the fixed ^{86}Sr/^{86}Sr ratio of 0.1194 (Nier, 1938), while stable Sr isotope ratios were determined by combining measurements on the unspiked and spiked samples via the Newton-Raphson iteration technique in ^{87}Sr denominator space (Pearce et al., 2015).

Analyses of splits of the same solution of the international NBS-987 Sr standard run during the course of this study yielded average ^{87}Sr/^{86}Sr ratios of 0.710259 +/- 5 (2σ; n = 11; Southampton) and 0.710251 +/- 5 (2σ; n = 18; Montreal). Analyses from both laboratories were normalized against a NBS-987 value of 0.710255. The calculated $\delta^{88/86}$Sr values for NBS-987 analyses for each analytical session were averaged and then normalized against a true NBS-987 $\delta^{88/86}$Sr value of zero. The resulting normalization value was used to correct the sample $\delta^{88/86}$Sr values for each session. Both laboratories yielded identical $\delta^{88/86}$Sr values for NBS-987 over the course of the study; -0.002 +/- 0.014 (2σ; n =9) at Southampton and -0.002 +/- 0.021 (2σ; n =11) for measurements at Montreal. The Sr blank at both institutions was less than 50 pg and represents <0.01% of the total Sr in each aliquot.

3. **Results**

3.1 Trace element geochemistry

The geochemical data used for this study is presented in Table A1 (supplementary data). Figure 2 illustrates the geochemical differences between these rivers based on the samples selected for this study. During the sampling period, the pH of the rivers varied between 6.1 and 8.1, with the Nelson River being significantly more alkaline than the three northern Quebec rivers. These different pH values reflect the varying geological compositions of the drainage basins (Rosa et al., 2012) as ~90% of the Nelson River drainage basin is underlain by sedimentary rocks that include calcareous sediments, whereas the three Quebec rivers are underlain by the intrusive and volcanic igneous rocks of the Canadian Precambrian Shield (70-99%). These differences are also reflected in the plot of pH versus the

Ca/Mg ratio (Fig. 2a) in which the Nelson River has the highest pH and highest Ca content. Among the Quebec rivers, the pH and the Ca content increase from the La Grande to the Great Whale then to the Koksoak Rivers. Figure 2b shows that the Ca/1000Sr ratio increases with increasing pH, suggesting that Ca increases with alkalinity at the expense of Sr. Figure 2c shows the relationship between the Ca/1000Sr and Mg/1000Sr ratios among the four rivers. This plot underlines the higher Mg content of the Koksoak River compared to those of the other four rivers likely reflects the higher proportion of volcanic (largely mafic in composition) and sedimentary rocks (30%) within its drainage basin (Rosa et al., 2012). No correction was made for atmospheric deposition (*e.g.*, Gaillardet et al., 1999) in these basins, as it did not affect the observed correlations.

3.2 Radiogenic stable Sr isotope analyses

The stable and radiogenic isotope data for the four rivers are presented in Table 1 and plotted in Figures 3 and 4. Figure 3a displays $\delta^{88/86}$Sr vs $\delta^{84/86}$Sr values of samples and of the NBS-987 standard. It illustrates that the values obtained at both the UQAM and Southampton laboratories conformed to the mass dependent fractionation line of -0.9545. Figure 3b plots the ^{87}Sr/^{86}Sr isotope ratios for samples analyzed at both UQAM and Southampton and also demonstrate that samples analyzed at both laboratories yielded comparable ^{87}Sr/^{86}Sr isotope ratios. In Figure 4, the Nelson River has the lowest ^{87}Sr/^{86}Sr ratios with very little variation (0.71295 to 0.71315) whereas the three Quebec rivers are much more radiogenic than the majority of rivers surveyed for stable Sr isotopes (e.g., Pearce et al. 2015; Krabenhoft et al., 2010) but are comparable with the Ganges River of India (Pearce et al., 2015) as well as with rivers draining the Slave Craton of northwestern Canada (Millot et al., 2002). The Koksoak River has the lowest ^{87}Sr/^{86}Sr ratios among the Quebec rivers with values ranging between 0.72701 and 0.72985. The La Grande River yielded ^{87}Sr/^{86}Sr ratios between 0.73023 and 0.73156 and the Great Whale

River is (on average) the most radiogenic river with $^{87}Sr/^{86}Sr$ ratios varying from 0.73030 and 0.73424. The more radiogenic Sr isotope composition in Quebec rivers, compared to the Nelson River, reflects the older Precambrian crust underlying these rivers compared to the younger Phanerozoic sediment/carbonate-dominated rocks underlying the Nelson River.

The stable Sr isotope composition $\delta^{88/86}Sr$ of the four rivers varies from 0.29 to 0.39 (Fig. 4), effectively bracketing the terrestrial silicate average of 0.30‰ (Moynier et al., 2010; Charlier et al., 2012) and the flux weighted global river average of 0.32 +/- 0.008 (Krabbenhöft et al., 2010; Pearce et al., 2015). The Nelson River shows the largest variation from 0.30 to 0.38 followed by the Great Whale River with values from 0.29 to 0.36. The La Grande and Koksoak rivers show more narow ranges of 0.30 to 0.32 and 0.37 to 0.39, respectively. All rivers yield a range of $\delta^{88/86}Sr$ values that are also overall similar to those derived from glacial run-off in the Alaska Panhandle (0.26 ± 0.02 to 0.40 ± 0.02‰; Stevenson et al. 2016) and to rivers draining into the Milford Sound region of Fiordland, New Zealand (Andrews et al., 2016). As a group, the Quebec rivers show a slight negative trend of decreasing radiogenic Sr isotope ratios with increasing stable Sr isotope compositions. This likely reflects the relative proportion of felsic versus mafic silicate rocks in the three catchment basins and is discussed in section 4.2.

3.3. Seasonal variations in the radiogenic and stable Sr isotope ratios

The $^{87}Sr/^{86}Sr$ and $\delta^{88/86}Sr$ isotope data are plotted against their sampling date in Figure 5. Over a period of six months the $^{87}Sr/^{86}Sr$ ratios of the Koksoak River decrease from a high of 0.72985 in February 2009 to a low of 0.72714 in July 2009 (Fig. 5a). The time series $^{87}Sr/^{86}Sr$ profile for the Great Whale River is more radiogenic in the winter and summer, but shows an abrupt decrease in the $^{87}Sr/^{86}Sr$ ratio during the snowmelt period (Fig. 5b). The Nelson River yields a somewhat flat $^{87}Sr/^{86}Sr$ profile and the La Grande River yields a convex profile with slightly more radiogenic Sr dominating in late winter and through the snowmelt season (Fig. 5b),. The trends observed in the Koksoak and Great Whale Rivers are in the opposite direction with more radiogenic Sr isotope ratios dominating in the winter months (Fig. 5a, b).

The $\delta^{88/86}$Sr values of the Koksoak River varied little over the six month sampling period and yielded a flat profile (Fig. 5c). The Great Whale River time series profile (Fig. 5d) is relatively constant through the winter and spring flood season but increases during the summer before decreasing from 0.36 to 0.29 in the autumn. The La Grande River also has a relatively flat time series profile (Fig. 5d), except for a slight decrease in the $\delta^{88/86}$Sr values in December, 2007. The Nelson River time series profile (Fig. 5d) increases slowly from the winter to the fall, but it is the only river to show a significant shift, a decrease, in the $\delta^{88/86}$Sr values during the spring flood season.

4.0 Discussion

4.1. Temporal variations

Seasonality has been shown to have a marked influence on the dissolved ^{87}Sr/^{86}Sr composition of rivers (Douglas et al., 2013; Voss et al., 2014). For example, Voss et al. (2014) showed that ^{87}Sr/^{86}Sr isotope ratios from the Frazer River in Western Canada varied from as low as 0.709 in the winter to as high as 0.714 in the summer with the increase reflecting the release of radiogenic Sr from weathered clays and clay rich sedimentary rocks during summer months. Stevenson et al. (2016) also noted a slight increase in the ^{87}Sr/^{86}Sr ratio of water from the subglacial outflow of the Lemon Creek glacier (Juneau Ice Field, Alaska) during a one month period during the summer of 2012. Douglas et al (2013) documented a similar trend of more radiogenic Sr isotope ratios in the summer versus winter in the boreal Chena river of Central Alaska that they attributed to a higher proportion of silicate versus carbonate mineral dissolution in the summer months.

Unlike the Chena and Frazer river profiles noted above, none of the four rivers sampled for this study shows a consistent trend in their radiogenic Sr isotope composition over the sampled period. The $^{87}Sr/^{86}Sr$ ratios of the Koksoak decrease steadily during the summer from January to July, 2009 (Fig. 5a). The time series $^{87}Sr/^{86}Sr$ profile for the Great Whale River is more radiogenic in the winter and summer, but shows an abrupt decrease in the $^{87}Sr/^{86}Sr$ ratio during the snowmelt period (Fig. 5b) which suggests a greater contribution from a less radiogenic source, such as carbonates, or an increased dissolution of silicate minerals derived from mafic rocks. The lack of a strong time-series $^{87}Sr/^{86}Sr$ profile for the La Grande and Nelson Rivers (Fig. 5b) may be related to the fact that these rivers are extensively developed for hydroelectric power and that the damming of the rivers results in a longer residence time of the river water that buffers seasonal gradients. For example, a study of dammed rivers in China, found that the weathering rate increased with the impoundment time of the water in the reservoir (Gao et al., 2013). This greater weathering could lead to an averaging out of geochemical variations on a yearly basis. Another factor is that given the large size of the Nelson River drainage basin, it is unlikely that snowmelt is concurrent across the basin, leading to an averaging out of the meltwater pulse over time. The trends observed in the Koksoak and Great Whale Rivers are in the opposite direction with more radiogenic Sr isotope ratios during winter months (Fig. 5a, b). Given their similar climatic conditions, the Sr isotope composition of the Quebec rivers will reflect the Sr isotopic composition of the most easily altered and eroded rock-type. In the subarctic environment of Northern Quebec, mafic rocks are abundant and among the most easily altered and eroded rock-type. During the summer months and/or snowmelt period, the friable mafic mixture would be prone to chemical weathering and the release of larger amounts of less radiogenic Sr to the rivers resulting in a decrease in the $^{87}Sr/^{86}Sr$ ratio as observed for the Koksoak and Great Whale Rivers. Water derived from the melting of the snow in the spring is not viewed as a significant contributor to the Sr budget because of the very low Sr contents in snow (typically less than 0.5 ppm; e.g. Simonetti et al., 2000) compared to the larger Sr reservoirs of the rocks, mineral and soils.

The time series variations observed in the $\delta^{88/86}$Sr values for the four rivers are not consistently associated with any one season and do not correlate with time series changes observed for the radiogenic Sr isotopes. The $\delta^{88/86}$Sr values for the Koksoak remain essentially constant throughout the year (within error, Fig 5c). The $\delta^{88/86}$Sr values for the La Grande River show no sbrupt changes bu display a small decrease during the winter (Fig. 5d). The $\delta^{88/86}$Sr values of the Great Whale River rise through the winter and spring months and decrease abruptly in the summer (Fig. 5d), but there is no abrupt change in the stable Sr isotope composition during the snowmelt period as seen in Figure 5b for the radiogenic Sr isotope compositions. The $\delta^{88/86}$Sr values of the Nelson River show an abrupt decrease during the snowmelt period (April 2008) and returned to an average value during the summer (Fig. 5d). Here again, the abrupt decrease in the $\delta^{88/86}$Sr values of the Nelson River is not accompanied by a corresponding change in the radiogenic Sr isotope composition. Thus although the $^{87}Sr/^{86}Sr$ ratios may respond to seasonal forcing in still "pristine" rivers (*e.g.*, Great Whale River), the $\delta^{88/86}$Sr values appear to be largely immune to the forces that act upon the radiogenic Sr isotope ratios. The $^{87}Sr/^{86}Sr$ and $\delta^{88/86}$Sr isotope systems are therefore decoupled from one another in these river systems. This decoupled behavior has also been observed for time-series $^{87}Sr/^{86}Sr$ and $\delta^{88/86}$Sr isotope data for the Hou-Ku River in Taiwan (Chao et al., 2013) and glacial out flow in Southeast Alaska (Stevenson et al., 2016), although Wei et al. (2013) documented a strong correlation between $^{87}Sr/^{86}Sr$ and $\delta^{88/86}$Sr isotope compositions for the Xijiang River in China, that was ascribed to variable carbonate *vs* silicate weathering.

In a $^{87}Sr/^{86}Sr$ isotope and geochemical study of a boreal stream environment, Land et al. (2000) divided water contributions to the streams into 3 compartments: deep ground water that contributed mostly during the late summer and fall base flow season (5-20%), soil water that dominated during the spring melt and shallow groundwater that dominates during base flow (during summer/fall). These observations could explain some of the observed variations in the rivers of this study. The Nelson River is distinct from the three Quebec rivers in that it drains the well-developed soils of the North American Prairie grasslands. The relatively constant $^{87}Sr/^{86}Sr$ isotope ratio over the nine month sampling period likely reflects the buffering of the radiogenic Sr isotope composition of these soils on the Nelson River. The decrease in the stable Sr isotope composition of the Nelson river during the spring melt could reflect the flushing of the soils by the spring run-off and the addition of soil water that is typically depleted in ^{88}Sr (Andrews et al., 2016). In contrast, the radiogenic Sr isotope composition of the Great Whale River decreases during the spring melt, but shows no change in its stable Sr isotope composition during the same period. The change in source indicated by the decrease in the $^{87}Sr/^{86}Sr$ may reflect the erosion of glaciofluvial and glaciomarine sediments containing younger crustal components during the spring flood that form the shores of the lower reaches of the river (Paradis and Parent, 1997). The lack of response in the stable Sr isotope composition suggests that the eroded Archean rocks and glaciofluvial/glaciomarine sediments in Great Whale River catchment have a similar mineralogical composition. The subsequent decrease in the stable Sr isotope composition of the Great Whale River in the late summer may reflect the addition of groundwater that has been depleted in ^{88}Sr due to its interaction with silicate rocks and/or the formation of secondary minerals (*e.g.*, clay minerals, micas).

4.2. Silicate *vs* carbonate weathering

Insights to the decoupled behavior of radiogenic and stable Sr isotope compositions in boreal rivers can be obtained by comparing the Sr isotope compositions with the geochemistry of the rivers. There is a broad negative correlation between the pH of the rivers (especially among the Quebec rivers) and the radiogenic Sr isotope ratios with the $^{87}Sr/^{86}Sr$ ratio generally increasing with decreasing pH (Fig 6a). Wei et al. (2013) also noted a negative correlation between pH and the $^{87}Sr/^{86}Sr$ ratio in a year-long observation of the Xijiang River water of Southeast China and suggested that this reflected increased chemical weathering of silicate rocks under low pH conditions, yielding an increase in the $^{87}Sr/^{86}Sr$ ratio. These variations also reflect the difference in the geology of the drainage basins. The weathering of granitic rocks, of greatest abundance in the Great Whale watershed (Rosa et al., 2012), yields a higher abundance of acidic cations and results in the lower pH and a higher $^{87}Sr/^{86}Sr$ ratio of Great Whale River. Conversely, the weathering of mafic rocks such as basalt (Koksoak River) release greater amounts of basic cations such as Mg, and less radiogenic Sr. The even higher pH and lower $^{87}Sr/^{86}Sr$ ratios of the Nelson River result from the higher abundance of carbonates in the hinterland of its drainage basin.

The $^{87}Sr/^{86}Sr$ ratios of the three Quebec rivers show a positive correlation with the Ca/Mg ratios and broadly negative correlations with the Ca/1000Sr and Ca/Na ratios (Fig. 6b-d). These correlations can also result from some control by relative contributions of granitic versus mafic rocks (extrusive and intrusive). Drainage basins within the Canadian Shield that contain significant amounts of mafic igneous rocks (e.g., Koksoak River) would have high Ca/Na and Ca/Sr ratios, low Ca/Mg ratios and low $^{87}Sr/^{86}Sr$ ratios. The higher $^{87}Sr/^{86}Sr$ ratios and Ca/Mg ratios, and lower Ca/Na and Ca/Sr ratios in the La Grande and Great Whale rivers reflects the greater proportion of granitic versus mafic rocks in their respective watersheds.

In contrast to the rivers of northern Quebec, Andrews et al. (2016) documented a positive correlation between the $^{87}Sr/^{86}Sr$ and Ca/Sr ratios in rivers draining into the Milford Sound of New Zealand. The authors attributed their positive correlation to the mixing of radiogenic soil water with riverine water. Soils are thin and poorly developed in the sub-arctic environment of northern Quebec. In the scarce and thin soils that characterize these drainage basins, both the interpretation above and that of Andrews et al. (2016) are consistent. In northern Quebec, the exchangeable Sr would yield $^{87}Sr/^{86}Sr$ isotope ratios similar to that of the bedrock considering the reduced chemical weathering that is present in the subarctic versus temperate environment of New Zealand. The abundance of carbonate and evaporite deposits in the watershed of the Nelson River results in the low Ca/Mg and higher Ca/Na and Ca/Sr ratios with lower $^{87}Sr/^{86}Sr$ ratios. It is noteworthy that the territory drained by the three Quebec rivers was the first area to be regionally sampled to obtain an average composition of the Earth's crust (Shaw et al. 1967), and the $^{87}Sr/^{86}Sr$ isotope ratio of this composite (0.7283; McCulloch and Wasserburg 1978) is comparable with the average Koksoak River $^{87}Sr/^{86}Sr$ composition of 0.7286.

The $\delta^{88/86}Sr$ isotope values also vary with the composition of the river waters. The pH of the Quebec rivers fall into discrete ranges with minor overlaps and, generally, the higher the pH of the river, the higher the stable Sr isotope composition of the river (Figure 7a). A number of studies have indicated that high $\delta^{88/86}Sr$ values in rivers are the product of weathering that releases heavy ^{88}Sr from silicates while the light ^{86}Sr is precipitated in secondary carbonate minerals (De Souza et al., 2012; Wei et al., 2013; Pearce et al., 2015; Andrews et al., 2016; Stevenson et al., 2016). Carbonate precipitation is also greater at higher pH and this would lead to higher $\delta^{88/86}Sr$ values in the river water after the carbonate precipitation.

However, as seen in the correlations with the radiogenic Sr isotope compositions, the increase in $\delta^{88/86}Sr$ values with pH may also be a product of the underlying geology with the heavier values reflecting weathering of the mafic rock that dominate the Koksoak drainage basin. The alteration and metamorphism of mafic rocks (basalt, gabbro) are accompanied by extensive formation of serpentine, talc and calcite; the formation of calcite in these assemblages likely traps the light Sr leaving the heavy Sr to be released to the environment. Alternatively, the weathering and metamorphism of mafic rocks releases abundant heavy Sr from silicate minerals such as pyroxene and calcic plagioclase that are less resistant to alteration compared to the more resistant K-feldspar and quartz that dominate in granite domains. The Nelson River does not follow this correlation, presumably due to the buffering effect of the abundant carbonate and evaporites in its drainage basin.

The $\delta^{88/86}$Sr values also correlate with the Ca/Na ratios, Ca/Mg and Ca/1000Sr ratios (Fig. 7b-d). The correlation with the Ca/Na ratio underlines the relationship of the $\delta^{88/86}$Sr variation with the degree of differentiation present in the bedrock underlying the drainage basins. The Quebec rivers show a decrease in the $\delta^{88/86}$Sr values with a decrease in the Ca/Na ratio. As the abundance of mafic rock in the drainage basin decreases and the amount of granitic rock increases, the $\delta^{88/86}$Sr values decrease due to a lesser contribution from weathered mafic rocks. Note that the Nelson River also follows this trend. This likely reflects the contribution of carbonate/evaporite *vs* silicate weathering products. The negative trend on the Ca/Mg versus $\delta^{88/86}$Sr diagram (Fig. 7c) could also be interpreted the same way. The high Ca/Mg ratio is found among the rivers draining basins underlain by greater proportions of granitic bedrocks whereas the lower Ca/Mg ratios are associated with the rivers underlain by mafic and sedimentary rocks (Koksoak and Nelson Rivers). The higher $\delta^{88/86}$Sr values associated with lower Ca/Mg ratios reflect the breakdown of the mafic silicates containing heavy Sr and the addition of this heavy Sr to river waters. The correlation between the Ca/1000Sr and $\delta^{88/86}$Sr values (Fig. 7d) behaves similarly with the heaviest $\delta^{88/86}$Sr isotope values correlating with the highest Ca/Sr ratios in the Quebec rivers. This reflects the higher proportion of Ca in the rivers (Koksoak) that have a greater abundance of mafic rocks in their watershed.

4.3 Global comparisons

Figure 8 provides a comparison of the Ca/1000Sr ratios and the $\delta^{88/86}$Sr values for the rivers of this study with those measured in other river water studies (Chao et al., 2013; Wei et al., 2013; Pearce et al., 2015; Andrews et al., 2016; Stevenson et al., 2016). The black arrows indicate the positive correlation between the Ca/1000Sr ratios and $\delta^{88/86}$Sr values as a result of carbonate and silicate weathering. This trend has been documented for carbonate dominated rivers in France (Pearce et al., 2015) and China (Wei et al., 2013) and is evident in the Upper Holly River catchment of New Zealand (Andrews et al., 2016). Low $\delta^{88/86}$Sr and Ca/1000Sr ratios reflect intense carbonate weathering with the release of light Sr and large amounts of Sr to the rivers, while the high $\delta^{88/86}$Sr and Ca/1000Sr ratios reflect carbonate precipitation and increased silicate weathering. In the absence of significant carbonate dissolution, the positive correlation is controlled by the silicate weathering process. Weathering of Ca-rich mafic bedrock releases heavy Sr to the rivers because light Sr is retained in secondary carbonate. Drainage basins that are underlain by more differentiated bedrock (granites) yield lower $\delta^{88/86}$Sr values due to release of lighter Sr from weathered feldspars and micas. Charlier et al. (2012) documented stable Sr isotope values as low as 0 to -0.2 for highly differentiated volcanic tuffs and rhyolitic glasses and suggested that magmatic fractional crystallization could result in these low $\delta^{88/86}$Sr values. The high Ca content of the modern glacier meltwater studied by Stevenson et al. (2016) likely reflects the high Ca content of the underlying tonalite rocks.

Andrews et al. (2016) also found a strong correlation between $\delta^{88/86}$Sr values and the Ca/Sr ratios in rivers draining into the Milford sound of New Zealand. They argued, based on the analysis of soil waters and leaching experiments of the bedrock, that this correlation was the result of the incorporation of isotopically heavy soil water (due to the uptake of light Sr by plants) in the rivers, with secondary mineral formation and precipitation playing a secondary role. This mixture is likely responsible for the negative trend indicated by the dashed line in Figure 8 that is defined by the data from the Lower Hollyford River (LHR) catchment of Andrews et al. (2016). Andrews and Jacobson (2017) found that the $\delta^{88/86}$Sr isotopic composition of Icelandic rivers could also be ascribed to a mixture of basalt and calcite and atmospheric deposition. The three Quebec rivers drain an area in which soils are very thin and often absent and affected by permafrost in the case of the Koksoak River. Thus the uptake of isotopically light Sr by plants, and residual soil waters are not expected to significantly impact the composition of the

Quebec rivers. Samples from the Nelson River drain a soil-rich region and define less of a positive trend in Figure 8 compared to the Quebec rivers, thus plant uptake and soil waters may play a greater role in defining the stable Sr isotope composition of the river. Andrews and Jacobsen (2018) found that the $^{87}Sr/^{86}Sr$ and $\delta^{88/86}Sr$ isotope composition of Icelandic rivers could be modeled as a mixture of Sr derived from hydrothermal calcite, atmospheric deposition and weathered basalt. A comparison with this study is not easily made due to the complex geology of the drainage basins of the rivers of this study.

The $^{87}Sr/^{86}Sr$ and $\delta^{88/86}Sr$ isotope compositions from this study and those of rivers from a number of previous studies are plotted together in Figure 4 (Andrews et al., 2016; Stevenson et al., 2016; Pearce et al., 2015; Wei et al., 2013). In a study of global rivers, Pearce et al. (2015) noted a general lack of correlation between the $^{87}Sr/^{86}Sr$ ratios and the $\delta^{88/86}Sr$ values of the rivers and suggested that the lack of correlation of the stable Sr isotope with other isotopic systems was likely an artefact of the complexity of weathering in multi-lithological catchments. This is supported by the fact that Wei et al (2013) and Andrews et al. (2016) documented both positive and negative correlations in this plot stemming from the competing effects of carbonate and silicate weathering (Wei et al., 2013) and mixing of river water dominated by either silicate or carbonate weathering with soil water (Andrews et al., 2016). The somewhat negative correlation defined by the three Quebec rivers can be interpreted within this context as reflecting a higher contribution of isotopically light and radiogenic Sr released from the weathering of K-feldspar-rich lithologies such as granites (Charlier et al., 2012) and TTG series that dominate the Great Whale River and La Grande River catchments, versus the isotopically heavy and less radiogenic Sr that is released via the weathering of pyroxenes and calcic plagioclase that are more abundant in the Koksoak River catchment.

The watersheds of the three Quebec rivers drain an area that is dominated by silicate rocks and bereft of limestone and/or dolomite. Carbonates are present in the form of secondary weathering/alteration minerals such as calcite, especially in terrains dominated by mafic and ultramafic rocks, as well as in more discrete biogenic carbonates and carbonate concretions from glaciomarine deposits (*e.g.*, Hillaire-Marcel, 1980a and b). It is interesting that the scope of $\delta^{88/86}$Sr values present in the three Quebec rivers combined is comparable to the range of $\delta^{88/86}$Sr values found in Nelson River that has abundant limestone, dolomite and evaporites in its watershed. Given that the amount of carbonate in the catchments of the Quebec rivers that can be weathered is extremely small and that calcite precipitation would be more limited in these northern latitudes, the variation in the $\delta^{88/86}$Sr values is most likely controlled by silicate weathering. Neymark et al. (2014) analyzed a K-feldspar standard (SRM-607) and found $\delta^{88/86}$Sr values as low as 0.18 and ^{87}Sr/^{86}Sr ratios as high as 1.2. The erosion of this type of material would contribute light Sr in weathered granitic terrains such as La Grande and Great Whale Rivers. Stevenson et al. (2016) found that the $\delta^{88/86}$Sr composition of suspended sediment in subglacial outflow from a weathered granitic terrain yielded $\delta^{88/86}$Sr values that were uniformly lower than the glacial outflow water and as low as 0.12. The authors attributed these low values to the leaching of light Sr from micas (biotite) and feldspars.

5. Conclusions

We presented new radiogenic and Sr isotope data for water samples collected over a 6-12 month period for four Canadian boreal rivers. The data demonstrate that underlying geology exerts a primary influence on both the radiogenic and stable Sr isotope compositions. Three rivers draining the Precambrian Shield of Northern Quebec yield highly radiogenic ^{87}Sr/^{86}Sr ratios whereas the Nelson River that drains a catchment dominated by carbonate and clastic sedimentary of the mid-continent has much lower ^{87}Sr/^{86}Sr ratios. The $\delta^{88/86}$Sr compositions straddle the global river average (Krabenhöft et al., 2010; Pearce et al., 2015), but values from the three Quebec rivers vary as a consequence of the proportion of mafic versus felsic silicate rocks within the catchment basin, with heavier $\delta^{88/86}$Sr values correlating with higher proportions of mafic rocks. This correlation is interpreted to reflect the formation of secondary carbonates during the weathering of the mafic rocks that trap the lighter Sr isotopes and underlines the importance of chemical weathering in a northern boreal environment. Samples of the river waters collected in different seasons to monitor changes in river composition during the snow melt period yielded inconsistent results for both radiogenic and stable Sr isotope compositions. Only the Great Whale River showed a variation during the spring thaw with a decrease in the radiogenic Sr isotope composition that was interpreted to result from increased winnowing of younger glacio-fluvial glacio-marine sediments from the banks of the river. The absence of variations in the other rivers may reflect the development of these rivers for hydroelectricity leading to longer residence time for the water. The Great Whale River is the only river of the study that is not developed or diverted for hydroelectricity. Thus, development of rivers appears to affect the isotopic composition of the river in that it smooths out seasonal variations due to longer residence time of the water.

Acknowledgements

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Figure Captions

Figure 1. Locations of the watersheds sampled for this study. 1 = Koksoak River; 2 = Great Whale River; 3 = La Grande River, 4 = Nelson River. Modified from Rosa et al. (2012).

Figure 2. Examples of the Water chemistry of the rivers sampled in this study. A. Ca/Mg vs pH and b. Ca/Sr vs pH. Chemical data from Rosa et al. (2012).

Figure 3. Figure depicts the general coherence of stable Sr isotope data to mass dependent fractionation line (a.) and the similarity of the radiogenic isotope compositions obtained by the UQAM and Southampton laboratories (b).

Figure 4. Plot of stable versus radiogenic Sr isotope compositions. The plot illustrates the radiogenic nature of the three Quebec rivers with respect to the Nelson River and the majority of global river waters studied to this point. See text for details. Terrestrial silicate average from Moynier et al. (2010). Global river average from Krabenhoft et al. 2010 and Pearce et al. (2015).

Figure 5. Time series radiogenic and stable isotope plots for the studied rivers. Solid symbols and large X's are data from UQAM; open symbols and small X's are data from Southampton. Figures b and d share the same legend. Average error for stable Sr isotope analyses indicated in figure c. See text for details..

Figure 6. Plots of the $^{87}Sr/^{86}Sr$ composition of the river water samples versus a. pH; b. Ca/Mg; c. Ca/1000Sr and d. Ca/Na. The trends reflect the lithological control on the isotope composition and the geochemistry of the water. Catchments with greater carbonate or mafic rock contents yield lower $^{87}Sr/^{86}Sr$ ratios and higher Ca, Mg and pH. The red star is the Sr isotope composition and Ca/Mg ratio of the Canadian Shield composite from McCulloch and Wasserburg (1978) and Shaw et al. (1967).

Figure 7. Plots of $\delta^{88/86}Sr$ versus a. pH; b. Ca/Na; c. Ca/Mg; d. Ca/1000Sr. The trends reflect the chemical weathering of mafic versus silicate rocks. See text for details.

Figure 8. A compilation of river water stable Sr isotope data versus Ca/1000Sr. The bulk of the data define sub-parallel positive correlations. These correlations reflect differing degrees of carbonate and silicate weathering. Some data such as that from the Milford Sound LHR catchment illustrate the effects of mixing between river water and soil water (Andrews et al. (2016).

Figure 1

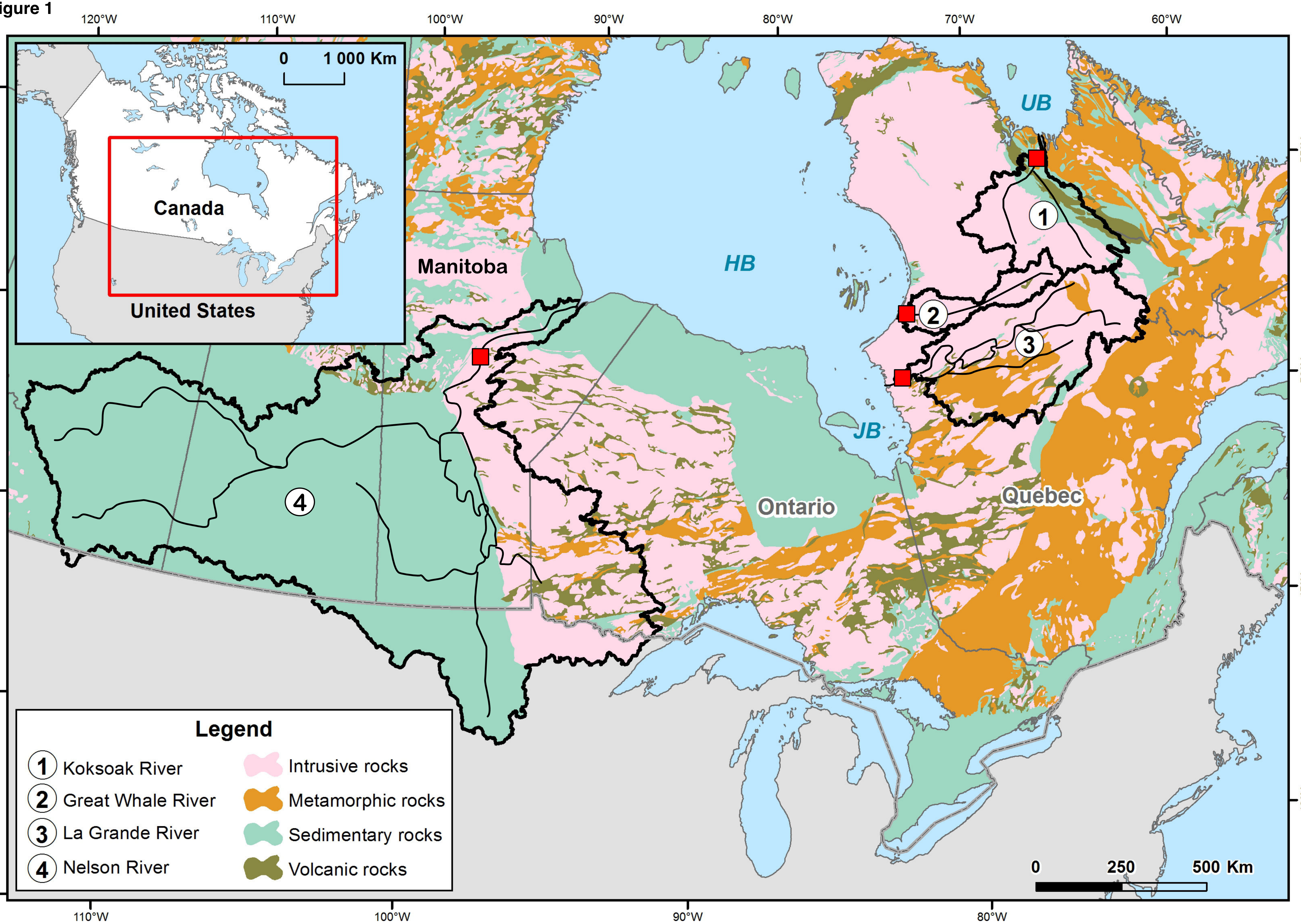
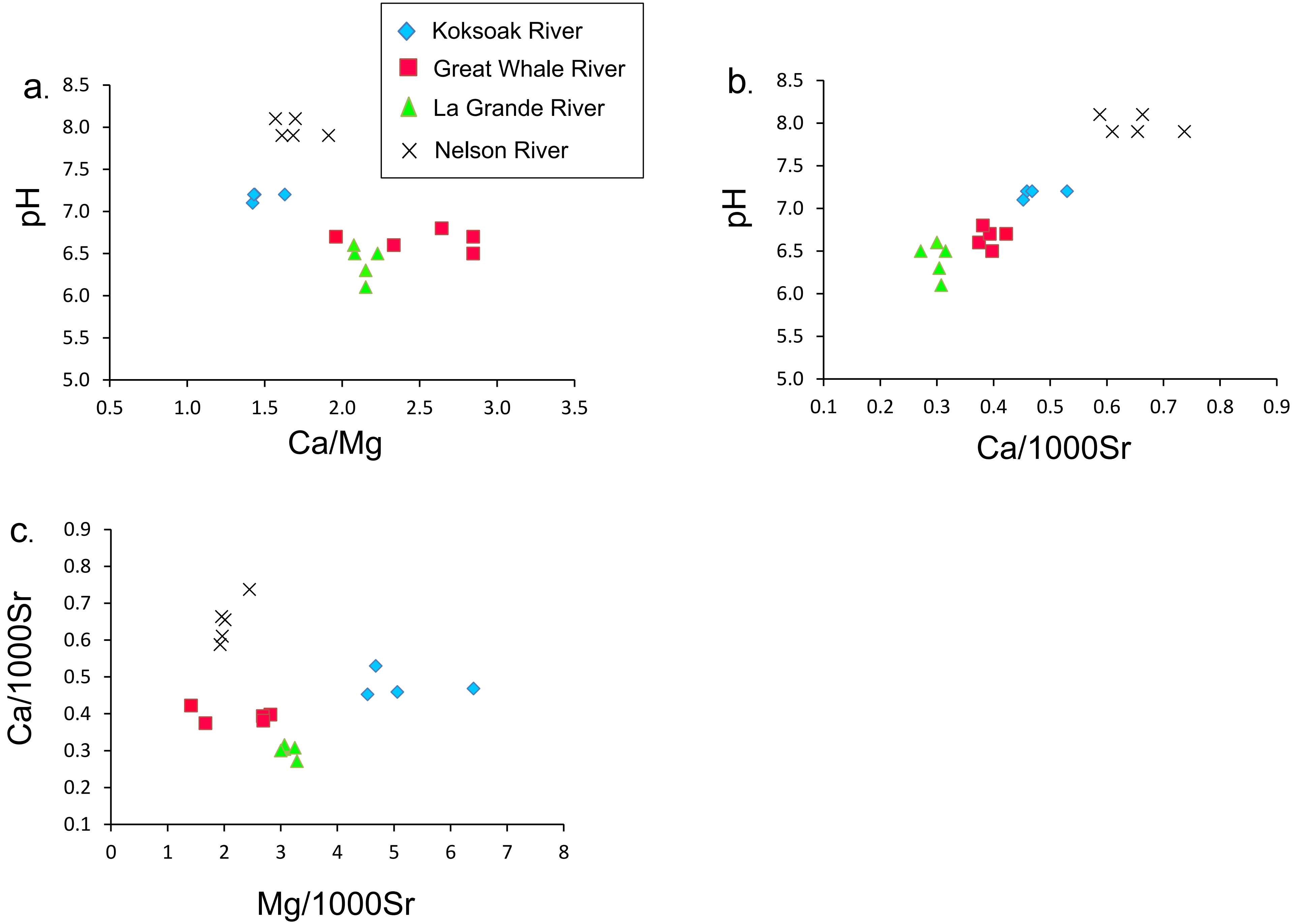
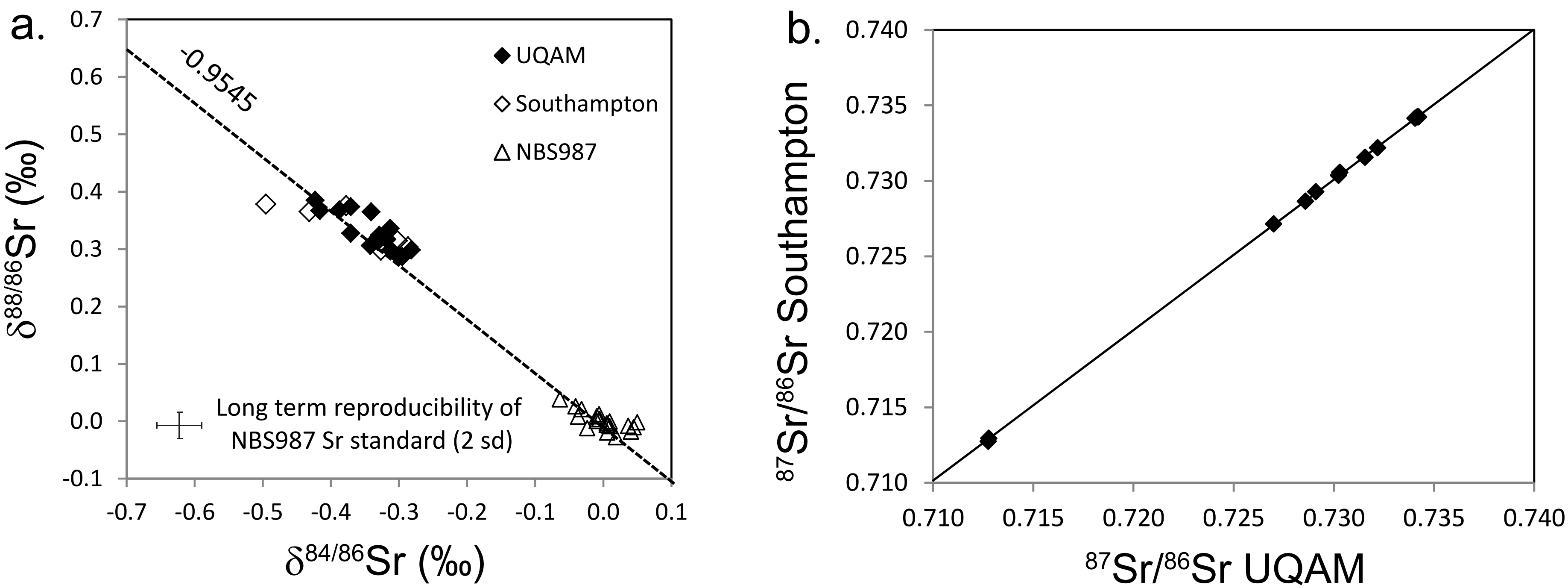

120°W
110°W
100°W
90°W
80°W
70°W
60°W
60°N
55°N
50°N
45°N
40°N
0
1 000 Km
Canada
United States
Manitoba
Ontario
Quebec
HB
JB
UB
1
2
3
4
Legend
1 Koksoak River
2 Great Whale River
3 La Grande River
4 Nelson River
Intrusive rocks
Metamorphic rocks
Sedimentary rocks
Volcanic rocks
0
250
500 Km

Figure 2



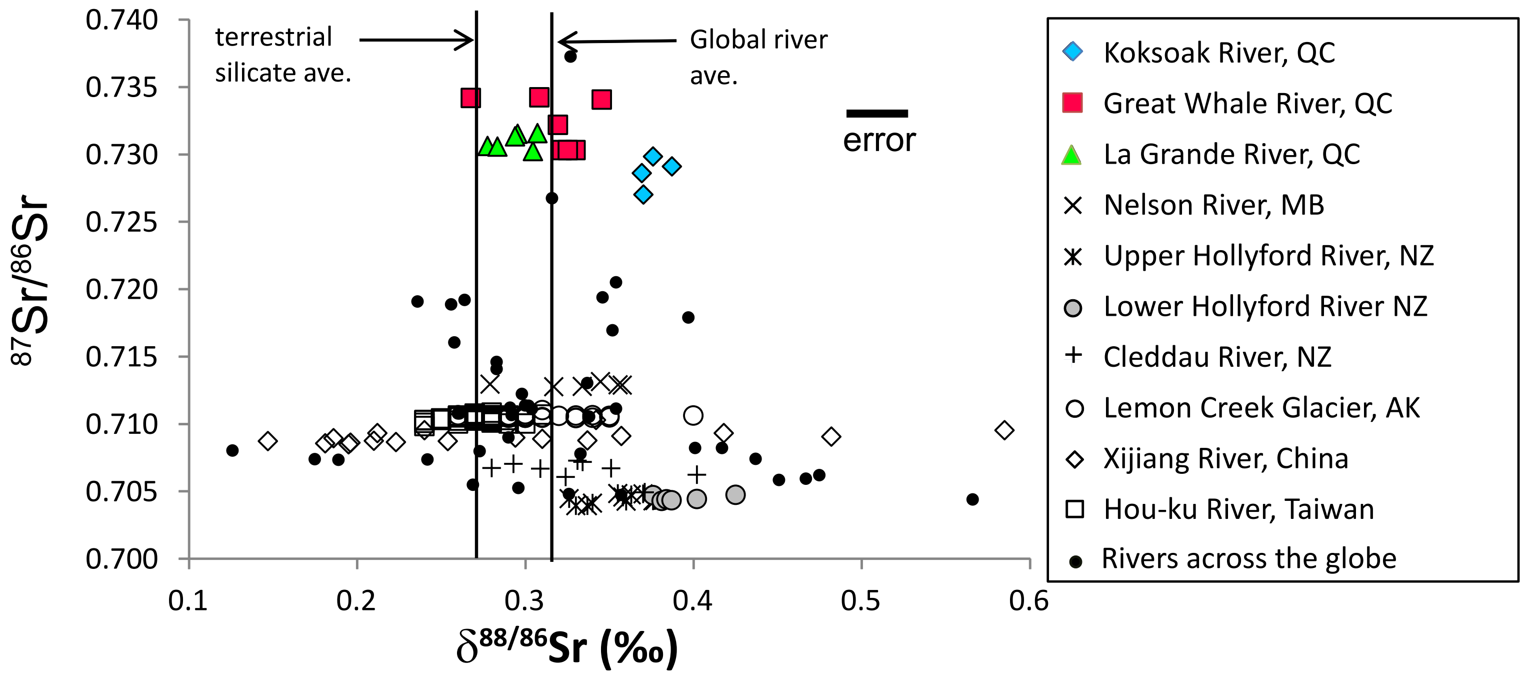
Koksoak River
Great Whale River
La Grande River
Nelson River
a.
pH
Ca/Mg
b.
pH
Ca/1000Sr
c.
Ca/1000Sr
Mg/1000Sr

Figure 3



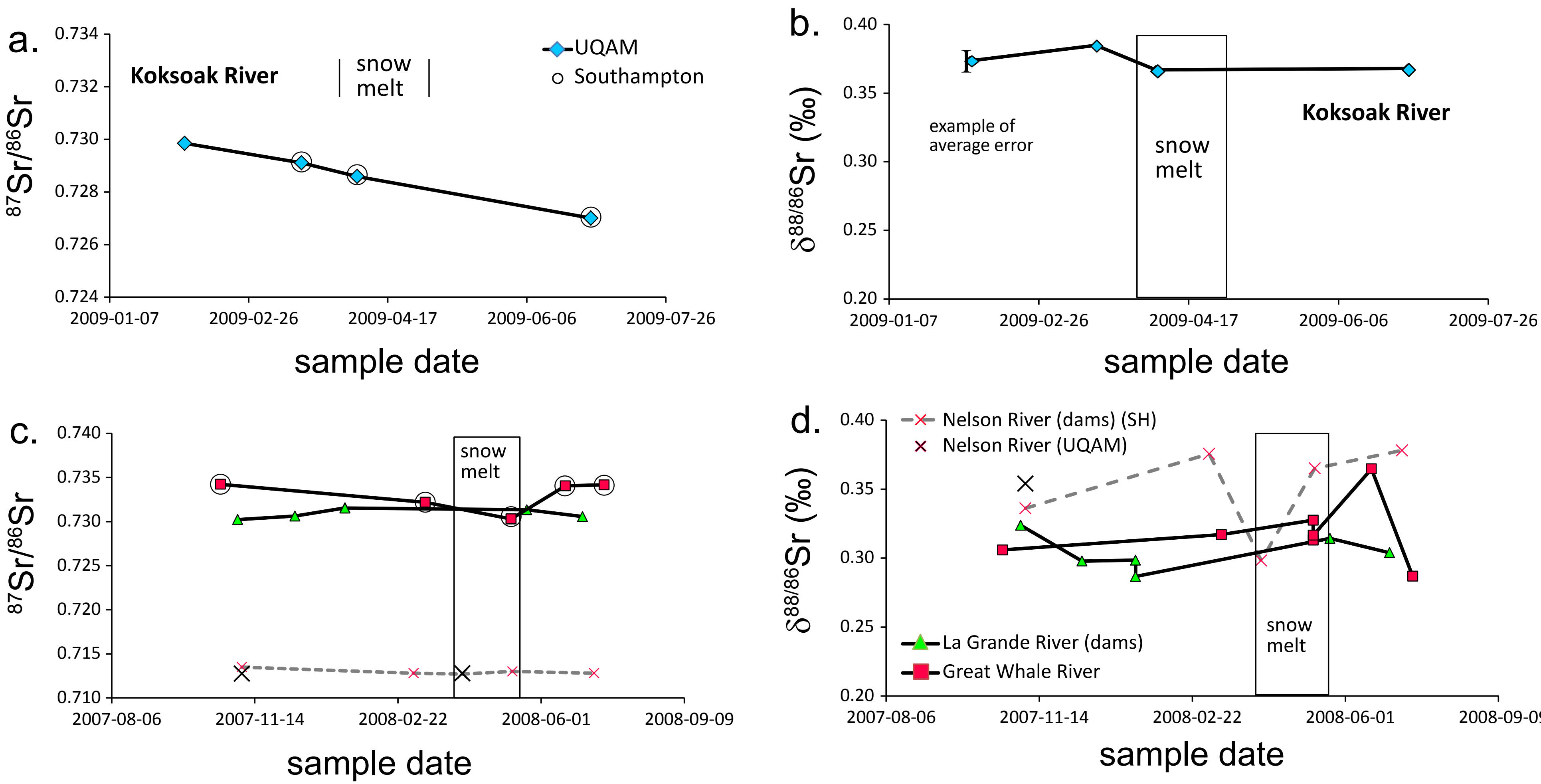
a.
b.
-0.9545
UQAM
Southampton
NBS987
Long term reproducibility of
NBS987 Sr standard (2 sd)
$\delta^{88/86}$Sr (‰)
$\delta^{84/86}$Sr (‰)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.7
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
0.1
^{87}Sr/^{86}Sr Southampton
^{87}Sr/^{86}Sr UQAM
0.740
0.735
0.730
0.725
0.720
0.715
0.710

Figure 4



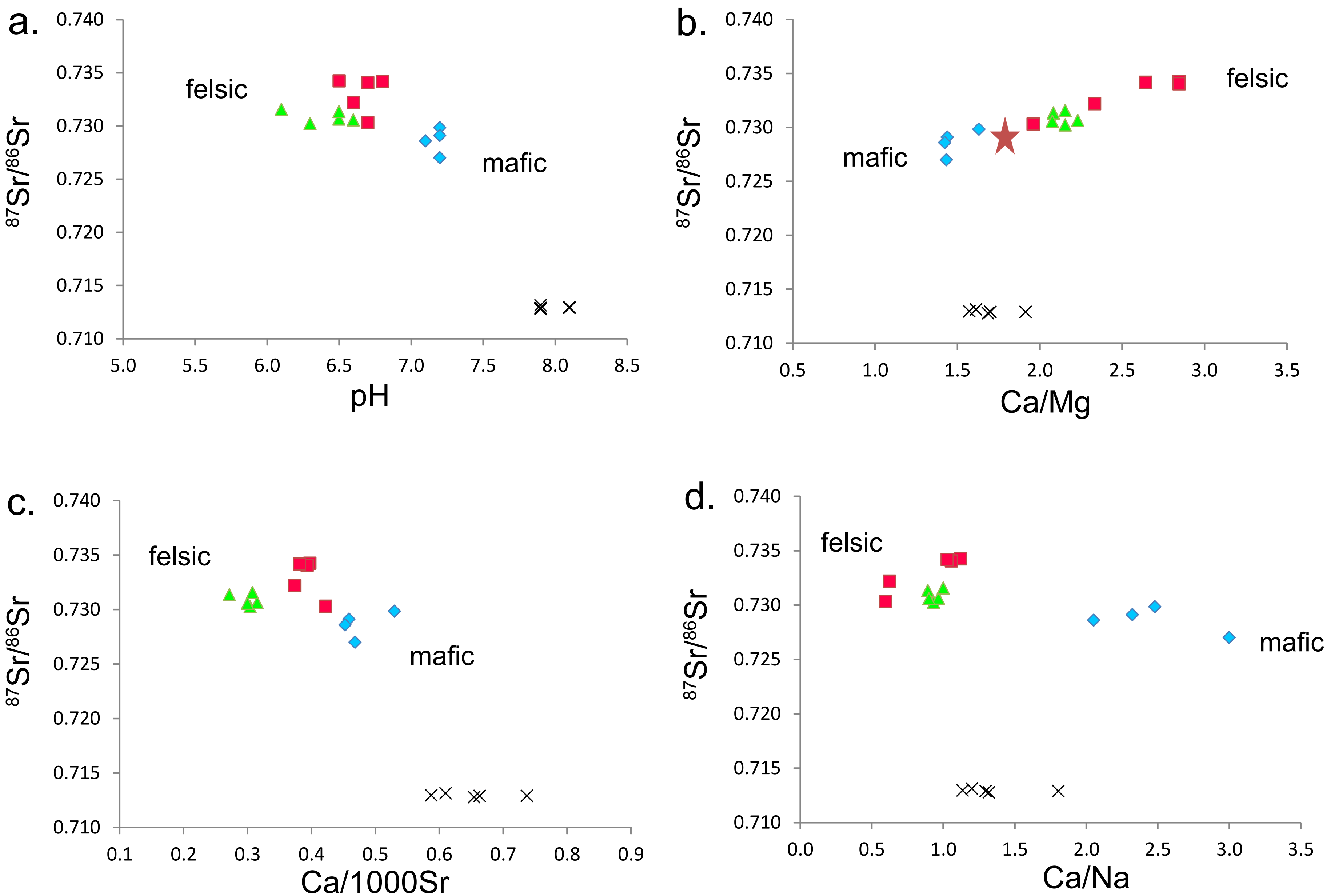
0.740
0.735
0.730
0.725
0.720
0.715
0.710
0.705
0.700
$^{87}Sr/^{86}Sr$
0.1
0.2
0.3
0.4
0.5
0.6
$\delta^{88/86}Sr$ (‰)
terrestrial silicate ave.
Global river ave.
error
Koksoak River, QC
Great Whale River, QC
La Grande River, QC
Nelson River, MB
Upper Hollyford River, NZ
Lower Hollyford River NZ
Cleddau River, NZ
Lemon Creek Glacier, AK
Xijiang River, China
Hou-ku River, Taiwan
Rivers across the globe

Figure 5



a.
Koksoak River
snow melt
UQAM
Southampton
$^{87}Sr/^{86}Sr$
0.734
0.732
0.730
0.728
0.726
0.724
2009-01-07
2009-02-26
2009-04-17
2009-06-06
2009-07-26
sample date
b.
$\delta^{88/86}Sr$ (‰)
0.40
0.35
0.30
0.25
0.20
example of average error
snow melt
Koksoak River
2009-01-07
2009-02-26
2009-04-17
2009-06-06
2009-07-26
sample date
c.
$^{87}Sr/^{86}Sr$
0.740
0.735
0.730
0.725
0.720
0.715
0.710
snow melt
2007-08-06
2007-11-14
2008-02-22
2008-06-01
2008-09-09
sample date
d.
$\delta^{88/86}Sr$ (‰)
0.40
0.35
0.30
0.25
0.20
Nelson River (dams) (SH)
Nelson River (UQAM)
La Grande River (dams)
Great Whale River
snow melt
2007-08-06
2007-11-14
2008-02-22
2008-06-01
2008-09-09
sample date

Figure 6



a.
0.740
0.735
0.730
0.725
0.720
0.715
0.710
87Sr/86Sr
felsic
mafic
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
pH
b.
0.740
0.735
0.730
0.725
0.720
0.715
0.710
87Sr/86Sr
mafic
felsic
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Ca/Mg
c.
0.740
0.735
0.730
0.725
0.720
0.715
0.710
87Sr/86Sr
felsic
mafic
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Ca/1000Sr
d.
0.740
0.735
0.730
0.725
0.720
0.715
0.710
87Sr/86Sr
felsic
mafic
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Ca/Na

Figure 7

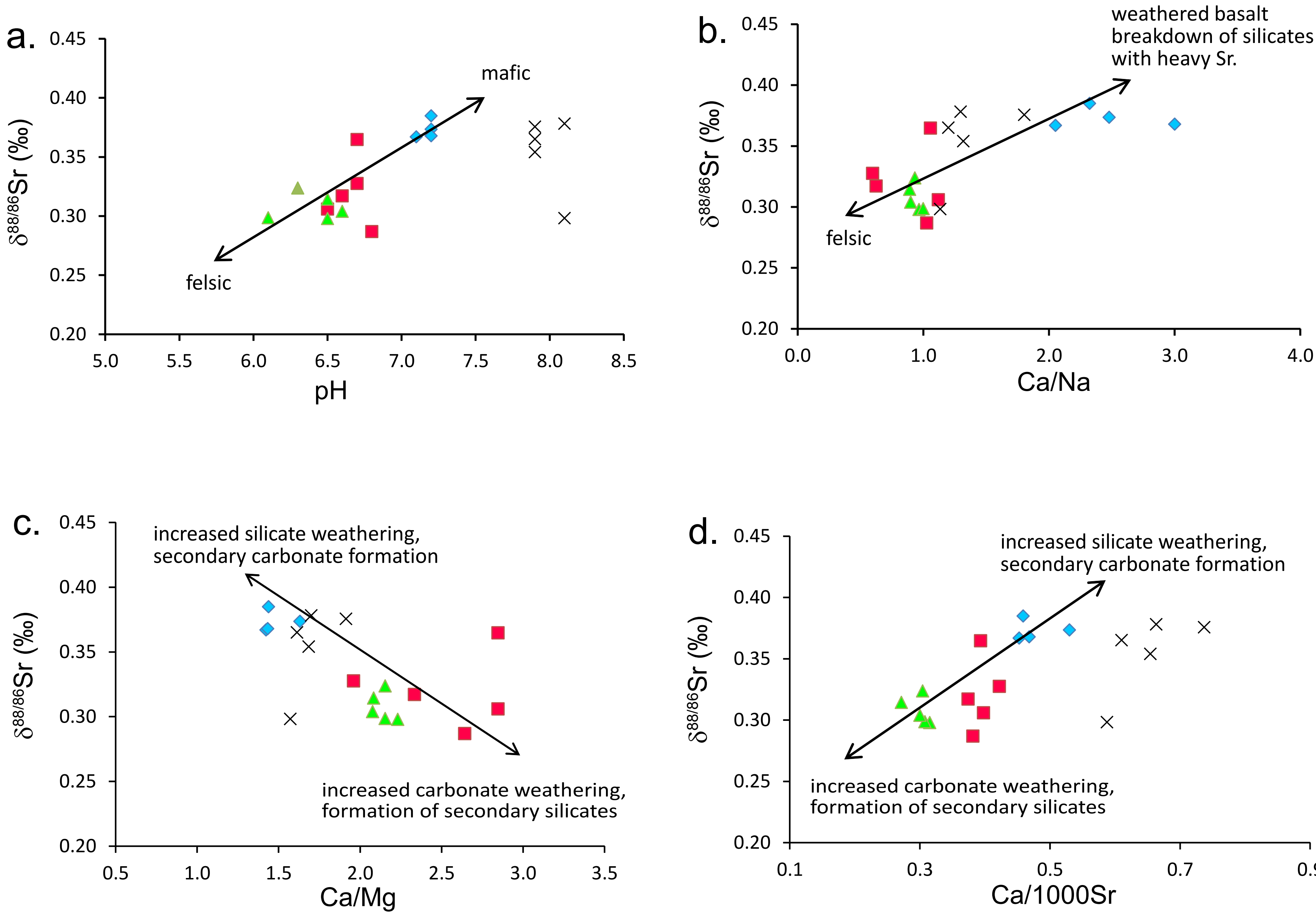
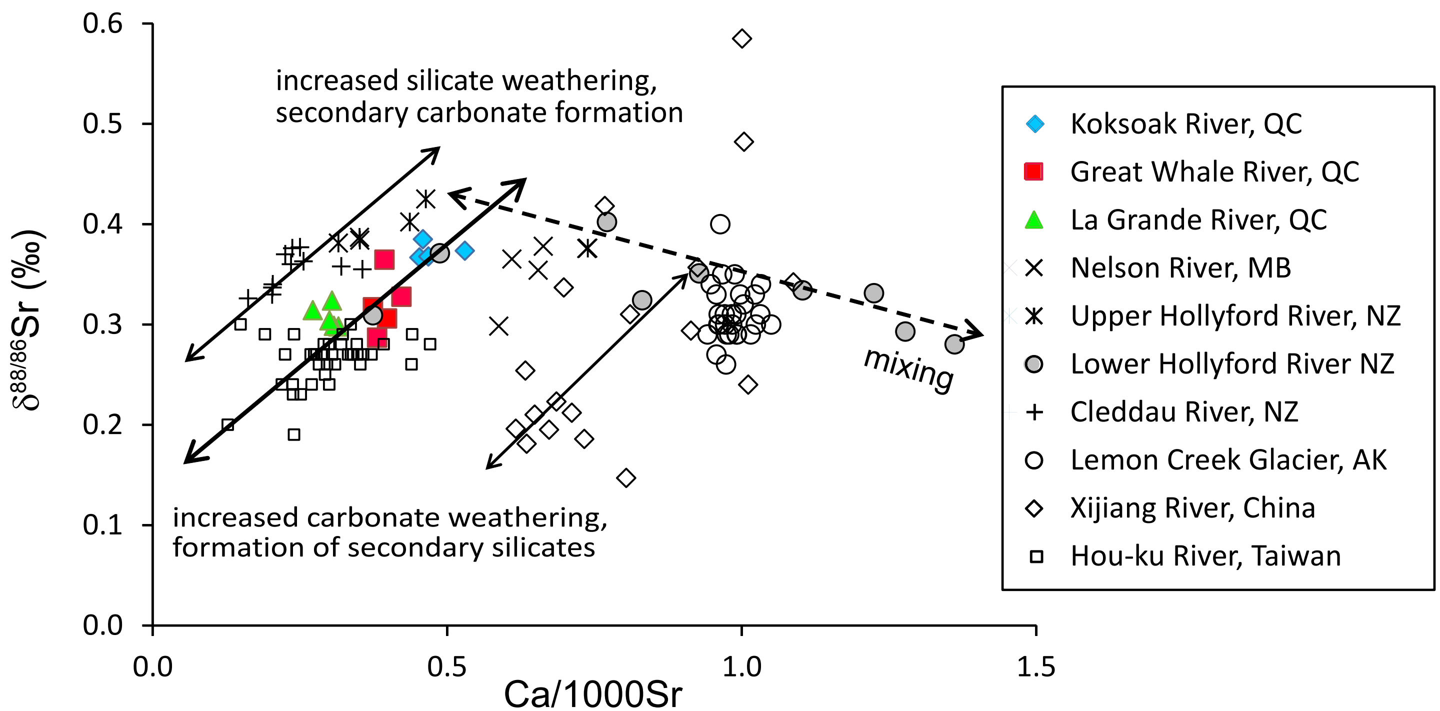

a.
0.45
0.40
0.35
0.30
0.25
0.20
δ88/86Sr (‰)
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
pH
mafic
felsic
b.
0.45
0.40
0.35
0.30
0.25
0.20
δ88/86Sr (‰)
0.0
1.0
2.0
3.0
4.0
Ca/Na
weathered basalt
breakdown of silicates
with heavy Sr.
felsic
c.
0.45
0.40
0.35
0.30
0.25
0.20
δ88/86Sr (‰)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Ca/Mg
increased silicate weathering,
secondary carbonate formation
increased carbonate weathering,
formation of secondary silicates
d.
0.45
0.40
0.35
0.30
0.25
0.20
δ88/86Sr (‰)
0.1
0.3
0.5
0.7
0.9
Ca/1000Sr
increased silicate weathering,
secondary carbonate formation
increased carbonate weathering,
formation of secondary silicates

Figure 8



0.6
0.5
0.4
0.3
0.2
0.1
0.0
δ88/86Sr (‰)
0.0
0.5
1.0
1.5
Ca/1000Sr
increased silicate weathering,
secondary carbonate formation
increased carbonate weathering,
formation of secondary silicates
mixing
Koksoak River, QC
Great Whale River, QC
La Grande River, QC
Nelson River, MB
Upper Hollyford River, NZ
Lower Hollyford River NZ
Cleddau River, NZ
Lemon Creek Glacier, AK
Xijiang River, China
Hou-ku River, Taiwan

Table 1

Table 1. Radiogenic and stable Sr isotope data for four boreal rivers of Canada

				UQAM		Southampton		UQAM				Southampton			
Sample No	**River**	**Sample date**	**Discharge Rate**	**$^{87}Sr/^{86}Sr$**	**2 σ error**	**$^{87}Sr/^{86}Sr$**	**2 σ error**	**$\delta^{84/86}Sr$**	**2 σ error**	**$\delta^{88/86}Sr$**	**2 σ error**	**$\delta^{84/86}Sr$**	**2 σ error**	**$\delta^{88/86}Sr$**	**2 σ error**
			m^3/s												
1	Koksoak	2009-02-03	377	0.729848	0.000004			-0.371	0.040	0.376	0.011				
2	Koksoak	2009-03-17	243	0.729107	0.000003	0.729276	0.000003	-0.423	0.034	0.387	0.014				
3	Koksoak	2009-04-06	227	0.728591	0.000003	0.728656	0.000003	-0.416	0.037	0.369	0.009				
4	Koksoak	2009-06-29	6335	0.727007	0.000003	0.727142	0.000003	-0.387	0.040	0.370	0.022				
5	Great Whale	2007-10-21	874	0.734236	0.000003	0.734236	0.000003	-0.342	0.052	0.308	0.011				
6	Great Whale	2008-03-12	179	0.732193	0.000004	0.732193	0.000004	-0.318	0.039	0.319	0.009				
7	Great Whale	2008-05-11	602	0.730302	0.000005	0.730558	0.000004	-0.371	0.051	0.330	0.018				
7	repeat	2008-05-11	602	0.730312	0.000004			-0.331	0.030	0.322	0.008				
7	Great Whale	2008-05-11	602	0.730310	0.000004			-0.318	0.034	0.325	0.008				
8	Great Whale	2008-06-18	1254	0.734051	0.000006	0.734157	0.000003	-0.341	0.054	0.345	0.012				
9	Great Whale	2008-07-15	716	0.734174	0.000005	0.734236	0.000004	-0.295	0.043	0.268	0.015				
10	La Grande	2007-11-02	n.d.i.	0.730234	0.000008	0.730363	0.000003	-0.328	0.062	0.305	0.013				
11	La Grande	2007-12-12	n.d.i.	0.730630	0.000003							-0.327	0.030	0.277	0.011
12	La Grande	2008-01-16	n.d.i.	0.731557	0.000003	0.731557	0.000003	-0.312	0.030	0.307	0.008				
12	repeat	2008-01-16	n.d.i.	0.731530	0.000003			-0.300	0.030	0.295	0.008				
13	La Grande	2008-05-22	n.d.i.	0.731341	0.000004							-0.302	0.035	0.294	0.009
14	La Grande	2008-06-30	n.d.i.	0.730567	0.000003							-0.287	0.027	0.283	0.008
15	Nelson	2008-04-07	3961	0.712783	0.000004	0.712946	0.000003	-0.282	0.044	0.279	0.023				
16	Nelson	2007-11-05	4421			0.712780	0.000003					-0.384	0.027	0.354	0.007
16	repeat	2007-11-05	4421	0.712752	0.000010			-0.313	0.094	0.317	0.019				
17	Nelson	2008-03-04	4154			0.712896	0.000003					-0.378	0.026	0.355	0.007
18	Nelson	2008-05-12	3541			0.713124	0.000003					-0.432	0.030	0.345	0.008
19	Nelson	2008-07-08	4041			0.712886	0.000003					-0.495	0.035	0.358	0.008

Latitude/longitude sampling sites for Koksoak River (58.029/68.475), Great Whale River (55.279/77.650), La Grande River (53.781/77.530) and Nelson River (56.685/93.790).

n.d.i. : discharge rates are confidential as per non-disclosure agreement with Hydro-Quebec.