# COMPARISON OF LAKE-SEDIMENT RESULTS FROM LABRADOR AND ADJACENT QUÉBEC: PRELIMINARY RESULTS 

S.D. Amor<br>Geochemistry, Geophysics and Terrain Sciences Section


#### Abstract

As part of a GEM-2-sponsored initiative to merge lake-sediment geochemical data from Labrador and the adjacent part of Québec, levelling has been attempted between two independently gathered datasets. Although many of the same elements have been determined in the two programs, in most cases the analytical methods and more importantly, the digestion methods were different, with a partial (aqua-regia) digestion applied to the Québec samples and a multi-acid ('total') digestion applied to their Labrador counterparts. Because of the resistance to digestion, by the former reagent, of certain minerals this has the potential to lead to a serious discontinuity between the two datasets if they are displayed together.

Initial investigation of the relationship between analyses of the same samples after aqua-regia and multi-acid digestions shows extreme differences for certain elements, such as Al and Sr, but a surprising level of concordance for others, including the transition and rare-earth elements. The latter close relationships can also be seen in the relationship between nearestneighbour sample pairs from the Québec and Labrador datasets. For elements showing this close relationship, regression equations have been derived between the nearest-neighbour pairs to relate the Québec and Labrador analyses, and convert the former to 'levelled'values more compatible with the latter. Results are presented in the form of cross-border transect profiles, and colour-contour maps.


## INTRODUCTION

## BACKGROUND

Regional lake-sediment sampling has been carried out over all of Labrador, with the exception of the northern Torngat Mountains where lake development is poor, and the adjacent portion of Québec. In the former case, the sampling work was carried out under the auspices of the Geological Survey of Canada (GSC)'s National Geochemical Reconnaissance (NGR) program. Sampling and initial analysis, by Atomic-Absorption Spectrometry (AAS) and certain other methods, were carried out in 1977-78 and 1982-85 with additional Instrumental Neutron Activation analyses (INAA) carried out in the 1990s The references to this work, 40 in all, are listed by Amor (2014). More recently, the samples were subjected to Inductively Coupled Plasma Emission Spectrometry (ICP-ES) analysis after multi-acid digestion (HCl-HF- $\mathrm{HClO}_{4}$; McConnell and Finch, 2012) The Québec program was carried out independently of the NGR program by the province's Ministère des Ressources naturelles et de la Faune (Ministry of Natural Resources and Wildlife) in 1982-84, 1997 and 2009 (Maurice and Labbé, 2009). Analyses were mostly by ICP-ES and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after aqua-
regia digestion, with additional analyses of selected samples by ICP-MS after multi-acid digestion, INAA and certain other methods (Maurice, 2011).

As part of a collaborative effort between the GSC and the provinces of Newfoundland and Labrador and Québec, under the auspices of the Geo-mapping for Energy and Minerals (GEM-2) program of the GSC, an attempt is made to combine the data from Labrador and adjacent Québec so that geochemical maps can be created for a contiguous area of more than $500000 \mathrm{~km}^{2}$ that includes both regions. Because the operating parameters of the two surveys were established independently, analyses of many elements on either side of the border show a distinct discontinuity when they are displayed together on the same map. In the case of 'wet-chemical' (AAS, ICP-ES and ICP-MS) analyses, this can normally be attributed to the different digestion methods applied to the two suites of samples, and different susceptibilities to the respective reagents of the minerals and other compounds in the lake sediment. The possibility also exists that slight calibration differences may give rise to a fixed shift in all analyses, in one dataset with respect to the other, even when digestions and other analytical parameters are ostensibly the same.

## SCOPE

This preliminary report first examines the relationship between ICP-ES and ICP-MS analyses after aqua-regia $\left(\mathrm{HCl}-\mathrm{HNO}_{3}\right)$ and multi-acid ( $\mathrm{HCl}-\mathrm{HF}-\mathrm{HClO}_{4}$ or $\mathrm{HNO}_{3}-\mathrm{HCl}-$ HF- $\mathrm{HClO}_{4}$ ) digestion on the same samples. Datasets from both Québec and Labrador are tested. The strength of the relationship between paired analyses of samples located on the Labrador side, and their nearest neighbours on the Québec side, is then quantified. For elements displaying acceptably close cross-border relationships, linear equations are derived relating the analyses in the two datasets; these are then applied to the Québec analyses in an attempt to harmonize the two datasets, and the results are assessed in the form of pre- and post-correction cross-border profiles and test plots.

## DATABASE

The Québec dataset comprises 26727 samples, which were analyzed, in varying numbers and for various elements, by ICP-ES, ICP-MS and AAS (all after aqua-regia digestion, AAS and INAA). A subset of the Québec dataset, comprising 1870 samples, has also been subjected to ICPMS analysis, after both aqua-regia and a variant multi-acid digestion consisting of $\mathrm{HNO}_{3}-\mathrm{HCl}-\mathrm{HF}-\mathrm{HClO}_{4}$. The samples in question are from an area bounded by $65.5^{\circ} \mathrm{W}$ to the west, $57^{\circ} \mathrm{N}$ to the north, and the Labrador border to the south and east, and have been referred to as the George River Survey (Maurice, 2011).

The Labrador dataset comprises 19836 samples, most of which were analyzed by AAS (after aqua-regia digestion), INAA and ICP-ES (after multi-acid digestion). The databases are summarized, in terms of sample totals and analyzed elements, in Table 1. As will be described below, only a limited subset of these elements is considered, in detail, in this paper.

The sample densities sustained over the two territories are illustrated in Figure 1A and B. Because of the extremely high sample density over the southern part of the Labrador Trough, with respect to coverage elsewhere (Figure 1 A ), a random selection of $24 \%$ of the samples in this subset was made to create a more homogeneous point distribution (Figure 1B). Fortuitously, this resulted in the number of samples in the Québec (18 595 samples) and Labrador datasets being approximately the same.

## RELATIONS BETWEEN AQUA-REGIA AND TOTAL DIGESTION

A key issue in the merging of the Labrador and Québec lake-geochemical data, the investigation of whose feasibili-
ty is the focus of this paper, lies in the different digestions applied to the samples for the majority of analyses: in Québec, aqua-regia digestions were applied to most samples whereas in Labrador, most elements were analyzed by the 'total' methods INAA and ICP-ES after multi-acid digestion (HCl-HF- $\mathrm{HClO}_{4}$; McConnell and Finch, 2012), although a few elements were also analyzed by AAS after aqua-regia digestion. Multi-acid digestions have the objective of total dissolution of the sample, although in practice certain minerals, notably zircon, are known to resist these reagents. However, many rock-forming minerals, notably quartz and feldspar but also including muscovite and some amphiboles, are resistant to aqua-regia digestion, although biotite and chlorite are almost completely dissolved (Snäll and Liljefors, 2000).

Although the multi-acid digestion is not identical to that applied to the Labrador samples (because of the inclusion of $\mathrm{HNO}_{3}$ ), the George River dataset affords a useful opportunity to compare the efficiency of the multi-acid and aquaregia digestions, and the equivalency of the subsequent analyses. It also provides preliminary indications of which analyses may be amenable to the combination of the data from Québec and Labrador, as well as clues as to what mineral phases each element may be residing in. Some data comparisons of this kind have already been described by Maurice (2011). In the latter study, the relation between the Al and Ti content of the samples, as measured after multiacid and aqua-regia digestions, was interpreted in terms of solubilities of certain minerals in which these elements would be expected to occur, although the possibility that some of these and other elements are hosted in the organic gels that predominate in most lake sediments (Cook and McConnell, 2001) was not addressed.

## QUÉBEC

The relationships between measured multi-acid- and aqua-regia-soluble content fall into six categories:

1. Close concordance with the $1: 1$ line throughout the concentration range; demonstrated by Cu (Figure 2), Mo, P and U .
2. A close linear relationship by most samples throughout the concentration range, with incomplete digestion by aqua regia by some samples in mid-range: $\mathrm{Ce}, \mathrm{Co}, \mathrm{Fe}$ (Figure 3), La, Li, Mn, Rb.
3. No relationship (or even a negative relationship) between aqua-regia and multi-acid digestion: $\mathrm{Ca}, \mathrm{Hf}$, $\mathrm{Na}, \mathrm{Sr}$ (Figure 4), Zr.
4. A linear relationship over the lower part of the concentration range, with incomplete digestion by aqua regia at higher concentration levels: Al (Figure 5), Ba, $\mathrm{Cr}, \mathrm{Ga}$, $\mathrm{K}^{*}, \mathrm{Mg}, \mathrm{Nb}^{*}, \mathrm{~Pb}, \mathrm{Sc}^{*}, \mathrm{Ti}, \mathrm{V}, \mathrm{Y}$.

Table 1: Summary of analyses in Québec and Labrador databases

| Dataset | Digestion | Finish <br> Method | Number of samples | Elements |
| :---: | :---: | :---: | :---: | :---: |
| Québec | Aqua regia | ICP-ES | 26497 | $\mathrm{Ag}, \mathrm{Al}, \mathrm{As}, \mathrm{B}, \mathrm{Ba}, \mathrm{Be}, \mathrm{Bi}, \mathrm{Ca}, \mathrm{Cd}, \mathrm{Ce}, \mathrm{Co}, \mathrm{Cr}, \mathrm{Cu}, \mathrm{Eu}$, $\mathrm{Fe}, \mathrm{Ga}, \mathrm{Ge}, \mathrm{In}, \mathrm{K}, \mathrm{La}, \mathrm{Li}, \mathrm{Mg}, \mathrm{Mn}, \mathrm{Mo}, \mathrm{Na}, \mathrm{Ni}, \mathrm{P}, \mathrm{Pb}$, Sc, Sm, Sr, Th, Ti, V, Y, Zn, Zr |
|  | Aqua regia | ICP-MS | 24261 | $\mathrm{Ag}, \mathrm{Al}, \mathrm{As}, \mathrm{Au}, \mathrm{B}, \mathrm{Ba}, \mathrm{Be}, \mathrm{Bi}, \mathrm{Ca}, \mathrm{Cd}, \mathrm{Ce}, \mathrm{Co}, \mathrm{Cr}, \mathrm{Cs}$, $\mathrm{Cu}, \mathrm{Fe}, \mathrm{Ga}, \mathrm{Ge}, \mathrm{Hf}, \mathrm{Hg}$, In, K, La, Li, Mg, Mn, Mo, Na, $\mathrm{Nb}, \mathrm{Ni}, \mathrm{P}, \mathrm{Pb}, \mathrm{Pd}, \mathrm{Pt}, \mathrm{Rb}, \mathrm{Re}, \mathrm{Sc}, \mathrm{Sb}, \mathrm{Sc}, \mathrm{Se}, \mathrm{Sn}, \mathrm{Sr}, \mathrm{Ta}$, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr |
|  | Multi-acid $\left(\mathrm{HNO}_{3}-\mathrm{HCl}-\right.$ $\mathrm{HF}-\mathrm{HClO}_{4}$ ) | ICP-MS | 1869 | $\mathrm{Ag}, \mathrm{Al}, \mathrm{As}, \mathrm{Au}, \mathrm{Ba}, \mathrm{Be}, \mathrm{Bi}, \mathrm{Ca}, \mathrm{Cd}, \mathrm{Ce}, \mathrm{Co}, \mathrm{Cr}, \mathrm{Cs}, \mathrm{Cu}$, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, $\mathrm{Mo}, \mathrm{Na}, \mathrm{Nb}, \mathrm{Nd}, \mathrm{Ni}, \mathrm{P}, \mathrm{Pb}, \mathrm{Pr}, \mathrm{Rb}, \mathrm{Sb}, \mathrm{Sc}, \mathrm{Sm}, \mathrm{Sn}, \mathrm{Sr}$, $\mathrm{Ta}, \mathrm{Tb}, \mathrm{Th}, \mathrm{Ti}, \mathrm{Tm}, \mathrm{U}, \mathrm{V}, \mathrm{W}, \mathrm{Y}, \mathrm{Yb}, \mathrm{Zn}, \mathrm{Zr}$ |
|  | Aqua regia | AAS | 17169 | As |
|  |  |  | 268 | Cr |
|  |  |  | 18116 | Hg |
|  |  |  | 12132 | Sn |
|  |  | INAA | $\begin{aligned} & 15393- \\ & 15881 \end{aligned}$ | As, Au, Br, Cs, Sb, Se, Tm, U, W |
|  |  | Gravimetry | 26489 | Loss on Ignition (L.O.I.) |
| Labrador | Multi-acid <br> $\left(\mathrm{HNO}_{3}-\mathrm{HCl}-\right.$ <br> $\mathrm{HF}-\mathrm{HClO}_{4}$ ) | ICP-ES | 18357 | $\mathrm{Al}, \mathrm{Ba}, \mathrm{Be}, \mathrm{Ca}, \mathrm{Ce}, \mathrm{Co}, \mathrm{Cr}, \mathrm{Cu}, \mathrm{Dy}, \mathrm{Fe}, \mathrm{Ga}, \mathrm{K}, \mathrm{La}, \mathrm{Li}$, $\mathrm{Mg}, \mathrm{Mn}, \mathrm{Mo}, \mathrm{Na}, \mathrm{Nb}, \mathrm{Ni}, \mathrm{P}, \mathrm{Pb}, \mathrm{Sc}, \mathrm{Sr}, \mathrm{Th}, \mathrm{Ti}, \mathrm{V}, \mathrm{Y}, \mathrm{Zn}$, Zr |
|  | Aqua regia | AAS | $\begin{aligned} & 18753 \\ & 10285 \\ & 19821 \\ & 10285 \end{aligned}$ | $\begin{aligned} & \mathrm{Co}, \mathrm{Cu}, \mathrm{Fe}, \mathrm{Mn}, \mathrm{Ni}, \mathrm{~Pb}, \mathrm{Zn} \\ & \mathrm{Cd} \\ & \mathrm{Mo} \\ & \mathrm{~V} \end{aligned}$ |
|  | Aqua regia | Cold-vapour AAS | 18613 | Hg |
|  | Aqua regia | Hydride AAS | $\begin{aligned} & 15111 \\ & 2412 \end{aligned}$ | $\begin{aligned} & \mathrm{As} \\ & \mathrm{Sb} \end{aligned}$ |
|  | Aqua regia | Colorimetry | 4636 | As |
|  | $\mathrm{K}_{2} \mathrm{CO}_{3}-$ <br> $\mathrm{KNO}_{3}$ <br> fusion | Ion-specific electrode (ISE) | 18579 | Fluoride |
|  |  | INAA | 18756 | $\mathrm{As}, \mathrm{Au}, \mathrm{Ba}, \mathrm{Br}, \mathrm{Ce}, \mathrm{Co}, \mathrm{Cr}, \mathrm{Cs}, \mathrm{Eu}, \mathrm{Fe}, \mathrm{Hf}, \mathrm{La}, \mathrm{Lu}, \mathrm{Mo}$, $\mathrm{Na}, \mathrm{Ni}, \mathrm{Rb}, \mathrm{Sb}, \mathrm{Sc}, \mathrm{Sm}, \mathrm{Ta}, \mathrm{Tb}, \mathrm{Th}, \mathrm{U}, \mathrm{W}, \mathrm{Yb}$ |
|  |  | Delayed neutron counting (DNC) | 18763 | U |
|  |  | Gravimetry | 18745 | Loss on Ignition (L.O.I.) |



Figure 1. Lake-sediment sample density in Labrador and adjacent Québec. A) Québec samples unedited; and B) With dense sample coverage over southern Labrador Trough reduced by 24\% random subselection.


Figure 2. Comparison of $\mathrm{Cu} I C P-M S$ analyses of Québec lake-sediment samples after multi-acid ( $\mathrm{HNO}_{3}-\mathrm{HCl}-\mathrm{HF}$ $\mathrm{HClO}_{4}$ : x-axis) and aqua-regia (y-axis) digestions. Correspondence is close to 1:1 throughout the concentration range, suggesting that almost all of the Cu in the lake-sediments resides in aqua-regia-soluble phases.


Figure 3. Comparison of Fe ICP-MS analyses of Québec lake-sediment samples after multi-acid and aqua-regia digestions. Correspondence is close to 1:1 below about $1.7 \%$ and above $7 \%$ total Fe ; between these concentration levels, as much as $80 \%$ of the Fe is held in an aqua-regia resistant phase.
5. A linear relationship at higher concentration levels, with incomplete digestion by aqua regia at lower concentration levels: Cd, Cs, Zn (Figure 6).
6. Variable relationship between aqua-regia and multiacid analyses throughout the concentration range (although the 1:1 line forms an upper boundary; in other words, aqua-regia analyses rarely exceed their multiacid counterparts): K* (Figure 7), Ni, Sb, Sn, Th, W.
(*all analyses of these elements, even those that line up parallel to the $1: 1$ line, show a downward shift with respect to


Figure 4. Comparison of $\mathrm{Sr} I C P-M S$ analyses of Québec lake-sediment samples after multi-acid and aqua-regia digestions. Aqua-regia analyses are consistently lower than their multi-acid counterparts.There is also evidence of a low-(total) Sr type, where aqua regia is capable of solubilizing most of the Sr, and a high-Sr, more refractory type.


Figure 5. Comparison of Al ICP-MS analysis of Québec lake-sediment samples after multi-acid and aqua-regia digestions. In samples whose total Al content is less than about 4.5 weight $\%$, the efficiency of the aqua-regia digestion is consistently about $80 \%$. Above this level, much of the Al appears to be hosted in a more refractory phase.
it, suggesting a slight difference in the calibration of the instrument between the two phases of analysis).

## LABRADOR

The results after multi-acid and aqua-regia digestions may be compared in the same way for a few elements from the Labrador dataset, since $\mathrm{Co}, \mathrm{Cr}, \mathrm{Cu}, \mathrm{Fe}, \mathrm{Mn}, \mathrm{Mo}, \mathrm{Ni}, \mathrm{Pb}$, V and Zn were analyzed by AAS, after aqua-regia digestion, during the early stages of the NGR program, and later by


Figure 6. Comparison of $\mathrm{Zn} I C P-M S$ analysis of Québec lake-sediment samples after multi-acid and aqua-regia digestions. There is a gradual increase in the efficiency of aqua-regia digestion with increasing total Zn .


Figure 7. Comparison of $K$ ICP-MS analysis of Québec lake-sediment samples after multi-acid and aqua-regia digestions. Efficiency of the aqua-regia digestion is very variable; with an upper limit of about $60 \%$ at all concentration levels.


Figure 8. Comparison of Co analyses after multi-acid (x-axis) and aqua-regia (y-axis) digestion. A) Results from Québec (ICP-MS finish; multi-acid digestion consists of $\mathrm{HNO}_{3}-\mathrm{HCl}-\mathrm{HF}-\mathrm{HClO}_{4}$ ); and B) Results from Labrador (AAS finish; multiacid digestion consists of $\mathrm{HCl}-\mathrm{HF}-\mathrm{HClO}_{4}$ ). Below about 25 ppm total Co , some aqua-regia analyses exceed their multi-acid counterparts; this is probably a consequence of inferior precision of the AAS method.


Figure 9. Comparison of Ni analyses after multi-acid and aqua-regia digestion. A) Results from Québec (ICP-MS finish; multiacid digestion consists of $\mathrm{HNO}_{3}-\mathrm{HCl}-\mathrm{HF}-\mathrm{HClO}_{4}$ ); and B) Results from Labrador (AAS finish; multi-acid digestion consists of $\mathrm{HCl}-\mathrm{HF}-\mathrm{HClO}_{4}$ ). Effects of imprecision in the AAS analyses persist up to about 80 ppm Ni .

ICP-ES, after multi-acid digestion (McConnell and Finch, 2012). For Co, the distribution of points is very similar to that displayed in Québec (Figure 8), except that at lower concentration levels (below about 25 ppm , as analyzed after multi-acid digestion), more aqua-regia analyses exceed their multi-acid counterparts; this apparently paradoxical relationship is probably a consequence of inferior precision (i.e., precision of greater absolute magnitude) at these levels, which is a widely documented phenomenon (e.g., Thompson and Howarth, 1978). This is also observable in the behaviour of Cu , although the level at which the effects of imprecision are apparent is much higher, at about 70 ppm ; and of Fe (where the effects of imprecision are detectable about up to $3 \%$, although a few 'rogue' samples, with Fe contents up to about $6 \%$, have aqua-regia analyses that
exceed them). Nickel shows the effects of imprecision at concentration levels up to about 80 ppm , with somewhat better convergence onto the $1: 1$ line, above this concentration level, than that displayed by this element in the Québec analyses (Figure 9). Zinc shows a similar pattern in both datasets although the effects of imprecision are discernible in this case up to 600 ppm . The behaviour of Mn is particularly similar to its counterpart in the Québec dataset, with the relationship falling away at about 1000 ppm in both cases (Figure 10).

The Labrador dataset also affords the opportunity to study the relationship between supposedly 'total' metal content (measured by ICP-ES after multi-acid digestion) and what probably constitutes a more truly total analysis by


Figure 10. Comparison of Mn analyses after multi-acid and aqua-regia digestion. A) Results from Québec (ICP-MS finish; multi-acid digestion consists of $\mathrm{HNO}_{3}-\mathrm{HCl}-\mathrm{HF}-\mathrm{HClO}_{4}$ ); and B) Results from Labrador (AAS finish; multi-acid digestion consists of $\mathrm{HCl}-\mathrm{HF}-\mathrm{HClO}_{4}$ ). Efficiency of aqua-regia digestion increases markedly and sharply above 1000 ppm Mn.

INAA. Correspondence is reassuringly close (although subject to the effects of inferior precision at lower concentration levels) between the analyses for $\mathrm{Ce}, \mathrm{Co}, \mathrm{Fe}, \mathrm{La}$ and Mo , whereas for Cr there is evidence of consistent underestimation, by about $20 \%$, by the multi-acid method. For Ba and Sc , overestimation is more serious at higher concentration levels ( $>1000 \mathrm{ppm}$ and $>10 \mathrm{ppm}$, respectively).

Similarly, comparison of ICP-ES and ICP-MS analyses is possible on essentially the entire Québec lake-sediment dataset. It is to be expected (and indeed, it is one of the underlying assumptions of this study) that while different digestions may result in analyses of different magnitude for the same element, the result will be independent of the finish, although individual result pairs may vary as a consequence of the precision of the respective methods. In a separate study (S. Amor, unpublished data, 2015) it was established that this is indeed the case for $\mathrm{Al}, \mathrm{Ba}, \mathrm{Co}, \mathrm{Fe}, \mathrm{K}, \mathrm{Ni}$, $\mathrm{P}, \mathrm{Pb}, \mathrm{Y}$ and Zn , while the ICP-MS analyses show systematic overestimation (with respect to ICP-ES) of $\mathrm{Ce}, \mathrm{Cd}, \mathrm{Cr}$, $\mathrm{Cu}, \mathrm{La}, \mathrm{Li}, \mathrm{Mg}, \mathrm{Sr}, \mathrm{Ti}$ and V and underestimation of $\mathrm{Ag}, \mathrm{Mo}$, Pb and Sc . There is little or no relationship between the ICPES and ICP-MS analyses for $\mathrm{B}, \mathrm{Be}, \mathrm{Na}$ and Th .

Extremes of disparity between ICP-ES analyses of two elements after aqua-regia digestion, in Québec, and multiacid digestion, in Labrador, are illustrated in Figure 11 where colour-contoured values of Al and Sr are displayed. In both cases, the latter analyses are greatly in excess of the former. Alternatively, when the Québec ICP-ES analyses of Pb , after aqua-regia digestion, are combined with AAS analyses of the same element from Labrador (Figure 12A), it is the former that show a conspicuous upward shift, whereas the match between the two datasets is better if the Québec aqua-regia analyses are combined with multi-acid
analyses from Labrador (Figure 12B). There also appears to be an internal levelling issue within the Labrador analyses, not addressed in the current study, with a discontinuity at the boundary between NTS map areas 14D and 14E.

## LEVELLING

## NEAREST-NEIGHBOUR ANALYSIS

The close correspondence between analyses of certain elements after the partial (aqua-regia) and near-total (multiacid) digestion described above suggests that it may be possible to merge the Québec and Labrador analyses without major adjustment of either dataset, even though the digestions were different.

The procedure whereby geochemical (and geophysical) data from two different sources, and two adjacent areas, are combined in such a way that discontinuities between the two datasets are eliminated (or at least minimized) is known as levelling. A levelling method that involves quantile regression of two adjacent strips, of equal width, from two NTS 1:250 000 map areas was described by Daneshfar and Cameron (1998). However, because of the convoluted (and extremely long) border between Labrador and Québec, this method is considered unsuitable for the current study. Instead, a nearest-neighbour regression method has been applied. To locate each sample's nearest neighbour, the databases were first subsetted so that only those sample points lying within 25 km of the border were selected, using the 'Buffer' option in ArcGIS. This speeds up subsequent computations, whereby the ArcGIS nearest-neighbour option was used to create a series of nearest-neighbour sample pairs, whose analytical values were then compared by means of the Pearson correlation coefficient. To determine


Figure 11. Unlevelled areal distribution of $A l(A)$ and $S r(B)$ in Labrador and adjacent Québec. For both elements the Labrador ICP-ES analyses, which followed multi-acid digestion, are generally much higher than their Québec counterparts which followed aqua-regia digestion.
the influence of inter-sample distance on the strength of the correlation between neighbours, the pairs were split into two: proximal sample pairs (those separated by distances of 5 km or less), and distal sample pairs (those separated by distances of $5-10 \mathrm{~km}$ ). Sample pairs separated by distances of more than 10 km were not numerous, and were discarded.

Although most of the comparisons are between ICP-ES analyses after aqua-regia digestion in Québec, and multiacid digestion in Labrador, in some cases the ICP-ES/aquaregia analyses from Québec are paired with analyses from Labrador by another method. These consist of $\mathrm{Cu}, \mathrm{Fe}, \mathrm{Mn}$, Ni and Zn (which were analyzed by AAS, after aqua-regia digestion, as well as ICP-ES, and might be expected to be more directly comparable with their Québec counterparts), and Sm and Th , for which the Labrador samples were analyzed by INAA.

## SEPARATION OF ORGANIC-RICH AND ORGANICPOOR SAMPLES

Geochemical relationships between elements are expected to be different in samples rich, and poor, in organ-
ic material (Garrett et al., 1990). Consequently, relationships were investigated in two subpopulations of the data: samples whose LOI content is above, and below $30 \%$. Although there are no strong discontinuities in the LOI frequency distributions when the latter are viewed graphically, this figure represents a compromise between the cutpoints identified by Jenks' (1967) optimization in the Labrador ( $26 \%$ LOI) and Québec ( $34 \%$ LOI) datasets. Some advantage would probably result from dividing the data into more than two subpopulations but this falls outside the scope of this preliminary investigation. The point density of the highLOI and low-LOI samples, so defined, is shown in Figure 13. The former are concentrated in Labrador, south of about $54^{\circ} \mathrm{N}$, and in the southern catchment basin of Ungava Bay in northern Québec. The latter concentrate along the border between the two territories between latitudes $56^{\circ}$ and $58^{\circ} \mathrm{N}$, in the southwest corner of the sampled area west of Schefferville, and in Ungava Bay's western catchment basin.

## ELEMENTS CONSIDERED

The number of elements whose behaviour was examined was reduced considerably from the original datasets. Elements were omitted if they failed to meet the following


Figure 12. Unlevelled areal distribution of Pb analyses. A) Québec analyses by ICP-ES after aqua-regia digestion, Labrador analyses by ICP-ES after multi-acid digestion; and B) Québec analyses by ICP-ES after aqua-regia digestion, Labrador analyses by $A A S$ after aqua-regia digestion.
criteria:

- The elements must be common to both the Labrador and Québec datasets
- For each element, no more than $25 \%$ of the analyses in each dataset can fall below the analytical detection limit

Elements were not excluded because they displayed poor correlation between analyses after aqua-regia and multiacid digestions but as will be seen, the nearest-neighbour correlations for these elements were invariably too low to justify the derivation of levelling equations. Figures 14 and 15 show the relationship between the correlation coefficients of various elements in proximal (X-axis) and distal (Y-axis) sample pairs, as defined above, in high-LOI and low-LOI samples, respectively. It is clear from both plots that certain elements display conspicuously strong correlations in both proximal and distal pairs, and plot as a cluster in the upper right-hand corner of the plot. Others display correlations that plot separately from this cluster but are still probably statistically significant. Because tables of significance of the Pearson correlation coefficient appear to be restricted to populations of no greater than 100 bivariate pairs, the critical level of the correlation coefficient can only
be estimated by extrapolation for these nearest-neighbour datasets. The behaviour of these elements can be separated into five groups, as listed in Table 2.

For elements whose nearest-neighbour correlation is equally high in both proximal and distal pairs, the entire nearest-neighbour datasets, comprising 599 low-LOI pairs and 273 high-LOI pairs, can be used to create levelling equations. This applies particularly to $\mathrm{Ce}, \mathrm{Cr}, \mathrm{La}$ and Ni (where correlations are particularly strong in proximal and distal pairs, for both high-LOI and low-LOI samples), but also to $\mathrm{Cu}, \mathrm{Li}, \mathrm{Mg}, \mathrm{P}, \mathrm{Sc}, \mathrm{Sm}$ and Th in which correlations are strong or significant in both proximal and distal pairs, for both high-LOI and low-LOI samples. In addition, the smaller, proximal datasets can be used to derive equations for $\mathrm{Fe}, \mathrm{Ti}, \mathrm{V}$ and Zn (because the correlations in the distal sets were insignificant for these elements). The regression equations are listed in Table 3.

The remaining elements ( $\mathrm{Al}, \mathrm{Ba}, \mathrm{Be}, \mathrm{Ca}, \mathrm{Co}, \mathrm{K}, \mathrm{Mn}$, $\mathrm{Na}, \mathrm{Pb}$, and Sr ) display insignificant correlation in at least one proximal category and are considered to have no levelling potential. Therefore, they are omitted from further consideration.


Figure 13. Point density (per $100 \mathrm{~km}^{2}$ ) of (A) low-LOI ( $\leq 30 \%$ ); and (B) high-LOI ( $>30 \%$ ) lake-sediment samples in Labrador and adjacent Québec.

## EVALUATION OF LEVELLING RESULTS PROFILES

A preliminary examination of the effectiveness of the levelling equations consists of examining a series of profiles across the border between Québec and Labrador. The profile lines are shown in Figure 16, and the lines are described in terms of their underlying geology in Table 4. The quality of the levelling on each section line has been assigned a score, in order to identify the lines, and the elements, where levelling has been most successful. Where levelling appears to have been successful, a score of 2 is assigned to that element, on that line. Where levelling has resulted in slight overcompensation, a score of -1 is assigned, and where the overcompensation is more severe, the score is -2 . These scores are displayed in Table 5, and summing them downward, and from left to right, shows that the levelling has been most successful on Line 0 (the most northerly) and of the elements, for Fe ; that is, iron analyzed after aqua-regia digestion in both datasets, by ICP-ES in Québec, and AAS in Labrador. The line profiles of selected elements, as well as corresponding contour maps of unlevelled and levelled data, are shown in Figures 17-21 and described in the next section.

The contours were computed using an inverse square distance weighting and a search radius of 25 km . Contour intervals are based on 20-percentile intervals of the entire unlevelled or levelled dataset.

## DESCRIPTION OF LEVELLING OF SELECTED ELEMENTS

## Cerium (Ce)

Direct comparison of the Ce analyses after multi-acid digestion, similar to that applied in Labrador, and aquaregia digestion, as applied to the Québec samples, indicated that correspondence was good at the low and high ends of the distribution range, with incomplete digestion in midrange. The correlation between nearest neighbours was exceptionally good, even for sample pairs separated by more than 5 km (Figures 14 and 15). The application of the levelling equations to the Ce analyses from Québec has achieved satisfactory results on profile lines $0,2,3,4$ and 7 . On lines 1,5 and 6 the equations have overcompensated for the discrepancy between the two datasets (Figure 17A) although this is more apparent on the profile lines than on the map itself (Figure 17B), where the discontinuity in raw values


Figure 14. Pearson correlation coefficients for proximal and distal nearest-neighbours in Labrador and Québec. High- (> 30\%) LOI only. Québec analyses are by ICP-ES after aqua-regia digestion. Labrador analyses are by ICPES after multi-acid digestion, except those with suffix of " 3 ", analyzed by ICP-ES after aqua-regia digestion, and those with a suffix " 1 ", analyzed by INAA. Red lines indicate boundary between significant and insignificant correlation at 99\% confidence limit.
north of $56^{\circ}$ is resolved. A sharp east-west boundary at about $54.5^{\circ} \mathrm{N}$, between high Ce values to the north and low values to the south, shows excellent continuity across the border between the datasets. The positive Ce features in Labrador are moderated slightly by the levelling process but they are still present, and conspicuous. Similar features are displayed by La and Sm.

## Chromium (Cr)

Investigation of the relationship between aqua-regia and multi-acid digestion in the Québec samples indicated incomplete aqua-regia digestion at higher concentration levels of total Cr , whereas comparison of multi-acid/ICP-ES and INAA analyses of the Labrador samples suggested that the multi-acid digestion itself was incomplete. Levelling has resulted in overcompensation on lines 3 and 4 but is satisfactory on lines 0-2 and 5-7 (Figure 18A). In Figure 18B, it can be seen that a discontinuity in the north, in the unlevelled data, has been resolved to some extent by the levelling equation. The continuity between the two datasets in the southwest is not seriously affected by this correction. Like $\mathrm{Ce}, \mathrm{Cr}$ shows a good example of the successful application


Figure 15. Pearson correlation coefficients for proximal and distal nearest-neighbours in Labrador and Québec. Low ( $\leq 30 \%$ ) LOI only. Québec analyses are by ICP-ES after aqua-regia digestion. Labrador analyses are by ICPES after multi-acid digestion, except those with suffix of " 3 ", analyzed by ICP-ES after aqua-regia digestion, and those with a suffix " 1 ", analyzed by INAA. Red lines indicate boundary between significant and insignificant correlation at 99\% confidence limit.
of the levelling process, although the discrepancy between the unlevelled datasets is admittedly not very strong.

## Lithium (Li)

The levelling exercise resulted in satisfactory compensation on lines $0-2,4$ and $6-7$ and overcompensation on lines 3 and 5 (Figure 19A). In map form (Figure 19B) the levelling appears to have been successful everywhere except in the southwest. However, there has been a general depression of concentration levels throughout southern Labrador to the extent that a positive feature corresponding to the Central Mineral Belt is effectively erased by the levelling process.

## Scandium (Sc)

The only transect lines where application of the levelling equations resulted in overcompensation were numbers 3 and 5, and the shift between datasets is serious in neither case (Figure 20A). Levelling has resulted in a very significant improvement in cross-border continuity in northern Labrador and adjacent Québec, but there has been serious

Table 2. Nearest-neighbour correlations between Québec and Labrador datasets, sorted by strength

|  | High LOI samples only | Low LOI samples only | High and Low LOI samples |
| :--- | :--- | :--- | :--- |
| Elements strongly correlated <br> in both proximal and distal <br> sample pairs | $\mathrm{Cu}^{2}, \mathrm{Cu}^{3}, \mathrm{Li}, \mathrm{Mg}, \mathrm{Sc}, \mathrm{Sm}^{1}$, |  |  |
| Elements significantly <br> correlated in proximal and <br> distal sample pairs | $\mathrm{Al}, \mathrm{K}, \mathrm{Ti}$ | $\mathrm{Cr}, \mathrm{Ce},{\mathrm{La}, \mathrm{Ni}^{2}, \mathrm{Ni}^{3}}^{2}$ |  |
| Elements significantly <br> correlated in proximal | $\mathrm{Fe}^{2}, \mathrm{Fe}^{3}, \mathrm{Zn}^{2}, \mathrm{Zn}^{3}$ | $\mathrm{Li}, \mathrm{Mg}, \mathrm{Zn}^{2}, \mathrm{Zn}^{3}, \mathrm{Sc}, \mathrm{Fe}^{2}$, | $\mathrm{P}, \mathrm{V}$ |
| sample pairs but not in <br> distal sample pairs |  | $\mathrm{Fe}^{3}, \mathrm{Be}, \mathrm{Co}^{3}, \mathrm{Th}^{1}$ |  |



Figure 16. Geochemical profile lines.
depression of concentration levels in southern and western Labrador (Figure 20B). This is an example of the profiles giving a misleadingly encouraging impression of the effectiveness of the levelling process. There is also a levelling issue within the Québec data, following the $57^{\text {th }}$ parallel through the middle of NTS map areas $24 \mathrm{~F}, 24 \mathrm{G}$ and 24 H

## Zinc (Zn)

In common with $\mathrm{Fe}, \mathrm{Cu}$ and Ni , the aqua-regia/ICP-ES analyses from Québec have been levelled with respect to both multi-acid/ICP-ES and AAS analyses from Labrador. Levelling has resulted in overcompensation on lines 1, 2, 4, 5 and 6 in the former case (Figure 21A) and in the latter (Figure 21B). These serious discontinuities (resulting in both Zn matches achieving the worst score in Table 5) are not apparent in the contoured geochemical maps (Figure 21C) where the cross-border continuity is very good, especially in the south, although once again, the mismatch was not particularly serious even before levelling was attempted.

## DISCUSSION

## SIGNIFICANCE OF WITHIN-DATASET COMPARISONS

A variety of relationships between analyses after aqua regia and multi-acid are displayed when these analyses are

Table 3. Labrador-Québec lake sediment nearest-neighbour regression equations

| Element | Dataset | Coefficient | Constant | $\mathbf{R}^{2}$ |
| :---: | :---: | :---: | :---: | :---: |
| Ce | Proximal and Distal High LOI | 0.9205 | 53.022 | 0.3959 |
|  | Proximal and Distal Low LOI | 0.7845 | 73.858 | 0.3532 |
| Cr | Proximal and Distal High LOI | 0.5263 | 17.457 | 0.4643 |
|  | Proximal and Distal Low LOI | 0.7132 | 33.792 | 0.439 |
| $\mathrm{Cu}^{2}$ | Proximal and Distal High LOI | 0.7456 | 12.87 | 0.3616 |
|  | Proximal and Distal Low LOI | 0.7834 | 21.487 | 0.243 |
| $\mathrm{Cu}^{3}$ | Proximal and Distal High LOI | 0.5306 | 13.645 | 0.308 |
|  | Proximal and Distal Low LOI | 0.7056 | 19.405 | 0.2344 |
| $\mathrm{Fe}^{2}$ | Proximal High LOI | 0.3124 | 2.0964 | 0.0776 |
|  | Proximal and Distal Low LOI | 0.4883 | 3.4581 | 0.0696 |
| $\mathrm{Fe}^{3}$ | Proximal High LOI | 0.323 | 1.7418 | 0.0766 |
|  | Proximal and Distal Low LOI | 0.4195 | 2.5314 | 0.0632 |
| K ${ }^{2}$ | Proximal and Distal High LOI | 0.8634 | 0.2477 | 0.1074 |
|  | Proximal and Distal Low LOI | 0.9755 | 0.8754 | 0.0536 |
| La | Proximal and Distal High LOI | 0.8883 | 31.996 | 0.3848 |
|  | Proximal and Distal Low LOI | 0.7069 | 39.396 | 0.3314 |
| Li | Proximal and Distal High LOI | 0.7763 | 3.4447 | 0.317 |
|  | Proximal and Distal Low LOI | 0.9435 | 10.597 | 0.2263 |
| Mg | Proximal and Distal High LOI | 0.4271 | 0.1568 | 0.2675 |
|  | Proximal and Distal Low LOI | 0.5667 | 0.482 | 0.1477 |
| $\mathrm{Ni}^{2}$ | Proximal and Distal High LOI | 0.4656 | 13.443 | 0.2119 |
|  | Proximal and Distal Low LOI | 0.5632 | 18.296 | 0.3653 |
| $\mathrm{Ni}^{3}$ | Proximal and Distal High LOI | 0.4864 | 9.8852 | 0.2122 |
|  | Proximal and Distal Low LOI | 0.5799 | 14.216 | 0.3447 |
| P | Proximal and Distal High LOI | 0.6181 | 391.65 | 0.1661 |
|  | Proximal and Distal Low LOI | 0.4704 | 802.71 | 0.0761 |
| Sc | Proximal and Distal High LOI | 0.5514 | 3.4869 | 0.2456 |
|  | Proximal and Distal Low LOI | 0.5828 | 8.0112 | 0.1468 |
| Sm ${ }^{1}$ | Proximal and Distal High LOI | 0.4403 | 4.4045 | 0.3026 |
|  | Proximal and Distal Low LOI | 0.3174 | 6.9143 | 0.2277 |
| Th ${ }^{1}$ | Proximal and Distal High LOI | 0.2749 | 2.5981 | 0.334 |
|  | Proximal and Distal Low LOI | 0.2132 | 7.0472 | 0.1607 |
| Ti | Proximal and Distal High LOI | 0.3922 | 867.97 | 0.0619 |
|  | Proximal Low LOI | 1.0614 | 1730.6 | 0.1846 |
| V | Proximal High LOI | 0.3756 | 28.427 | 0.0913 |
|  | Proximal Low LOI | 0.56 | 54.576 | 0.0989 |
| $\mathrm{Zn}^{2}$ | Proximal High LOI | 0.2553 | 122.95 | 0.0916 |
|  | Proximal and Distal Low LOI | 0.2635 | 112.09 | 0.1542 |
| $\mathrm{Zn}^{3}$ | Proximal High LOI | 0.2604 | 119.45 | 0.0697 |
|  | Proximal and Distal Low LOI | 0.4704 | 802.71 | 0.0761 |

[^0]Table 4. Profiling Traverse Lines; UTM Coordinates are NAD 1927, Zone 20

| Line |  |  |  | Length <br> (km) |
| :--- | :--- | :--- | :--- | :--- |
| 0 | Border | Rocks traversed |  |  |

Table 4. Profiling Traverse Lines (Continued)
UTM Coordinates are NAD 1927, Zone 20

| Line | Start | Border |  | Length <br> (km) |
| :--- | :--- | :--- | :--- | :--- |
| 3 |  | End | Rocks traversed |  |

Table 4. Profiling Traverse Lines (Continued)
UTM Coordinates are NAD 1927, Zone 20

| Line | Start | Border | Length <br> (km) |
| :--- | :---: | :---: | :--- |
| 6 |  | Rocks traversed |  |

Table 5. Summary of cross-border matches as observed in profiles

| Line Number |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | Totals |
| Ce | 2 | -1 | 2 | 2 | 2 | -2 | -1 | 2 | 6 |
| Cr | 2 | 2 | 2 | -2 | -1 | 2 | 2 | 2 | 9 |
| $\mathrm{Cu}^{2}$ | 2 | 2 | 2 | -2 | -1 | 2 | -2 | -1 | 2 |
| $\mathrm{Cu}^{3}$ | 2 | 2 | 2 | -2 | -1 | 2 | -1 | -1 | 3 |
| $\mathrm{Fe}^{2}$ | 2 | 2 | 2 | -2 | -1 | 2 | -2 | -1 | 2 |
| Fe ${ }^{3}$ | 2 | 2 | 2 | 2 | -1 | 2 | 2 | 2 | 13 |
| La | 2 | 2 | 2 | 2 | 2 | -2 | 2 | 2 | 12 |
| Li | 2 | 2 | 2 | -2 | -2 | -2 | -2 | 2 | 0 |
| Mg | 2 | 2 | 2 | -1 | 2 | -2 | 2 | 2 | 9 |
| $\mathbf{N i}^{2}$ | 2 | 2 | 2 | -2 | -1 | 2 | -1 | 2 | 6 |
| $\mathrm{Ni}^{3}$ | 2 | 2 | 2 | -2 | -2 | 2 | -1 | 2 | 5 |
| P | 2 | 2 | -1 | 2 | -1 | 2 | 2 | 2 | 10 |
| Sc | 2 | 2 | 2 | -1 | 2 | -1 | 2 | 2 | 10 |
| Sm | 2 | 2 | 2 | 2 | 2 | -2 | -1 | 2 | 9 |
| Th | -1 | 2 | 2 | 2 | 2 | 2 | -2 | -2 | 5 |
| Ti | 2 | 2 | 2 | -2 | -2 | -2 | -2 | 2 | 0 |
| V | 2 | 2 | 2 | -2 | 2 | 2 | 2 | 2 | 12 |
| $\mathbf{Z n}{ }^{2}$ | 2 | -2 | -2 | 2 | -2 | -2 | -2 | 2 | -4 |
| $\mathbf{Z n}{ }^{3}$ | 2 | -2 | -2 | 2 | -2 | -2 | -2 | 2 | -4 |
| Totals | 38 | 25 | 29 | -9 | -4 | -3 | -11 | 24 |  |

2: Good cross-border match between Labrador and (levelled) Québec datasets
-1: Slight overcompensation by levelling equation
-2: Strong overcompensation by levelling equation
${ }^{2}$ Labrador analyses by ICP-ES after multi-acid digestion
${ }^{3}$ Labrador analyses by AAS after aqua-regia digestion
plotted against one another. The poor relationship observed between the two digestion methods is to be expected for elements like $\mathrm{Al}, \mathrm{K}$ and Na , whose inorganic fraction concentrates in relatively refractory minerals like feldspars; whereas elements such as Cu , which concentrate in ferromagnesian minerals, are more readily released by aqua regia, which produces similar results to the multi-acid digestion. The apparent solubility of the rare-earth elements Ce and La , as well as Li , in the latter reagent is rather more surprising. The most common rock-forming mineral in which the former elements occur is monazite, however, this is described as a resistate mineral (that is, resistant not only to aqua regia) by a number of sources (e.g., Actlabs, 2014). Consequently, monazite may not be dissolved by either reagent and its presence would not give rise to a discrepancy between analyses that follow the two digestions. Since the multi-acid/ICP-ES and INAA analyses for rare-earth elements in the Labrador samples tend to be very similar, monazite is an unlikely host for them. Indeed, in Labrador the rare-earth elements do not seem to concentrate in either the clastic, inorganic fraction of lake sediments; nor do they correlate with LOI (Amor, 2014), which represents the
organic content, to a first approximation, at least in non-carbonate terrain.

In general, the strength of the relationship between nearest-neighbour sample pairs across the Labrador-Québec border is echoed in results from the internal comparisons, although the reverse is not necessarily the case. The elements displaying the strongest nearest-neighbour correlations are $\mathrm{Ce}, \mathrm{Cr}, \mathrm{Cu}, \mathrm{Ni}$ and Li , which were described earlier as having "close concordance with the 1:1 line throughout the concentration range" (Cu), "a close linear relationship by most samples throughout the concentration range, with incomplete digestion by aqua regia by some samples in mid-range" (Ce, La, Li) or "a linear relationship over the lower part of the concentration range, with incomplete digestion by aqua regia at higher concentration levels" (Cr). However, $\mathrm{Co}, \mathrm{Fe}$ and Mn display a close relationship between aqua-regia and multi-acid analyses in the same samples over much of the concentration range, but much weaker nearest-neighbour correlation, particularly in organ-ic-rich samples. In the case of the latter two elements, this confirms that local controls over the Fe and Mn content of


Figure 17A. Profiles of unlevelled and levelled Ce values on eight section lines across Québec-Labrador border. Québec analyses were by ICP-ES after aqua-regia digestion. Labrador analyses were by ICP-ES after multi-acid (HCl-HF-HClO ${ }_{4}$ ) digestion. (Caption and Figure 17B on next page.)
the lake sediment, such as precipitation of Mn hydroxides (and Co, by the scavenging effect) where a rapid change in $\mathrm{eH} / \mathrm{pH}$ conditions takes place, predominate over more regional geological controls; i.e., two lakes very close together may have radically different Fe and Mn contents.

One of the elements showing the best levelling, when the results are viewed in the form of a contoured map, is Cr. This is somewhat unexpected given the relationship between ICP-ES analyses after aqua-regia and multi-acid digestions, which diverge at higher concentration levels. Presumably, such high concentrations are rare (which would be typical of the frequency distribution of a geochemical variable) and have limited influence on the gridded values used to generate the contours.

## ORGANIC-RICH AND ORGANIC-POOR SAMPLES

Dividing the lake sediments into more than two classes, based on their LOI content, or experimenting with different cut-offs between 'high-LOI' and 'low-LOI' samples, becomes a complicated task, outside of the scope of this preliminary study, although such an approach may serve to improve the quality of the levelling between the two datasets. The effects on the quality of the levelling, and the resulting appearance of the geochemical maps, by applying high-LOI equations to low-LOI samples, or of applying a single LOI-independent equation to all samples (pace Garrett et al., 1990) have also to be investigated further.

Figure 17B. Areal distribution of unlevelled (Bi) and levelled (Bii) Ce in Labrador and adjacent Québec. The match between the unlevelled datasets is reasonably good, although levelling serves to accentuate certain features in Québec, while retaining features in Labrador in slightly diluted form.


Figure 18A. Profiles of unlevelled and levelled Cr values on eight section lines across Québec-Labrador border. Québec analyses were by ICP-ES after aqua-regia digestion. Labrador analyses were by ICP-ES after multi-acid (HCl-HF-HClO ${ }_{4}$ ) digestion. (Caption and Figure 18B on next page.)

## NEW ANALYSES

It is proposed (B. McClenaghan, personal communication, 2014) to re-analyze selected Labrador samples from the NTS 1:250 000 map areas closest to the Québec border. Analysis will be by ICP-ES after aqua-regia digestion; in other words, the same digestion and finish that have been applied to the Québec samples. When it takes place, this will undoubtedly improve the compatibility of the analytical results from either side of the border, and make some of the work done in the current study redundant. However, levelling may still be necessary for some elements, and even if it is not to be applied, the nearest-neighbour correlation and regression methods, applied in the current study, may find application in confirming the correctness of the latter decision.

## METHOD OF DISPLAY

A simple inverse-distance contour gridding method has been applied to the data; this seems to highlight serious shifts in concentration levels, where they exist as well as strong regional anomalies, such as the positive Zn feature extending on both sides of the border over rocks of the Labrador Trough in the western part of the study area. Other methods of displaying the data may be experimented with in future, both for existing data and for the new data that will be generated. The method of display adopted for the final products may differ from that used in this preliminary study.

Figure 18B. Areal distribution of unlevelled (Bi) and levelled (Bii) Cr in Labrador and adjacent Québec. The discontinuity between the two datasets has been addressed by applying the levelling equation, without seriously affecting the appearance in Labrador.


Figure 19A. Profiles of unlevelled and levelled Li values on eight section lines across Québec-Labrador border. Québec analyses were by ICP-ES after aqua-regia digestion. Labrador analyses were by ICP-ES after multi-acid ( $\mathrm{HCl}-\mathrm{HF}^{2}-\mathrm{HClO}_{4}$ ) digestion. (Caption and Figure 19B on next page.)

## CONCLUSIONS

The feasibility of combining large semi-regional lakesediment datasets from Labrador and the adjacent part of Québec is being investigated.

The Labrador samples were analyzed by ICP-ES following a multi-acid ( $\mathrm{HCl}-\mathrm{HF}-\mathrm{HClO}_{4}$ ) digestion that is capable of dissolving most rock-forming minerals, whereas most of their Québec counterparts were treated with an aquaregia digestion, to which many such minerals are resistant. This creates an incompatibility issue when the data are combined; most serious in the case of elements that are mainly hosted in aqua-regia-resistant minerals such as feldspars; these include $\mathrm{Al}, \mathrm{Sr}$ and Na . The correspondence between analyses after the two digestions is, on the other hand, much closer for siderophile or chalcophile elements such as Cu , $\mathrm{Fe}, \mathrm{Mn}$ and Mo , but also for $\mathrm{Ce}, \mathrm{La}$ and Li .

Some of the elements in the Québec and Labrador datasets have been levelled by establishing linear regression relationships between nearest neighbours on either side of the border. In most cases the levelling exercise has only been partially successful, with satisfactory matching of the data from either side of the border in one part of the map, and overcompensation in others. Among the elements that are least susceptible to overcompensation, and produce the most satisfactory results, are Ce and Cr .

Whereas re-analysis has been proposed, which may, when complete, make some of this work redundant, the method of testing the cross-border match between the analyses proposed in the current study may have application in the testing of the new analyses, which are unlikely to be entirely free of levelling issues.

Figure 19B. Areal distribution of unlevelled (Bi) and levelled (Bii) Li in Labrador and adjacent Québec. The discontinuities north of $56^{\circ} N$ have been alleviated, but this has resulted in overcompensation in the west and excessive dilution throughout southern Labrador.


Figure 20A. Profiles of unlevelled and levelled Sc values on eight section lines across Québec-Labrador border. Québec analyses were by ICP-ES after aqua-regia digestion. Labrador analyses were by ICP-ES after multi-acid (HCl-HF-HClO ${ }_{4}$ ) digestion. (Caption and Figure 20B on next page.)

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Figure 20B. Areal distribution of unlevelled (Bi) and levelled (Bii) Sc in Labrador and adjacent Québec. The very strong discontinuity north of $56^{\circ} N$ has been alleviated by the levelling, but overcompensation in the south is severe. An internal discontinuity is present in the Québec dataset, corresponding to the $57^{\circ}$ parallel, which bisects NTS map areas 24F, 24G and $24 H$.


Figure 21A. Profiles of unlevelled and levelled Zn values on eight section lines across Québec-Labrador border. Québec analyses were by ICP-ES after aqua-regia digestion. Labrador analyses were by ICP-ES after multi-acid (HCl-HF-HClO ${ }_{4}$ ) digestion. (Caption and Figure 21B on next page.)

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Figure 21B. Profiles of unlevelled and levelled Zn values on eight section lines across Québec-Labrador border. Québec analyses were by ICP-ES after aqua-regia digestion. Labrador analyses were by AAS after aqua-regia digestion.

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Figure 21C. Areal distribution of unlevelled (Ci) and levelled (Cii) Zn in Labrador and adjacent Québec. Zn2 (top row): Québec analyses by ICP-ES after aqua-regia digestion, Labrador analyses by ICP-ES after multi-acid digestion. Zn3 (bottom row): Québec analyses by ICP-ES after aqua-regia digestion, Labrador analyses by AAS after aqua-regia digestion.


[^0]:    ${ }^{1}$ Québec samples analyzed by ICP-ES after aqua-regia digestion; Labrador samples by INAA
    ${ }^{2}$ Québec samples analyzed by ICP-ES after aqua-regia digestion; Labrador samples by ICP-ES after multi-acid digestion
    ${ }^{3}$ Québec samples analyzed by ICP-ES after aqua-regia digestion; Labrador samples by AAS after aqua-regia digestion

