Regional geochemical data compilation and map preparation, Labrador, Canada*

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ABSTRACT

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Procedures used to compile geochemical data for some 20,000 lake sediment and stream sediment samples from 292,000 km^2 in Labrador, Canada, are described. A methodology for integrating the lake and stream sediment data is developed which compensates for the varying organic component in the matrix of the two sample media. It is shown that this procedure is effective in reducing the variability of the Zn and Ni data due to the organic matrix effect and for normalizing the data for regional-scale comparisons. No compensation was required for U data. In order to generate geochemical maps of the broad-scale patterns in the data, reflecting such features as structural provinces, litho-tectonic packages and metallogenic provinces, the use of medians for the data falling within square cells with a side varying from 10 to 50 km was investigated. An Analysis of Variance procedure is described which was used to select an optimal cell size. For the Labrador data 25×25 km cells were selected, resulting in a 97% reduction in the volume of data to be managed. The reduced data contained approximately 35%, 70% and 55% of the information for Zn, Ni and U, respectively. The final maps appear to reflect major features of the regional geochemistry related to the geological history of Labrador. It is proposed that the procedures developed should be further evaluated to determine their suitability in fulfilling the objectives of IGCP Project 259 on International Geochemical Mapping.

INTRODUCTION

Following a series of full-scale pilot studies the Geological Survey of Canada commenced a programme of systematic regional geochemical mapping in 1974 under the title of the National Geochemical Reconnaissance (NGR). To date in excess of 1.5 million km^2 have been mapped using stream and lake sediment sampling procedures (Lund, 1987). Funding for the activity has largely been from joint Federal-Provincial Mineral Development, or similar, agreements.

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    In recent years there has been an increased interest in regional geochemical mapping as an activity in support of broad-scale crustal-, environmental- and global-change investigations, in addition to the mineral exploration and regional metallogeny studies it was designed to assist. Many countries, or major portions of nations, are now covered by geochemical atlases, e.g., England and Wales (Webb et al., 1978), Alaska (Weaver et al., 1983), the Federal Republic of Germany (Fauth et al., 1985) and Northern Fennoscandia (Bölviken et al., 1986). The work in Fennoscandia is particularly noteworthy as it was an international cooperative project involving the Geological Surveys of Finland, Norway and Sweden.

    The increased interest in geochemical mapping and atlases has led to the proposal and acceptance of an International Geological Correlation Programme Project, Number 259, entitled International Geochemical Mapping, with the objective of developing methodologies and recommendations that will lead to consistent criteria for the presentation of international geochemical maps. This paper is a contribution to the activities of IGCP Project 259.

    The preparation of small-scale regional geochemical maps, for example at scales of 1:2 million, 1:5 million and larger, can follow two general procedures. Firstly, field sampling and analytical work may be undertaken specifically in support of the mapping programme; or secondly, suitable available data may be compiled and presented at the desired scale. The latter procedure is particularly attractive in Canada where geochemical survey data already exist, and the cost of undertaking new field sampling programmes in remote, largely uninhabited, areas is high.

    The Labrador area of some 292,000 km² was selected for a compilation study for three main reasons. Firstly, it was the first Canadian geo-political entity to be systematically covered, in surveys carried out between 1978 and 1986. Secondly, geochemical data compilations were being made independently by the Newfoundland and Labrador Department of Mines and Energy with whom the Geological Survey had undertaken the regional surveys (P.H. Davenport, pers. commun., 1990); and by the Quebec Department of Energy and Resources (Baumier, 1989) to the west, and by the Geological Survey of Greenland across the Labrador Sea to the northeast (Steenfelt, 1987). Finally, the data were derived from lake sediments in the southern and central parts of Labrador, and from stream sediments in the far north. This presented a challenge for combining the two data types in a single presentation.

    In the following sections we describe the procedures employed to compile the data in order to prepare colour 1:5 million scale geochemical maps of the regional variations in geochemical background levels across Labrador, and to merge the lake and stream sediment data into a unified whole. The scale 1:5 million was chosen as it is commonly used in north America for continental-scale geoscience compilations, e.g., geology, tectonic, magnetic and gravity

anomaly maps, where a Lambert Conformal projection is used with standard parallels at 49° and 77°N. The geochemical maps of Labrador were prepared using this projection with these same standard parallels and a central meridian of 61°W. For the purpose of publication in this paper the colour contour scheme was changed to a grey-scale and the maps plotted at 1:9 million scale. It should be noted that the purpose of this paper is to describe a data-compilation methodology for discussion as part of IGCP Project 259. It was not intended to carry out an in-depth interpretation of the regional geochemistry of Labrador; such a task is for geologists and geochemists with a far greater knowledge of Labrador than we possess.

DATA ACQUISITION

Records containing regional survey data, consisting of the geochemical field number, Universal Transverse Mercator (UTM) zone and coordinates, Zn (ppm), Ni (ppm), U (ppm), Mn (ppm), and loss-on-ignition (LOI, percent), were extracted from the archival geochemical data files held by the Geological Survey of Canada and organized by National Topographic System (NTS) sheet number and survey year. At the time of these retrievals the UTM coordinates were converted to Lambert Conformal coordinates consistent with the 1:5 million scale maps to be prepared. The geochemical analyses had been made on the < 177-μm fraction of the stream sediment, and the similar fraction of the disaggregated lake sediment. Zn, Ni, Fe and Mn data were derived by a hot, reverse aqua-regia leach followed by determination of the metals by atomic absorption spectrophotometry, U was determined by delayed neutron counting, and the loss-on-ignition was determined after heating to 500°C. Only records where the sample preparation and analysis procedures were consistent with the above criteria were retrieved. In total, 20097 records contained valid data, divided between lake sediments (18853) and stream sediments (1244). A subset of 19929 records contained data for Zn, Ni and LOI, but not necessarily the other elements, and a subset of 19982 records contains U data. The division between lake and stream sediment data lies at 58°N. However, in 1985 (lake sediments) and 1986 (stream sediments) the southern halves of NTS areas 14L and 24I were sampled for both lake and stream sediments. Surveys in both years were undertaken at the nominal NGR sample density of 1 site per 13 km^2 (5 mi^2) for both sample media. However, in the overlap area the stream sediments were sampled at a higher density in order to facilitate any sample media comparative studies that might be undertaken. Following a careful inspection of the sample location maps for both media, a set of 112 lake sediment–stream sediment pairs representing almost identical catchment basins was prepared for an effects-due-to-sampling-media study. Lastly, a subset of the total Labrador retrieval was prepared which represented a S–N meridional transect approximately 2° of longitude wide

from Lac Brulé (NTS 13D) to Grenfell Sound (NTS 25A). This spanned the physical environmental range of 8.5° of latitude between 52°N and 60.5°N, and crossed the open-woodland to tundra-open-woodland transition at approximately 56°N (National Atlas of Canada, 1973). In the southern parts of this meridional transect black spruce boreal forest is found.

MERIDIONAL TRANSECT STUDY AND THE EFFECTS OF SAMPLE MEDIA

Previous work at the Geological Survey had indicated the important role organic matter, estimated by loss-on-ignition (LOI), plays in controlling many trace-element levels in organic-rich centre-lake bottom sediments (e.g., Garrett and Hornbrook, 1976). With the knowledge that Labrador spanned vegetation zones from the boreal forest to tundra, and that stream sediments were collected in the northernmost part of Labrador due to the unavailability of suitable lakes to sample, an investigation of the meridional transect data was undertaken using the IDEAS (Garrett, 1988) interactive statistical computer graphics software. In order to focus on trends in the data they were divided into nine subsets corresponding to NTS areas 13D, 13E, 13L, 13M, 14D, 14E, 14L and 24I, 14M and 24P, and 25A from south to north. The southernmost six subsets, bounded by longitudes 62° and 64°W, are represented by lake sediment data, and the northernmost three subsets comprise those parts of Labrador between longitudes 62° and 66°W and are represented by stream sediment data.

The data for LOI are presented as box-and-whisker plots (Fig. 1). In these the data maxima and minima are indicated by a +, the ends of the whiskers mark the 5th and 95th percentiles of the data, and the central box spans the middle 50% of the data from the 25th to 75th percentiles. The central box is notched to indicate the median (50th percentile) and its 95% confidence interval. Firstly, the three northernmost, stream sediment sampled, areas are characterized by both low LOI levels and high geochemical relief. Secondly, the four southernmost, lake sediment sampled, areas consistently exhibit higher LOI levels but lower geochemical relief. Lastly, the northernmost two lake sediment areas, 14D and 14E between latitudes 56° and 58°N, exhibit a transitional nature with decreasing LOI levels and somewhat increased relief. This transition zone correlates well with the southern limit of the tundra at 56°N, indicating that LOI levels fall significantly once the tree line is crossed. The scaling in Figure 1 is logarithmic in order to provide scale expansion at low LOI levels. Previous work at the Geological Survey of Canada has indicated that once LOI levels in lake sediments fall below 12% there are decreases in many background trace-element levels unrelated to geological phenomena. Therefore, whilst it is very clear from Figure 1 that depressed Zn levels should be expected in the stream sediment data, there should also be a more subtle effect in the lake sediment data north of the tree line.
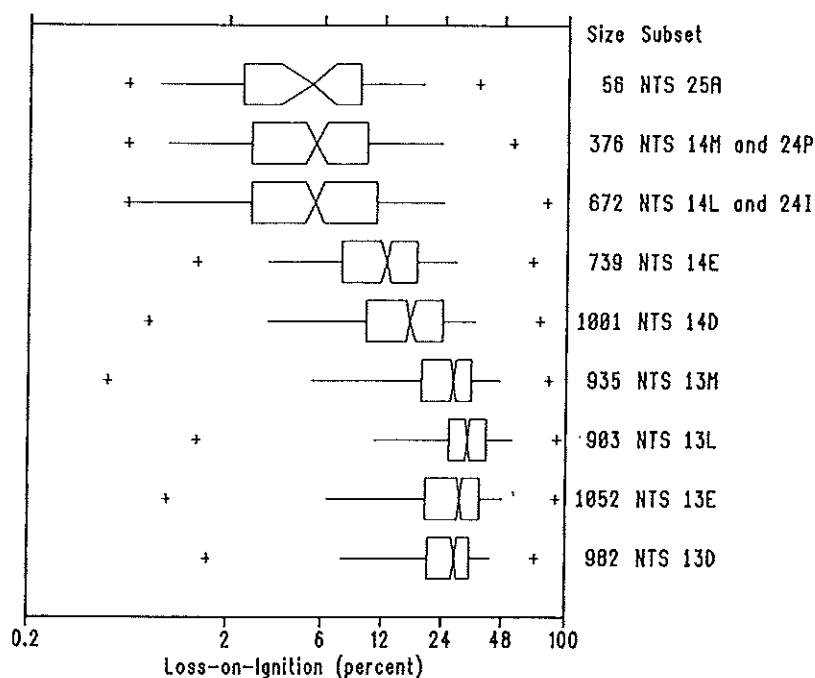
Size	Subset
56	NTS 25A
376	NTS 14M and 24P
672	NTS 14L and 24I
739	NTS 14E
1081	NTS 14D
935	NTS 13M
903	NTS 13L
1052	NTS 13E
982	NTS 13D

Loss-on-Ignition (percent)

Fig. 1. LOI levels along the meridional transect.

Size	Subset
56	NTS 25A
389	NTS 14M and 24P
715	NTS 14L and 24I
739	NTS 14E
1081	NTS 14D
936	NTS 13M
903	NTS 13L
1052	NTS 13E
982	NTS 13D

Zn (ppm)
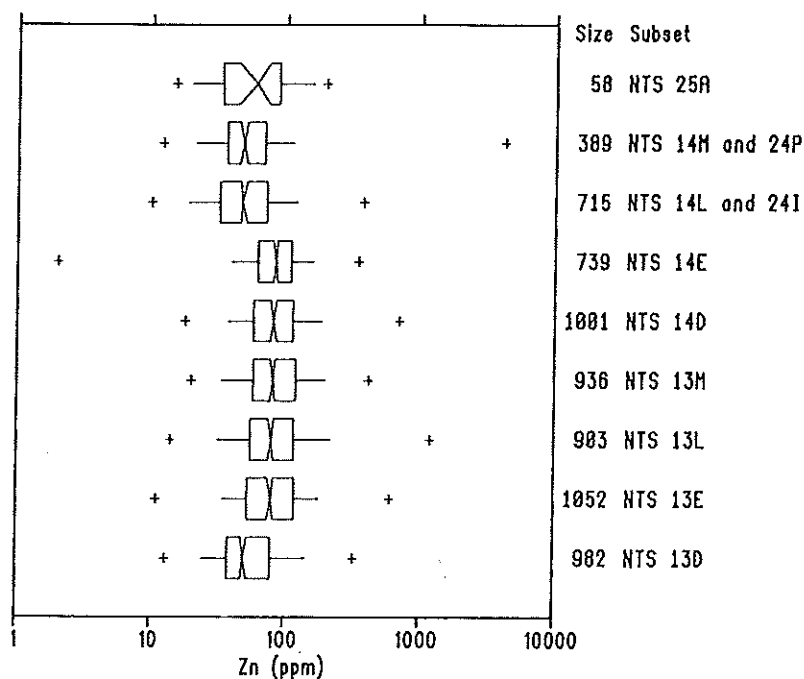
Fig. 2. Zn levels along the meridional transect.

The meridional transect data for Zn have also been plotted as box-and-whisker plots (Fig. 2). These show remarkably little geochemical relief across the 8.5° latitudinal span. However, the low LOI in stream sediment areas in the north clearly form a distinct low Zn level grouping. A decrease in regional

Zn levels also occurs at the southern extremity of the transect. It is postulated that this is a geological phenomenon and related to the Grenville Province, whose northern limit in the transect is at $53.5°N$ and which appears to be Zn depleted. An alternative hypothesis is that these low Zn levels could be due to year-to-year analytical variability. Significant long-term drift is unlikely as the analytical quality control procedures used in the NGR surveys were designed to detect such drift (Garrett et al., 1980). Further evidence that the variation is not due to long-term drift is provided by Figure 2. From south to north the sampling and analysis were undertaken in 1982 and 1983 (NTS 13D), 1982 (NTS 13E), 1978, 1982 and 1983 (NTS 13L), 1978 (NTS 13M and 14D) and 1985 (NTS 13E). If there was significant long-term drift it would be likely that the multi-year areas, NTS 13D and 13L, would exhibit markedly increased data variability, but none is observed. Therefore, the Zn patterns exhibited by the three southernmost NTS sheets sampled in 1978, 1982 and 1983 are not believed to be an artifact of the survey procedures.

The regional relationship for the Zn vs. LOI interaction is displayed in a box-and-whisker plot (Fig. 3) where the data are subdivided into 3% LOI wide groups up to 12% LOI and 12% wide groups from 12 to 48% LOI, after which the >48% LOI data are placed in a single group. The increase in median Zn levels between 1 and 12% LOI by a factor of about two is clear. From 12 to 48% LOI the Zn medians stabilize, and as observed previously (Garrett and Hornbrook, 1976) Zn levels decrease again less markedly at higher LOI levels, here by about 10%.

In order to study the trace-element vs. LOI relationship in greater detail an
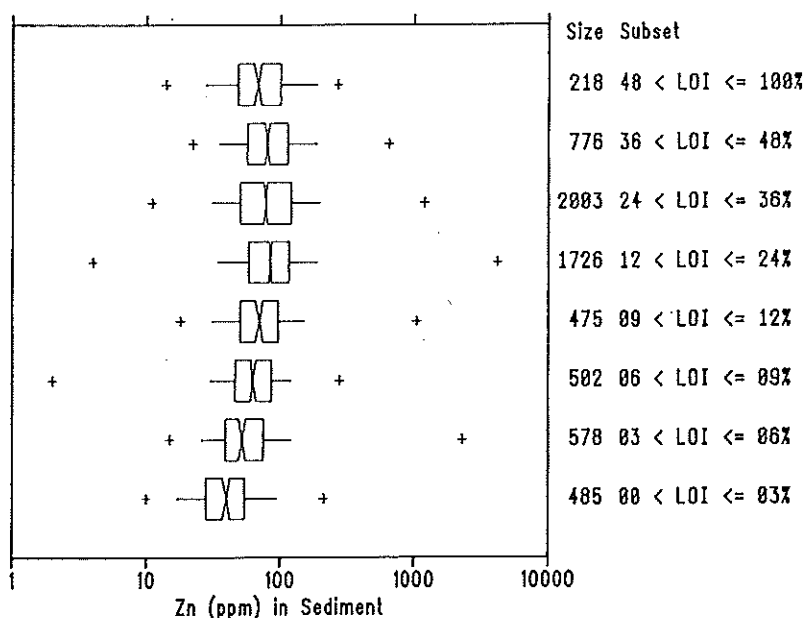

Fig. 3. Variation of Zn as a function of the organic matrix effect as estimated by LOI.

extensive graphical study was made of the Zn, Ni and U analyses for the paired lake sediment–stream sediment data of the catchment basin. Firstly, the three bivariate metals in lake sediment vs. stream sediment relationships were studied and any statistical outliers removed to obtain background data subsets (Garrett, 1989). The pairs common to the three background data subsets for which there were LOI determinations in stream sediment were then retrieved. This resulting core group of 92 lake sediment-stream sediment catchment pairs was used in the effects-due-to-sample-media study. Attention was then focused on Zn with the objective of finding a simple relationship between Zn in lake sediments and Zn and LOI in stream sediments. The most revealing display was of Zn in stream sediment plotted against Zn in lake sediment with the individual points being coded by the LOI content of the stream sediment (Fig. 4). The display clearly shows that at high LOI in stream sediment levels there is little difference between the Zn data for lake and stream sediments in the same catchment basins. However, as the LOI in stream sediment decreases there is a rapid decrease in Zn in stream sediment relative to lake sediment. Replotting the data as the Zn-in-lake-sediment/Zn-in-stream-sediment ratio against LOI in stream sediment (Fig. 5) produces a "noisy" plot. However, a trend can be seen where the ratio is close to one above about 15% LOI and generally increases through about 1.6 at 4% LOI to approximately 3.5 at 1% LOI. The value of the ratio used as a multiplier ap-

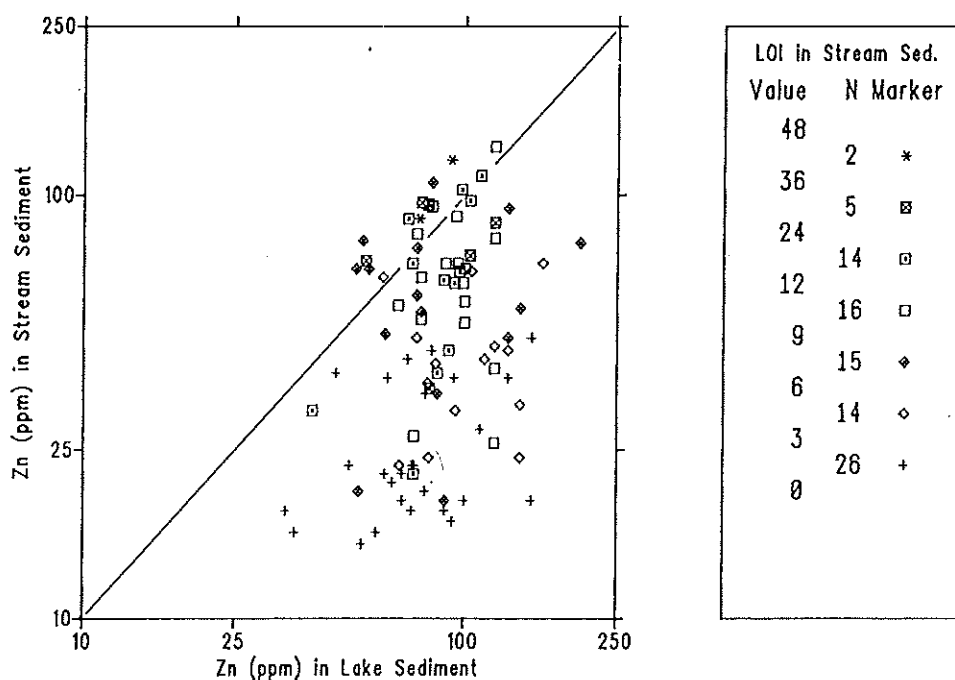| LOI in Stream Sed.		
Value	N	Marker
48		
	2	*
36		
	5	⊠
24		
	14	⊡
12		
	16	□
9		
	15	◆
6		
	14	◇
3		
	26	+
0		

Fig. 4. The relationship between Zn in lake sediment and Zn and LOI in stream sediment for the paired catchment basin study data from NTS areas 14L and 24I.
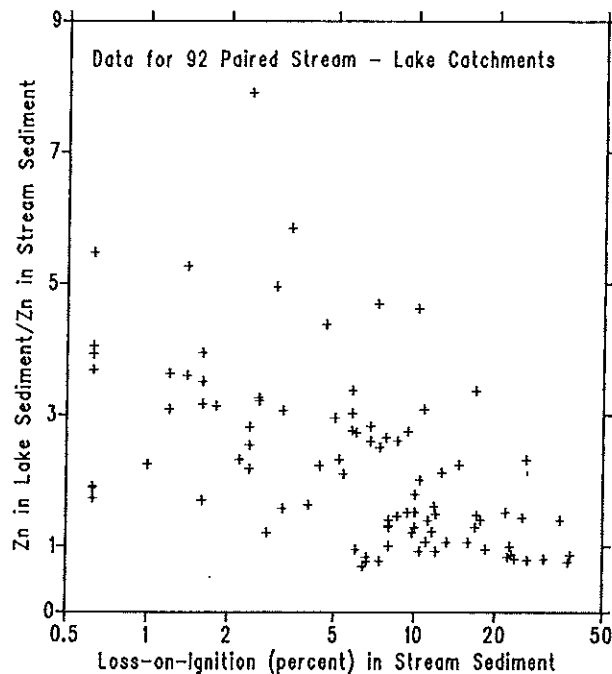
Fig. 5. The relationship between the Zn-in-lake-sediment to Zn-in-stream-sediment ratio and LOI in stream sediment for the paired catchment basin study data from NTS areas 14L and 24I.

plied to the Zn in stream sediment data would yield an equivalent Zn in lake sediment estimate, referred to as the LOI-corrected Zn value.

Several options are available to estimate the multiplier, or correction factor. Regression analysis is one candidate; however the correction factor is nonlinear which complicates estimation. If regression analysis is used some workers would argue that Fe and/or Mn should be included with LOI as the hydroxides of these elements readily scavenge many trace elements (Rose et al., 1979). However, it is not our intention to correct for the effects of varying Fe and Mn levels. These variations may be due to changes in catchment lithology, the presence of Fe- and/or Mn-containing mineral occurrences, or local surficial environmental phenomena, and appear to be nonlinear. A plot of Fe plus Mn vs. LOI for the meridional transect data (not shown) indicates a generally quadratic form with the combined elements rising from 1.8% at 1% LOI to 2.5% at 17% LOI, and falling to 1.1% at 50% LOI in a smooth and systematic fashion. As we cannot partition these effects and only correct for the surficial environmental component we chose not to include these elements in our correction procedure. Additionally, a regression analysis is data-based and would yield different results with different data sets, and the regression coefficients are particularly susceptible to distortion by any outliers in the data. Moreover, the clear non-linearity of the trace-element, LOI, Fe and Mn relationship would require at least the inclusion of quadratic terms in any regression model.

The approach we have taken is to only correct the Zn data for LOI using an empirical function that falls from a value of 3.7 at 1% LOI, through 1.8 at 4% LOI to 1.03 at 12% LOI. The basis for the selection of this function is the overall increase of Zn with LOI by a factor of two from low to 12% LOI levels (Fig. 3) and the factor of 3.5 derived from Figure 5. The actual form of the function is:

$$\text{Zn correction factor} = 1 + 4 \times 1.5^{-\text{LOI}}$$

which results in a less than 0.1% correction above 21% LOI (Fig. 6).

A similar study for Ni indicated that the LOI effect was less severe and that a function of the form:

$$\text{Ni correction factor} = 1 + 3 \times 1.5^{-\text{LOI}}$$

was appropriate. A study of the U data indicated that no correction could be justified on the basis of the data from the overlap area.

It is postulated that the reason for these changes in behaviour may be due to the mode of dispersion of the three elements. We hypothesize that the dispersion of the Zn determined is dominantly by hydromorphic processes, whilst clastic dispersion plays a more important role with U, and Ni falls in an intermediate position. Therefore, the organic matrix plays a more important role in controlling the Zn distribution than it does the U. It may be argued that the methods of analysis used could affect this model. The Zn and Ni data are "near-total", being derived by determination after a hot, reverse aqua-
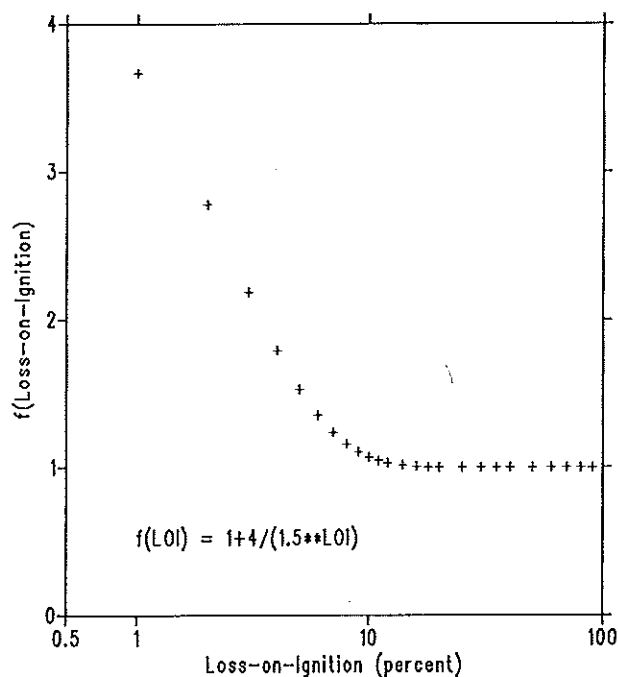

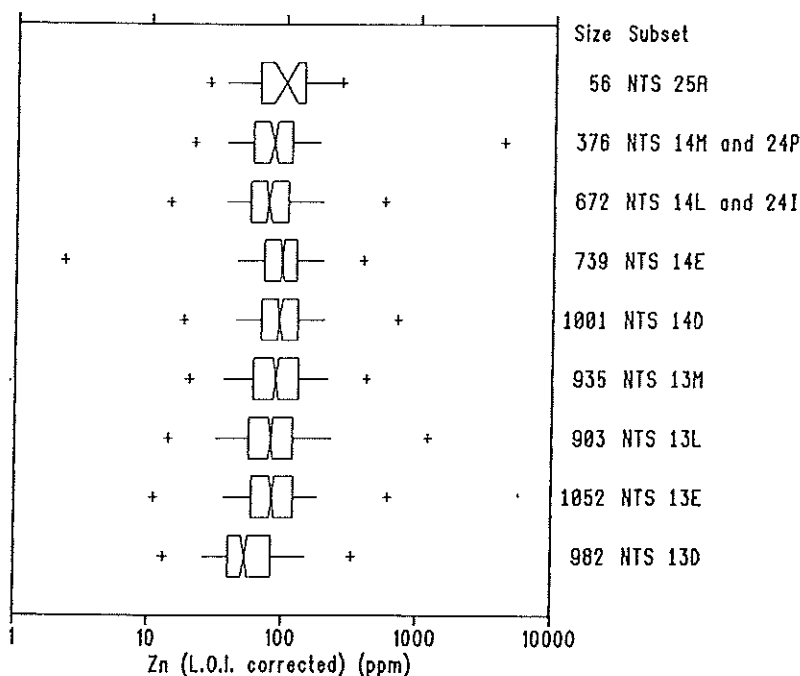Fig. 6. Values of the Zn correction factor as a function of LOI.

Fig. 7. LOI-corrected Zn levels along the meridional transect.

regia leach procedure, whereas the U data are "total" being derived by de-
layed neutron counting. However, we do not believe that differences induced
by the two analytical procedures are large enough to account for the different
elemental behaviours.

The LOI correction for the organic matrix effect has been applied to both
the lake and stream sediment data in an attempt to correct both data types to
a constant 12–48% LOI matrix. This facilitates the direct comparison of all
data in the 1–48% LOI range. We have taken this action as we believe that
north of the tree line the lakes are mainly a repository for the finer fractions
of the stream sediment bed load. The result of applying the correction to all
the Zn data is displayed as box-and-whisker plots (Fig. 7). A careful compar-
ison of Figures 2 and 7 reveals that the levels for NTS areas 13E, 14D and
14E have all increased, whilst those for the northernmost three areas have
increased markedly. In terms of statistical significance, the medians for the
five northernmost areas have all increased significantly as indicated by the
95% confidence interval notches in the box-and-whisker displays.

REGIONAL GEOCHEMICAL MAP PREPARATION

The large-scale broad regional geochemical maps envisioned in IGCP Proj-
ect 259 are maps of regional background levels. They do not necessarily re-
flect the presence of individual mineral occurrences or small bodies of geo-
chemically contrasted rock types. They should, however, reflect metallogenic

and geochemical provinces and changes in geochemical level and relief related to major litho-tectonic packages.

Given this objective one may ask whether the low sampling densities used in traditional regional geochemical surveys of the order of 1 site per 10 km² could be reduced even further and still reflect features of the scale of those to be studied on a continental or global scale. Work undertaken in Norway suggests that regional geochemical surveys with sampling densities of the order of 1 site per 300 to 500 km² can reflect the scale of regional features being discussed (Bölviken, 1988). A proposed West European survey would employ "overbank" samples, i.e., samples of alluvial material collected immediately adjacent to streams which was deposited during flood periods when the streams overflowed their banks, as the sampling media (Bölviken, 1988). In an area as small as Western Europe where, because of the diversity of sampling and analytical procedures used in different countries, the compilation of data to a single base would be extremely difficult, resampling at very low densities, e.g., 1 site per 20×20 km cell, would be a realistic approach.

However, in many of the areally extensive countries of the world, e.g., Canada, China, the U.S.A. and the U.S.S.R., very large volumes of internally consistent geochemical data already exist. In these countries the cost of resampling at very low densities, e.g., 1 site per 20×20 km cell, would be prohibitively high. The alternative is to compile the already existing data and prepare maps that would emulate those that would be generated from a very low-density survey. This alternative is relatively low cost as it involves only the use of computers and technical personnel without any additional field activities.

Two procedures are possible. Firstly, the data may be sampled by randomly selecting a subset of geochemical samples using sampling strata corresponding to the proposed very low density sampling grid, e.g., 20×20 km cells. Or secondly, all the data in each sampling stratum could be used to estimate a single representative value. The first procedure has been used to investigate the effects of sample density variation in regional geochemical surveys in Canada (Garrett, 1977). This work indicated that sampling densities over large parts of the Canadian Shield could be reduced from 1 site per 13 km² to 1 site per 30 km² without losing much of the resolution obtained by the higher-density survey. However, the objective in selecting the sample density was to preserve important local detail, not derive a map of the broad-scale regional background patterns. For the current study we have investigated a procedure where all the available data are used. Our reason for this choice is that the objective is to obtain a stable map of the broad patterns of regional variation.

Miesch (1976) described a statistic, V_m, used to measure map stability for use with Analysis of Variance (ANOVA) based structured sampling designs used by the U.S. Geological Survey in certain regional geochemical studies. V_m is computed as the ratio of the between-sampling-strata variability to the

pooled estimate of the standard error of the strata means. Intuitively the value of this ratio should be as high as possible, i.e., large variation between the sampling strata with a high precision (low standard error) for the strata means. Tidball, in simulation studies reported by Miesch (1976), noted that when V_m exceeded 3 the maps prepared from strata means appeared to reflect the true geochemical patterns well. When V_m was below 1 the true geochemical patterns were not clear, and for values between 1 and 3 the maps increased in reliability with V_m.

We have adapted the ANOVA and V_m approaches in order to objectively determine a strata size that would yield an acceptable data compilation. The original studies of V_m were made with balanced ANOVA designs, i.e., the same number of individuals per stratum. However, in the post-hoc imposition of regular strata on regional reconnaissance data each stratum will not contain an equal number of individuals; this leads to an unbalanced ANOVA design. The estimation of pooled standard error of the strata means under this situation is not routine. One procedure would be to use the arithmetic mean of the number of individuals per stratum in the estimation of standard error. However, this procedure underestimates the standard error, indicating the strata means to be more precise than they really are. Work by Rankin (1974) and Thomas and Hultquist (1978) indicates that the use of the harmonic mean provides a more suitable estimator for the average number of samples per stratum in unbalanced designs. The effect of the harmonic mean is to "penalize" the estimator for strata containing few individuals; hence the standard errors are larger (lower precision) and V_m will be lower. We are unaware of any studies of the significance of the V_m statistic in unbalanced designs employing the harmonic mean estimator. However, noting that our use of V_m is to obtain a comparative measure between strata size effects and that the proposed unbalanced V_m, $V_{\tilde{m}}$, is conservative relative to V_m we have continued to use the approximate values of 1 and 3 as guidelines for discussion purposes.

The Lambert Conformal coordinates of the 20097 lake and stream sediment samples were scanned and the maximum and minimum easting and northing coordinates determined. The minima were rounded down to the nearest 10 km and a series of nine square grid cell strata, 10, 15, 20, 25, 30, 35, 40, 45 and 50 km on a side were constructed from this origin. Then a series of nine ANOVA computations were undertaken for the corrected Zn, corrected Ni and U data. The data were logarithmically transformed in order to meet the ANOVA model's requirement for homogeneity of variance (Cochran, 1947; Bartlett, 1947). The use of a logarithmic transform also implies that the strata grid cell means are geometric rather than arithmetic. Procedures outlined by Garrett and Goss (1979) were employed to compute the variance components of the post-hoc unbalanced ANOVA designs. The ANOVA procedure permits the total variability, s_t^2, to be partitioned into between- and within-strata grid cell components, s_b^2 and s_w^2, so that:

$$s_t^2 = s_b^2 + s_w^2$$

If the number of strata grid cells is k and the number of individuals in the i-th of the k cells in n_i, then the harmonic mean number of individuals per cell, $\tilde{n}$, is:

$$\tilde{n} = k / \Sigma_{i=1}^{k} (1/n_i)$$

Then the unbalanced map stability estimator, $V_{\tilde{m}}$, is:

$$V_{\tilde{m}} = s_b^2 / (s_w^2/\tilde{n})^{0.5}$$

The results of the ANOVAs for the nine strata grid cell sizes are presented in Table 1. To aid discussion, $V_{\tilde{m}}$ and the harmonic mean number of individuals per cell, $\tilde{n}$, have been plotted against strata size (Figs. 8 and 9, respectively). Three features are immediately apparent on the plot of $V_{\tilde{m}}$ vs. grid cell size (Fig. 8). Firstly, the similar behaviour of the Ni and U data in contrast to Zn; secondly, the rise of $V_{\tilde{m}}$ for Ni and U to a "sill" at about 25 km; and lastly, the irregular nature of the Ni and U plots for grid cell sizes greater than 35 km. The probable reason for this last phenomenon is the erratic behaviour of the harmonic mean number of individuals per grid cell with increasing cell size after 35 km (Fig. 9). In turn, this is due to edge effects, i.e., a large proportion of the cells with data falling around the margins of the surveyed area and therefore only being partially covered by the original sampling programme. With the Labrador data this feature is accentuated because

TABLE 1

Total degrees of freedom and $\log_{10}$ variance, number of strata, harmonic mean number of individuals per strata, proportions of variability between and within strata and $V_{\tilde{m}}$ statistics for the post-hoc unbalanced Analyses of Variance by strata-grid-cell size (km)

| Grid (km)	No. of strata	Harm. mean	Zn 19929 0.07178			Ni 19929 0.1293			U 19982 0.2038		
	Total D.F.	$\text{Log}_{10}\,s_t^2$	s_b^2 (%)	s_w^2 (%)	$V_{\tilde{m}}$	s_b^2 (%)	s_w^2 (%)	$V_{\tilde{m}}$	s_b^2 (%)	s_w^2 (%)	$V_{\tilde{m}}$
10	3052	4.7	43	57	0.33	75	25	1.24	64	36	1.05
15	1445	8.5	40	60	0.40	74	26	1.59	61	39	1.27
20	846	12.9	37	63	0.45	72	28	1.84	57	43	1.41
25	561	16.0	35	65	0.47	71	29	1.96	55	45	1.45
30	408	16.8	34	36	0.46	69	31	1.94	53	47	1.43
35	303	26.0	32	68	0.54	68	32	2.30	51	49	1.69
40	238	25.3	31	69	0.50	67	33	2.21	47	53	1.47
45	192	22.4	31	69	0.47	66	34	2.04	45	55	1.34
50	157	32.3	31	69	0.56	66	34	2.44	44	56	1.51
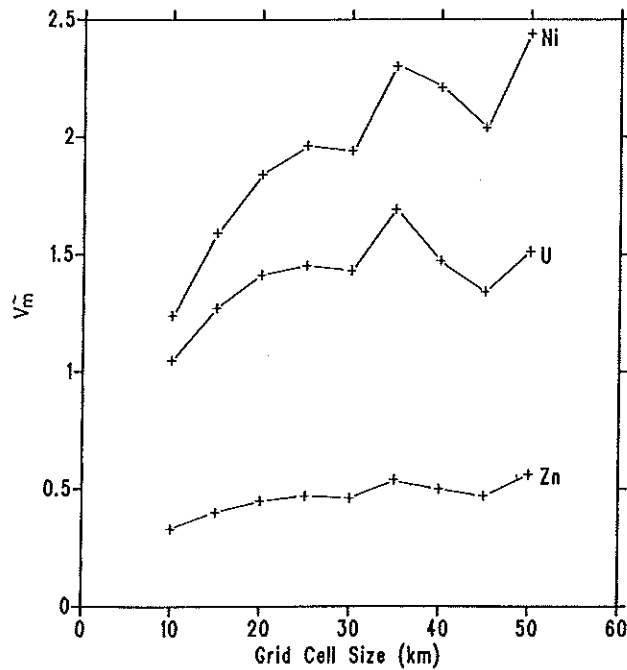
Fig. 8. Plot of the unbalanced map stability estimator, $V_{\tilde{m}}$, vs. the side length (km) of the strata grid cells.
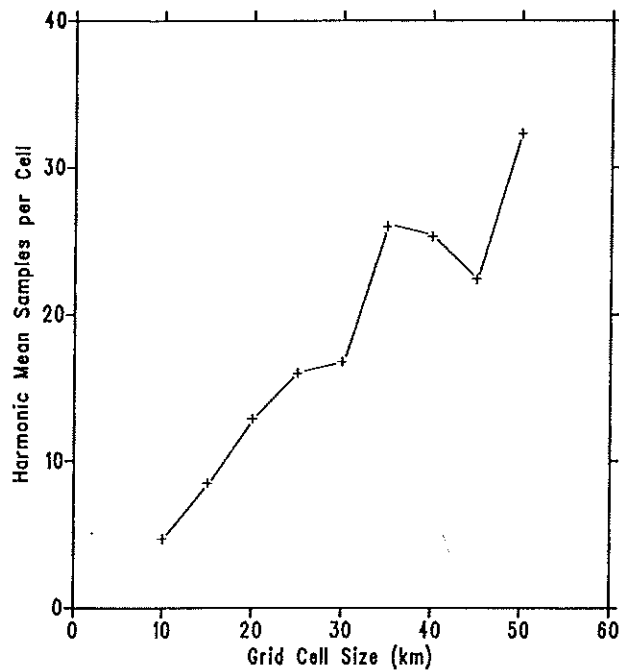

Fig. 9. Plot of the harmonic mean number of individuals per grid cell vs. the side length (km) of the strata grid cells.

of the long relatively narrow region in the north that lies between the Labrador Sea to the east and the Province of Quebec to the west.

On the basis of the post-hoc ANOVA results it was decided to employ a 25×25

km grid cell size, as $V_{\tilde{m}}$ for both Ni and U attains a local maximum with approximately 70 and 55% of the total variability of the data being contained in the 561 strata geometric means. The data for Zn are characterized by a large proportion of the variability being at the local level within the strata grid cells, and only some 35% is contained in the strata geometric means. However, for consistency the Zn data were also treated on a 25×25 km basis, as was LOI. It is useful to note that $V_{\tilde{m}}$ is reduced relative to Miesch's V_m by a factor equal to the square root of the ratio of the harmonic mean to the arithmetic mean of the average number of individuals per strata cell. With the Labrador data this ranges from 0.84 for 10×10 km cells to 0.48 for 45×45 km cells, thus $V_{\tilde{m}}$ can be reduced relative to V_m by a factor of up to two. For 25×25 km cells, values of $V_{\tilde{m}}$ would be 0.66 of V_m, and the corresponding Tidball guideline values would be 0.7 and 2.0. These values indicate the acceptability of the Ni and U maps as depictions of regional-scale patterns, but the Zn map should be interpreted with more caution.

In preference to strata geometric means, the grid cell medians have been used to create a subfile of 561 corrected Zn and Ni, and U values. The medians are resistant estimators, i.e., they do not change in the presence of a significant proportion of abnormally high or low values, and if a single individual had been collected or selected to represent the grid cell its most likely value would be the median. Additionally, for the positively skewed distributions usually observed in large regional geochemical data sets the median and geometric mean are more similar to each other than they are to the arithmetic mean. For these reasons we believe the medians are particularly appropriate for preparing maps of regional geochemical background levels. Medians have also been used by Björklund and Gustavsson (1987) to depict regional geochemical patterns on a national scale in Finland. However, their procedure is a little different from that presented in this paper.

The subfile ($N = 561$) of geochemical data, consisting of Lambert Conformal metre coordinates for the centre of each 25×25 km grid cell, the number of individuals in that cell, the LOI-corrected Zn, LOI-corrected Ni, and U medians was further processed using the APPMAP geochemical mapping software of the Geological Survey of Canada. APPMAP makes use of the UNIRAS (1986) device independent raster graphics software. Details of the gridding procedure are provided in the Appendix. After addition of cartographic and other information the resulting graphic is output to a Versatec 400 dot per inch colour electrostatic plotter.

For colour use the data are divided into 12 contour groups for plotting, i.e., min–5th percentile, 5th–10th, 10th–20th, ..., 90th–95th and 95th–maximum. However, the smaller monochrome displays at larger scales required for publication necessitate using only 8 contour groups, i.e., minimum–5th percentile, 5th–10th, 10th–25th, 25th–50th, ..., 90th–95th and 95th–maximum. These symmetric percentile based plotting schemes yield appropriate dis-

plays for regional geochemical studies where areas of low elemental content may be just as interesting as those characterized by high levels. The regional geochemical maps so produced are presented in Figures 10–15 and are discussed in more detail below. For geological reference the reader is referred to figure 1 of Kerr and Davenport (1990, this issue).

The distribution of the original 20,000 sample points may be seen in Figure 10. The contour intervals have been selected to be approximately linear in their square roots at lower levels on the basis of the estimation procedure for standard errors. As would be expected 25×25 km cells with fewer numbers of individual samples fall around the margin of the survey area and in the
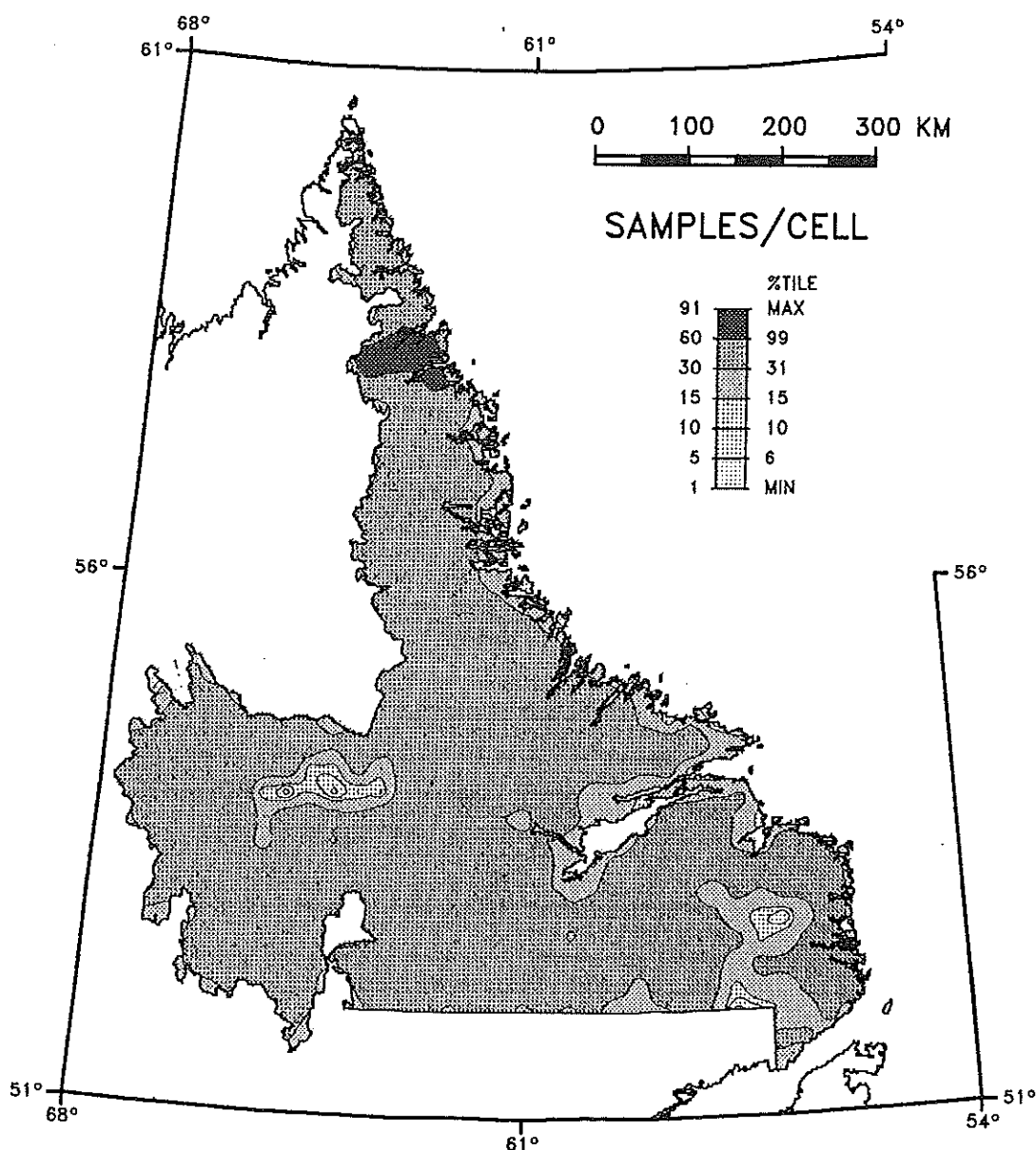

Fig. 10. The spatial distribution of the number of individuals occurring in each strata grid cell.

region of the Smallwood Reservoir in west-central Labrador. The lower-density area in the southeast correlates with an area of lower lake density compared with the rest of southern Labrador. In contrast, the narrow east-west strip of high-density cells in northern Labrador coincides with the southern half of NTS areas 14L and 24I where higher-density stream sediment sampling was undertaken to support sample-media comparative studies.

The regional distribution of loss-on-ignition (LOI) is presented in Figure. 11. The contour intervals are based on the percentiles of the 25×25 km cell median LOI values. However, the 10th percentile conveniently coincides with
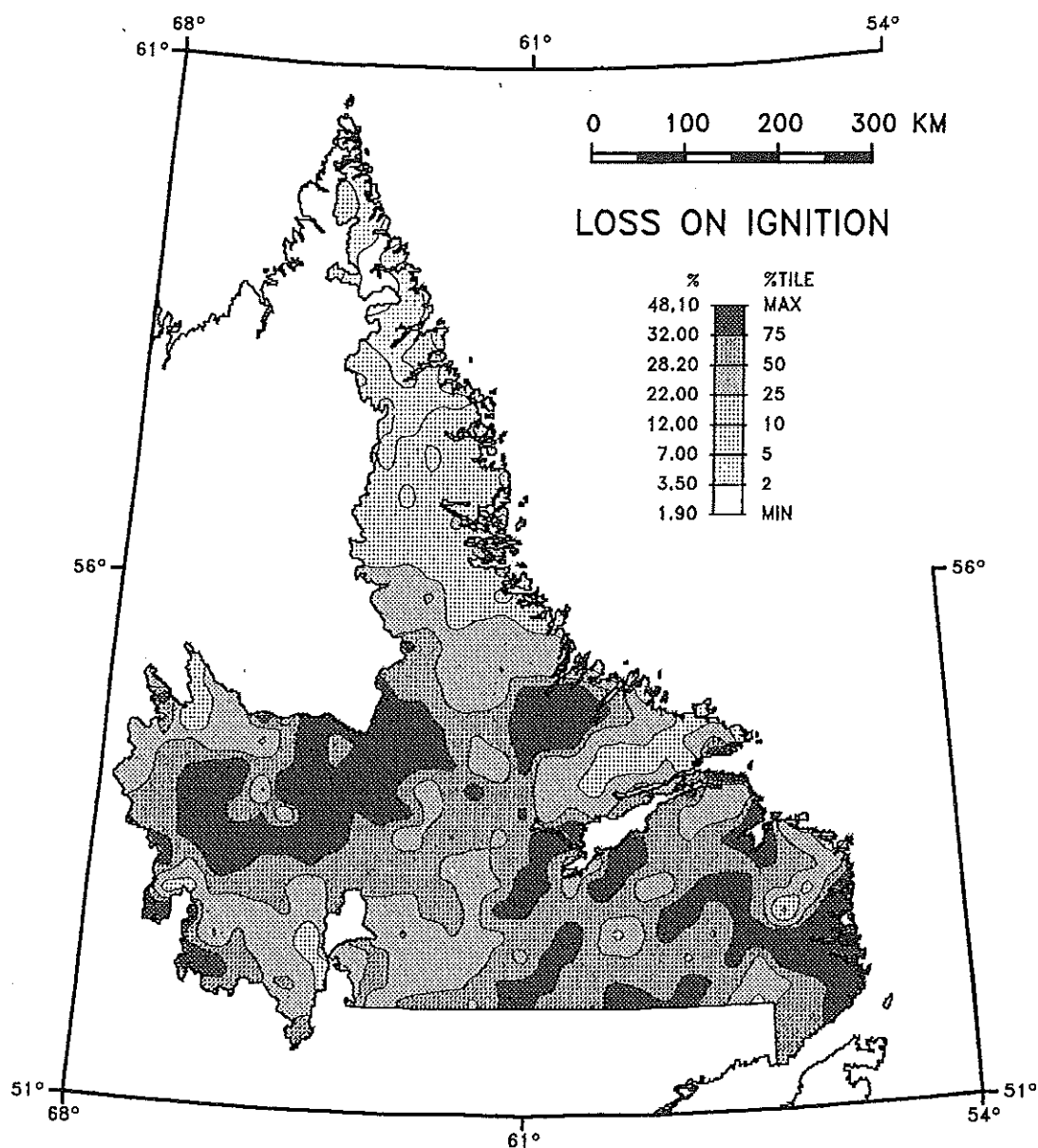

Fig. 11. Median ($N=561$) smoothed regional geochemistry for LOI (%) in lake and stream sediments, Labrador.

the 12% LOI level, below which significant corrections were made to the Zn and Ni data. The most notable feature is the decrease in LOI northwards as the terrain becomes treeless and barren. Also of note is that the northernmost lake sediment sampled areas exhibit LOI levels as low as some encountered in the areas which were sampled using stream sediments further to the north.

The LOI-corrected Zn distribution based on the 25×25 km cell medians is presented in Figure 12 using the standard symmetrical percentile display for regional geochemical mapping. A number of features of geological interest are apparent. Firstly, the eastern part of the Grenville province is characterized
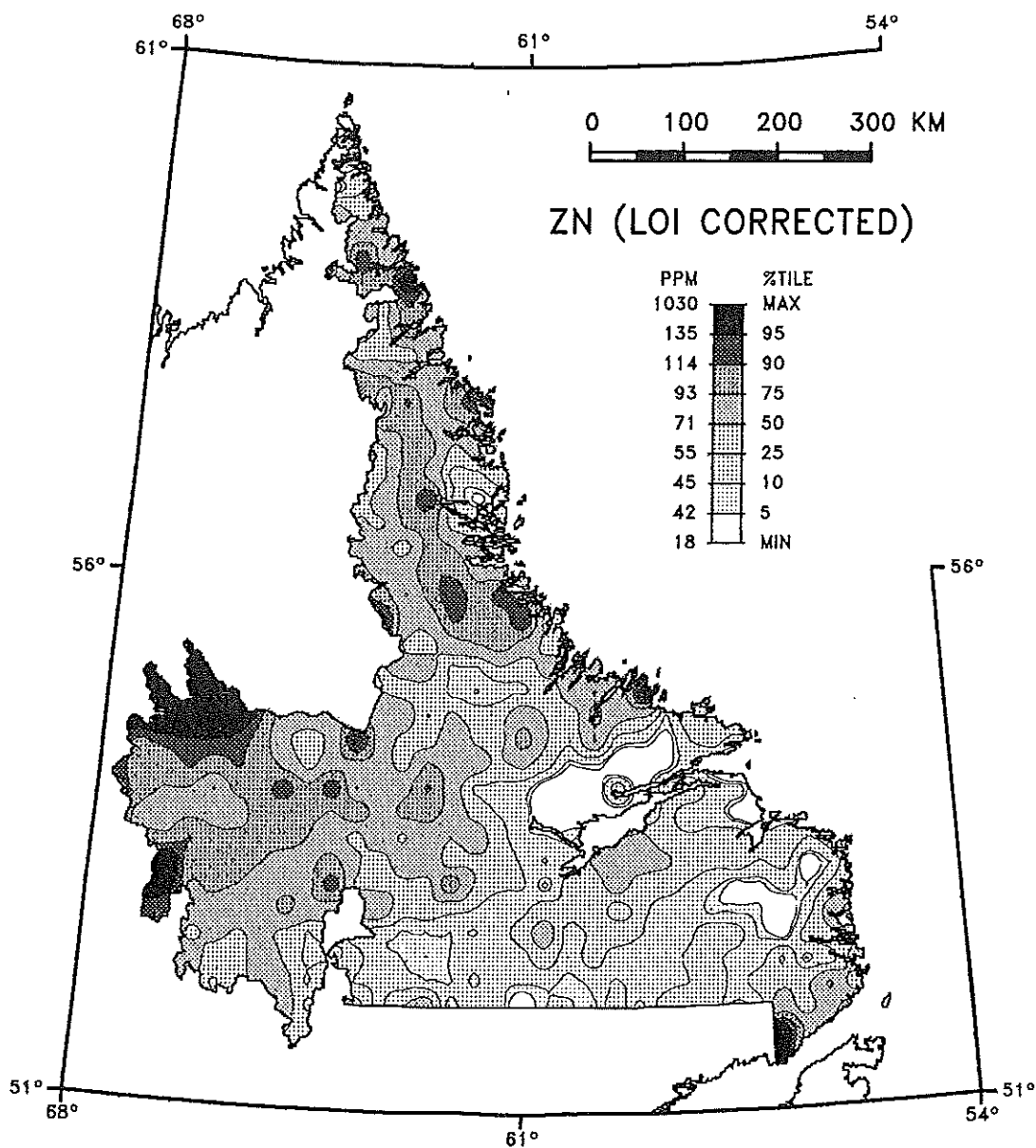

Fig. 12. Median (N=561) smoothed regional geochemistry for LOI-corrected Zn (ppm) in lake and stream sediments, Labrador.

by low Zn levels, as are several of the areas underlain by Paleohelikian anorthosites intruding Churchill Province rocks to the north. The northern part of the Aphebian volcano-sedimentary Labrador Trough of the Churchill Province, which is known to contain sulphide mineral occurrences, is, in contrast, characterized by high Zn levels.

The distribution of the LOI-corrected Ni 25×25 km cell medians is presented in Figure 13 using the symmetrical percentile display. The dominant features are, like Zn, low Ni levels in the eastern Grenville province, and low levels in areas of Paleohelikian syenites intruding Churchill Province rocks to
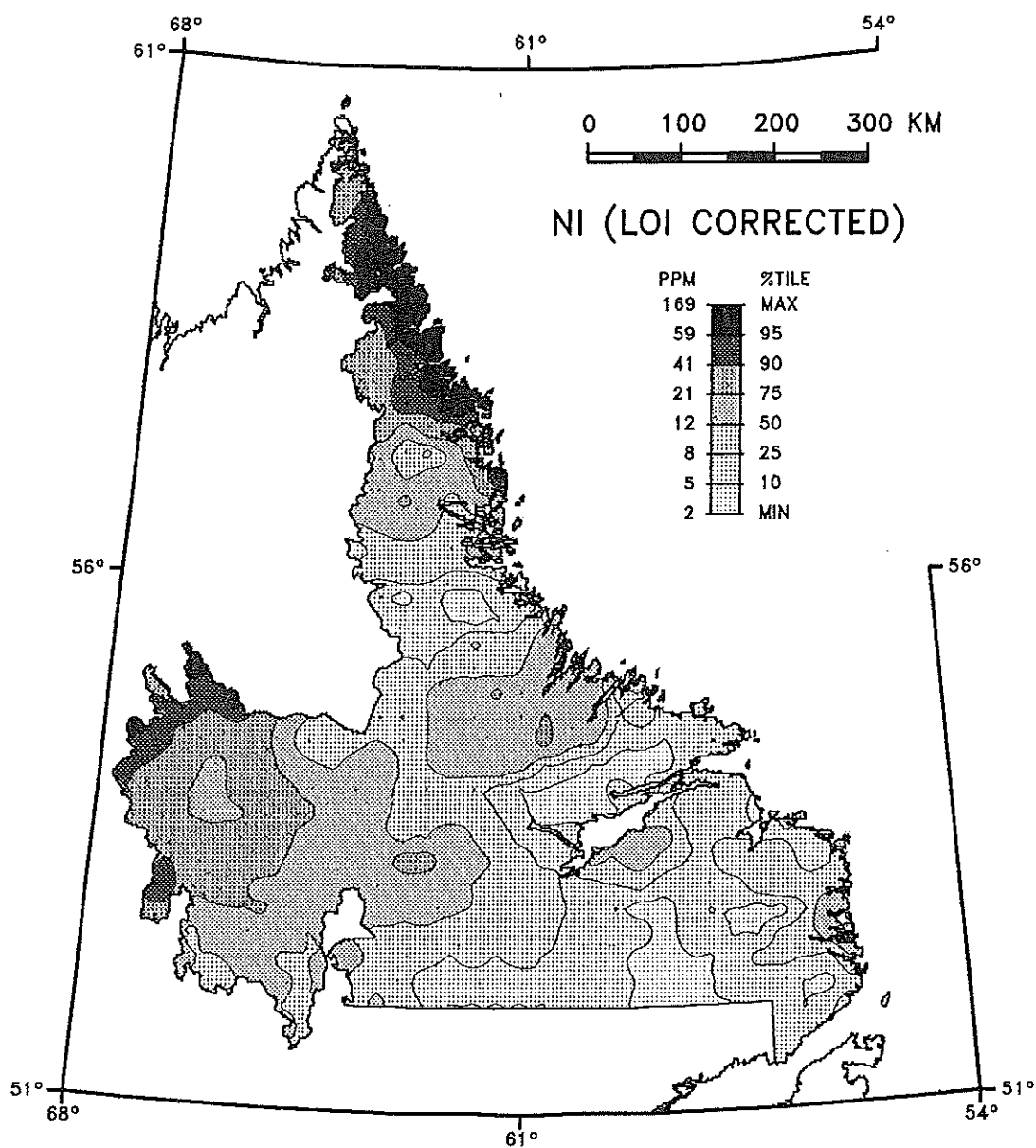

Fig. 13. Median ($N=561$) smoothed regional geochemistry for LOI-corrected Ni (ppm) in lake and stream sediments, Labrador.

the north. Higher Ni levels are found in the area of the Labrador Trough, to
the southwest in the Superior Province, and in the Nain Province of Superior
age in the east. Most notable are the high Ni levels in the north of the Nain
Province which appear to correlate with extensive small ultramafic intru-
sions. In terms of the tectonic history of Labrador these results are interesting.
The older Superior age rocks that have been depleted in LIL (large ionic-
radius lithophile) elements are relatively enriched in Ni, as are the younger
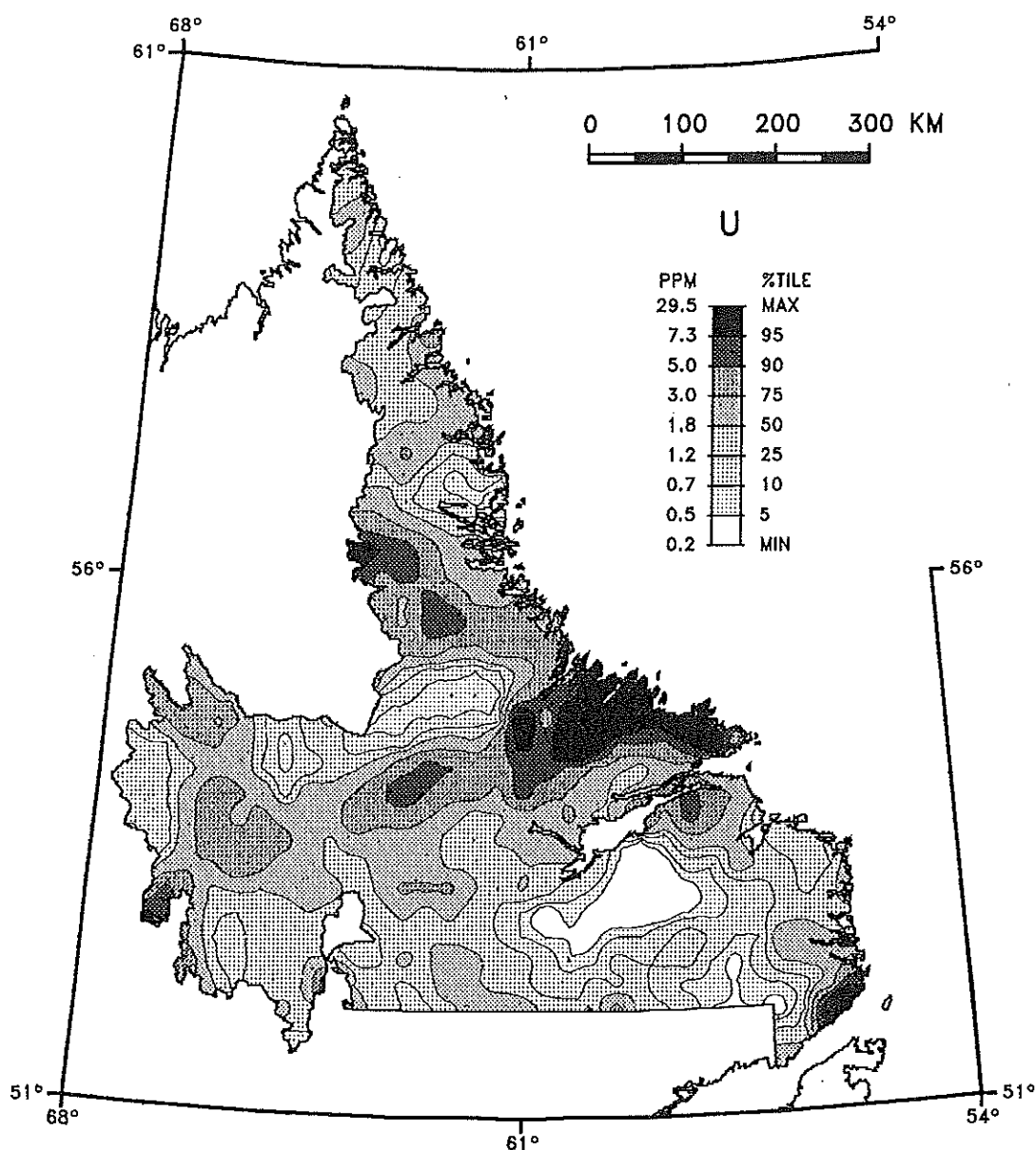volcano-sedimentary sequences of the Labrador Trough. In contrast the

Fig. 14. Median ($N=561$) smoothed regional geochemistry for U (ppm) in lake and stream
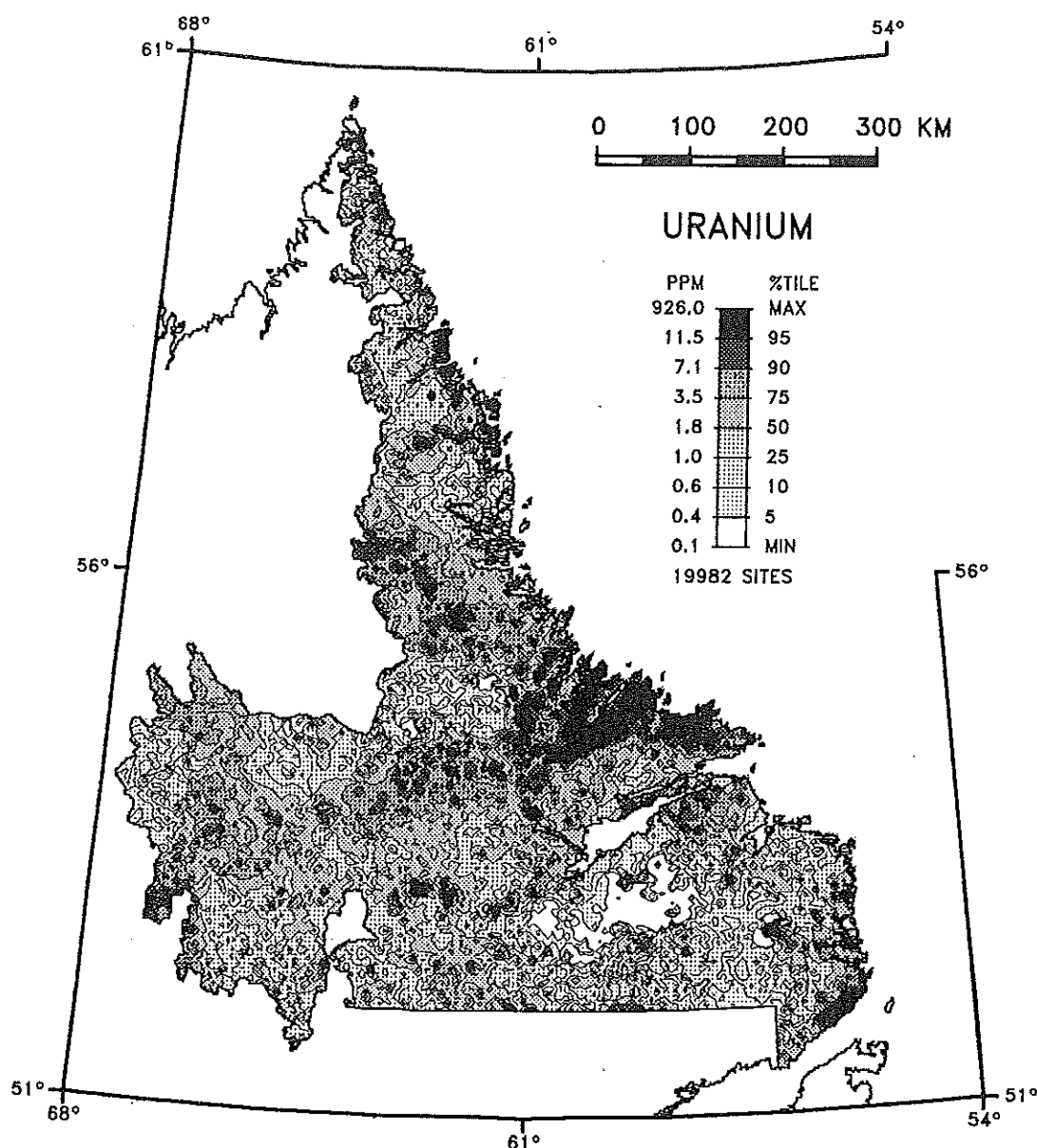sediments, Labrador.

Fig. 15. Regional geochemistry for U (ppm) in lake and stream sediments (N=19982), Labrador.

Grenville Province rocks and Paleohelikian units are not LIL depleted and Ni levels show as relative lows.

The regional distribution of U as 25×25 km cell medians is presented in Figure 14, again using the symmetrical percentile contour display. This map contains approximately 55% of the total variability of the U data, the approximation being due to plotting cell medians rather than geometric means. A number of important features relating to both fundamental geology and metallogeny are apparent. Again the Grenville Province is revealed as a region dominantly characterized by low U levels. Similarly, the small section of the

Superior Province in the westernmost part of Labrador, and parts of the Nain Province, appear regionally low in U due to LIL depletion. The Aphebian Labrador Trough rocks, in the west, are reflected as an area of elevated background striking down from the north-northwest. In central coastal Labrador the Makkovik Province, known to contain U mineral occurrences, is characterized by regionally very high background levels. Extending from this area southwestward, the Trans-Labrador Granitoid Batholith is also characterized by a region of high background, which is locally higher in the Letitia Lakes area to the west where there are known U mineral occurrences. Lastly, the Strange Lake alkaline intrusive suite on the Labrador–Quebec border at approximately 56°N, which is a known U–rare-earth-element resource, is reflected by high U levels. These levels are as high as those in the Makkovik Province, and a southeasterly trending belt of elevated U background levels connects these two areas.

In order to visually compare the effects of the loss of approximately 45% of the U information, a map (Fig. 15) was prepared from the U data subset ($N = 19982$). A comparison of the two maps (Figs. 14 and 15) show that apart from small isolated high and low "anomalies" the map based on 561 cell medians contains all the information relevant to broad crustal-scale regional geochemical studies. Thus the median-based map makes it easier to observe those large-scale features of litho-tectonic and metallogenic interest that are the focus of IGCP Project 259.

DISCUSSION

The simple correction procedure based on the loss-on-ignition content of the lake and stream sediment samples significantly reduces the organic matrix effect in the Labrador data. The correction procedure is data-based to the extent that it was derived from a detailed study of catchment basin geochemistry in the northern Labrador lake and stream sediment survey overlap zone. The correction function sets out to compensate for a matrix effect phenomena that has been known for a decade. However, the actual correction function used is empirical and therefore, hopefully, more generally applicable. The procedure needs to be evaluated in other areas of northern shield terrain where both lake and stream sediments have been collected. The effect of decreasing organic content as estimated by LOI requires correction to a constant 12–48% LOI matrix level.

The Analysis of Variance (ANOVA) approach to the post-hoc selection of a data density, i.e., "sample density", has proven effective. The grid cell size selected on the basis of the unbalanced map stability index, $V_{\tilde{m}}$, has led to maps that appear to meet the objectives of the current study. It could be argued that a geostatistical approach might have been appropriate. However, an inspection of the original 1:250,000 scale maps and earlier compilations

indicated that the spatial structure of the data varied across Labrador. To fully justify a geostatistical approach the data should be divided into different tectonic domains and the spatial structure determined for each mapping undertaken, and the final maps constructed from those of the different domains. Inasmuch as the maps presented in this paper are only those of underlying trends, and estimation variance was not considered to be of major interest as no additional sampling would be undertaken as a result of the mapping, the cost of a geostatistical approach was not considered justifiable. It is of note that Miesch (1975) has demonstrated the essential equivalence of some AN-OVA studies to variogram analysis in geostatistics. The procedure undertaken in this paper with spatial strata of varying size is just such a case, and the plots of $V_{\tilde{m}}$ vs. cell size are analogous to plots of "within cell variance", $\bar{\gamma}(v,v)$, vs. cell size, v (Journel and Huijbregts, 1978).

The 25×25 km cell median-based maps reflect the major features of the regional geochemistry of Labrador. The reduction in data volume is significant, from approximately 20000 to 560 values, i.e., a 97% reduction. Yet for elements that show high regional contrasts such as Ni and U, this drastic reduction in data volume only results in approximately 30% and 45% reductions of information, respectively. When compiling data on a continental scale such data volume reduction considerations become important at the practical level of data management and processing. We note that Labrador is only 3% of Canada's total land surface. Additionally, the cell median approach will meet many proprietary or national security concerns for regional geochemical data. The cell median is an estimate of the most likely value for an area under consideration. The median can withstand as much as 50% "anomalous" data, be they low or high values, and not change. It is therefore a most appropriate estimator for studies of broad-scale regional variations of geochemical background levels.

The fact that the optimum grid cell size is 25×25 km and that the cells contain an arithmetic mean of 36 individuals is of interest. Firstly, the 625-km²-area cells fall between the 50-km-radius circular cells using by Björklund and Gustavsson (1987) for their moving median maps, being smaller by a factor of about 12, and traditional very low density direct surveys at 1 site per 20–30 km², e.g., Steenfelt (1987). The 625-km²-area cells selected in this study are quite similar to the densities of 1 site per 300 to 500 km² proposed by Bölviken (1988) for the geochemical mapping of Western Europe.

Secondly, the fact that the 25×25 km cells contain on average 36 individuals is a curious coincidence. The concept of standard error is a primary element of classical statistics, and the inverse square root of the sample size is an essential part of its computation. If the inverse square root is plotted against sample size (not shown) it can be seen that the function begins to flatten out at about 35. This raises the question, if the original survey sample density had not been 1 site per 13 km² would the optimum grid cell size still have been

25×25 km, or would it have been that cell size that contained about 35 individuals on average? This whole question is related to the "fractalness" and scale independence of nature. It seems that no matter what the scale of the study, be it the cross-sectional chemistry of a mineral grain, a soil survey of a mineral prospect, or the regional geochemistry of a province, we find patterns of interest. This paper is not the place to discuss such fundamental aspects of our science; however, the observation does point to an intriguing area for future research.

APPENDIX

Interpolation and gridding procedures

Since the mid 1970s the Geological Survey of Canada has been preparing coloured regional geochemical maps employing an Applicon ink-jet colour plotter and software provided by the company. In 1988 a Versatec electrostatic colour plotter was acquired by the Survey and the contouring program was rewritten to use the UNIRAS (1986) GEOINT software. In order to achieve backwards compatibility of the new colour-contoured maps with those prepared previously with the Applicon software a series of experiments were undertaken to determine the UNIRAS parameters that would lead to the preparation of maps visually similar to the earlier Applicon maps. The present study offered an excellent opportunity to carry out this task with a regularly spaced data set that had been originally contoured using the Applicon software. The purpose of the following paragraphs is to describe the selected UNIRAS parameters that achieved the objective of visual compatibility and to permit other users with access to the UNIRAS software to reproduce the procedure we have followed.

Interpolation from the median data on 25-km centres was undertaken using the GINTP1 (UNIRAS, 1986) procedure to generate a grid of values on 5-km centres. The origin of the new grid was selected to be the same as that used for generating the median data. Therefore each median value fell in the centre of a 5×5 set of new 5×5 km cells. To interpolate values for the remaining 24 cells, GINTP1 first carries out two steps of linear interpolation. The radius of influence for this procedure was set to 36 km, i.e., the hypotenuse of a 25-km right angle triangle. From the median values within this area of influence values are interpolated linearly for points on the vertical and horizontal axes running through the node to be evaluated. Then by averaging the interpolations for the actual node position which are derived from the intermediate axis interpolations a value is finally estimated. These grid node values are then further smoothed by the GINTP1 default local quadratic interpolator. The effect of this latter procedure is to take "trends" in the data into account, and as a result values higher or lower than the limits observed in the input data

may be generated. Although this effect is not considered desirable by many geochemists contouring raw data, we feel that as we are working with cell medians this procedure is valid.

At the contour generation stage of UNIRAS the new 5-km values are further interpolated to the generic UNIRAS picture file. At this stage a hyperbolic smooth is used to remove angular discontinuities along the contour lines (UNIRAS, 1985). This is carried out at the maximum resolution of the dummy driver for the generic picture file.

In the instance of the irregularly spaced complete U data set ($N=19982$) the same 5-km grid size and grid origin was used as for the median compilation maps. In contrast to the median mapping procedure, data falling inside each 5×5 km cell were substituted by their mean placed at the nodes of a 5-km grid running through the cell centres. If the cell contained no data a value was interpolated exactly as described previously using the same 36-km radius of influence. Subsequent to this the same procedures of local quadratic smoothing and final hyperbolic contour smoothing were used as for the median compilation maps.

The grey-scale map displays consist of six dither patterns, together with solid black and white. The white is usable as the contours are explicitly drawn as a fine black line and the change of level boundaries are not just implied by a pattern change. The six patterns decrease in blackness geometrically by a factor of two, except for one jump of 2.5. The steps are 62.5, 31.25, 12.5, 6.25, 3.13 and 1.56%, each dither pattern being designed in a 32×32 matrix.

REFERENCES

Bartlett, M.S., 1947. The use of transformations. Biometrics, 3(1): 39–52.

Baumier, M., 1989. Multi-element geochemical domains – an aid to exploration. In: G. Garland (Editor), Proceedings of Exploration 87, The Third Decennial Conference on Geophysical and Geochemical Exploration for Minerals and Groundwater. Ont. Geol. Surv., Spec. Vol., 4: 439–447.

Björklund, A. and Gustavsson, N., 1987. Visualization of geochemical data on maps: New options. J. Geochem. Explor., 29(1/3): 89–103.

Bölviken, B., 1988. Plans for geochemical mapping of Western Europe. V.M. Goldschmidt Conference, Baltimore, Maryland, Abstr. Vol. 31.

Bölviken, B., Bergström, J., Björklund, A., Kontio, M., Lehmuspelto, P., Lindholm, T., Magnusson, J., Ottesen, R.T., Steenfelt, A. and Volden, T., 1986. Geochemical Atlas of Northern Fennoscandia. Geol. Survs. Finland, Norway and Sweden, 19 pp and 154 maps.

Cochran, W.G., 1947. The consequences when the assumptions of analysis of variance are not satisfied. Biometrics, 3(1): 22–38.

Fauth, H., Hindel, R., Siewers, U. and Zinner, J., 1985. Geochemischer atlas Bundesrepublik Deutschland. Bundesanst. Geowiss. Rohstoffe, Hannover, 79 pp.

Garrett, R.G., 1977. Sample density investigations in lake-sediment surveys for Canada's Uranium Reconnaissance Programme. In: Symp. on Hydrogeochemical and Stream Sediment

Reconnaissance in the United States. U.S. Dep. Energ., Grand Junction Office, Open-File Rep., GJBX-12(78): 173–185.

Garrett, R.G., 1988. IDEAS: An interactive computer graphics tool to assist exploration geochemists. Geol. Surv. Can., Pap., 88-1F: 1–13.

Garrett, R.G., 1989. The Chi-square plot – A tool for multivariate outlier recognition. In: S. Jenness (Editor), Geochemical Exploration 1987. J. Geochem. Explor., 32(1/3): 319–341.

Garrett, R.G. and Goss, T.I., 1979. The evaluation of sampling and analytical variation in regional geochemical surveys. In: J.R. Watterson and P.K. Theobald (Editors), Geochemical Exploration 1978. Assoc. Explor. Geochem. Rexdale, Ont., Spec. Publ., 7: 371–384.

Garrett, R.G. and Hornbrook, E.H.W., 1976. The relationship between zinc and organic content in centre-lake bottom sediments. J. Geochem. Explor., 5(1): 31–38.

Garrett, R.G., Kane, V.E. and Zeigler, R.K., 1980. The management and analysis of regional geochemical data. J. Geochem. Explor., 13(1/2): 115–152.

Journel, A.G. and Huijbregts, G.T., 1978: Mining Geostatistics. Academic Press, London, 600 pp.

Kerr, A. and Davenport, P.H., 1990. Application of geochemical mapping techniques in regional geology: An example from a polyorogenic Precambrian Shield area in Labrador, Canada. In: A.G. Darnley and R.G. Garrett (Editors), International Geochemical Mapping. J. Geochem. Explor., 39: 225–247.

Lund, N.G. (comp.), 1987. Index to National Geochemical Reconnaissance surveys, 1973–1986. Geol. Surv. Can., Map 1661A.

Miesch, A.T., 1975. Variagrams and variance components in geochemistry and ore evaluation. In: E.H.T. Whitten (Editor), Quantitative Studies in the Geological Sciences. Geol. Soc. Am., Mem., 142: 333–340.

Miesch, A.T., 1976. Geochemical survey of Missouri – methods of sampling, laboratory analysis and statistical reduction of data. U.S. Geol. Surv., Prof. Pap. 574-G, 47 pp.

National Atlas of Canada, 1973. Vegetation regions, map 45-46. Dep. Energ., Mines Resourc., Ottawa.

Rankin, N.O., 1974. The harmonic mean method for one-way to two-way analysis of variance. Biometrika, 61(1): 117–122.

Rose, A.W., Hawkes, H.E. and Webb, J.S., 1979. Geochemistry in mineral exploration, 2nd Ed. Academic Press, London, 657 pp.

Steenfelt, A., 1987. Geochemical mapping and prospecting in Greenland – A review of results and experience. J. Geochem. Explor., 29(1/3): 183–205.

Thomas, J.D. and Hultquist, R.A., 1978. Interval estimation for the unbalanced case of the one-way random effects model. Ann. Stats., 6(3): 582–587.

UNIRAS, 1985. GEOPAK Reference Manual, 1st Edition – version 5. European Software Contractors A/S, Lyngby, Denmark, 210 pp.

UNIRAS, 1986. GEOINT User's Manual: GEOPAK interpolation – version 5. European Software Contractors A/S, Lyngby, Denmark, 122 pp.

Weaver, T.A., Freeman, S.H., Broxton, D.E. and Bolivar, S.L., 1983. The geochemical atlas of Alaska. U.S. Dep. Energ., Grand Junction Office, Open-File Rep. GJBX-32(83), 57 pp.

Webb, J.S., Thornton, I., Thompson, M., Howarth, R.J. and Lowenstein, P.L., 1978. The Wolfson geochemical atlas of England and Wales. Oxford Univ. Press, Oxford, 74 pp.