



Natural Resources
Canada

Ressources naturelles
Canada

**GEOLOGICAL SURVEY OF CANADA
OPEN FILE 8962**

**Regional lake sediment geochemical data from east-central
Labrador (NTS 013-I, 013-J, 013-K, 013-N, and 013-O):
reanalysis data and QA/QC evaluation**

M.W. McCurdy, J.M. Rice, H.E. Campbell, and R.C. Paulen

2023

Canada

**GEOLOGICAL SURVEY OF CANADA
OPEN FILE 8962**

**Regional lake sediment geochemical data from east-central
Labrador (NTS 013-I, 013-J, 013-K, 013-N, and 013-O):
reanalysis data and QA/QC evaluation**

M.W. McCurdy¹, J.M. Rice¹, H.E. Campbell², and R.C. Paulen¹

¹Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario

²Geological Survey of Newfoundland and Labrador, 50 Elizabeth Avenue, St. John's, Newfoundland and Labrador

2023

© His Majesty the King in Right of Canada, as represented by the Minister of Natural Resources, 2023

Information contained in this publication or product may be reproduced, in part or in whole, and by any means, for personal or public non-commercial purposes, without charge or further permission, unless otherwise specified.

You are asked to:

- exercise due diligence in ensuring the accuracy of the materials reproduced;
- indicate the complete title of the materials reproduced, and the name of the author organization; and
- indicate that the reproduction is a copy of an official work that is published by Natural Resources Canada (NRCan) and that the reproduction has not been produced in affiliation with, or with the endorsement of, NRCan.

Commercial reproduction and distribution is prohibited except with written permission from NRCan. For more information, contact NRCan at copyright-droitdauteur@nrcan-rncan.gc.ca.

Permanent link: <https://doi.org/10.4095/331526>

This publication is available for free download through GEOSCAN (<https://geoscan.nrcan.gc.ca/>).

Recommended citation

McCurdy, M.W., Rice, J.M., Campbell, H.E., and Paulen, R.C., 2023. Regional lake sediment geochemical data from east-central Labrador (NTS 013-I, 013-J, 013-K, 013-N, and 013-O): reanalysis data and QA/QC evaluation; Geological Survey of Canada, Open File 8962, 1 .zip file. <https://doi.org/10.4095/331526>

Publications in this series have not been edited; they are released as submitted by the author.

ISSN 2816-7155
ISBN 978-0-660-47851-7
Catalogue No. M183-2/8962E-PDF

Table of Contents

1	Introduction	1
2	Bedrock geology of the Hopedale Block	4
3	Sampling and analytical techniques.....	5
3.1	Description of surveys and sample management.....	5
3.2	Analytical procedures 2022	6
4	QA/QC of geochemical data.....	7
4.1	Accuracy.....	8
4.2	Precision.....	9
4.3	Analysis of Variance (ANOVA).....	10
5	Conclusions	11
6	Acknowledgements.....	11
	References	11
	Appendices.....	15

Table of Figures

Figure 1. Location of the NTS sheets where the lake sediments were originally collected and reanalyzed. Inset shows the lake sediment sites reanalyzed for this report (black) and for a previous study of the Core zone in northern Labrador and northeastern Quebec (red; McCurdy et al., 2018)..... 2

Figure 2. Sample location map showing lake sediment sites in east-central Labrador reanalyzed for this report (red dots) with contiguous lake sediment sites previously reanalyzed using the same method of sample digestion and ICP-MS analysis..... 3

Figure 3. Generalized bedrock geology of eastern Quebec and Labrador. The study area is in east-central Labrador within NTS sheet 13I, 13J, 13K, 13N, and 13O. Modified from Hinchey et al. (2022)..... 5

List of Tables

Table 1. Lower detection limits published by Bureau Veritas for ‘partial’ aqua regia digestion followed by ICP-MS analysis.

Table 2. Appendix C1 workbook. The workbook contains the QA/QC results for this study.

Regional lake sediment geochemical data from east-central Labrador (NTS 013-I, 013-J, 013-K, 013-N, and 013-O): reanalysis data and QA/QC evaluation

Abstract

This report presents the geochemical data, quality assurance and quality control (QA/QC) results of the reanalysis of lake sediment samples collected from east-central Labrador (NTS 013-I, 013-J, 013-K, 013-N, and 013-O). The original lake surveys were conducted in 1977, 1978, 1983, 1987 and 1992, and the reanalysis was initiated in 2022. Original survey results are presented in Geological Survey of Canada open files 513, 558, 997, 1636, 1637, 2645, 2646, 2648, and 2650. Lake sediments from 3 736 archived site samples were re-analyzed, covering an approximate area of 44 000 km², with an average density of 1 sample per 18 km². Samples were measured for 65 elements via modified aqua-regia – ICP-MS. To ensure high quality geochemical data, the data were evaluated for accuracy, precision, and fitness-for-purpose. QA/QC results have identified several elements to be monitored carefully for future analyses.

1 Introduction

Between 1977 and 1992, lake sediment samples were collected in east-central Labrador. The geochemical data were published in Geological Survey of Canada (GSC) Open Files 513 (Hornbrook et al., 1977), 558 (Hornbrook et al., 1979), 997 (Hornbrook et al., 1984), 1636 (Hornbrook and Friske, 1989), 1637 (Hornbrook and Friske, 1988), 2645 (Friske et al., 1993a), 2646 (Friske et al., 1993b), 2648 (Friske et al., 1993c), and 2650 (Friske et al., 1993d). With recent improvements in analytical instrumentation, particularly the availability of lower detection limits, improvements in analytical precision, and the increase in the number of elements available for analysis, reanalysis of these samples was warranted. The original survey samples were collected from east-central Labrador, a region with known resource potential and an area of interest for the Geo-Mapping for Energy and Minerals in Canada's North (GEM-GeoNorth) Program (Geological Survey of Canada, 2018; Lebel, 2020).

Funding for the reanalysis was provided by the GEM-GeoNorth Program. The GEM-GeoNorth Program aims to advance regional geo-mapping of Canada's North to promote sustainable resource exploration and development (Geological Survey of Canada, 2018; Lebel, 2020). Geoscience knowledge produced by the GEM-GeoNorth Program will enable governments and communities to make informed decisions regarding the development of resources (Lebel, 2020). The program (2020-2027) is a continuation of the successful Geo-Mapping for Energy and Minerals (GEM) program (2008-2020). Other partners for this project include the Geological Survey of Newfoundland and Labrador (GSNL).

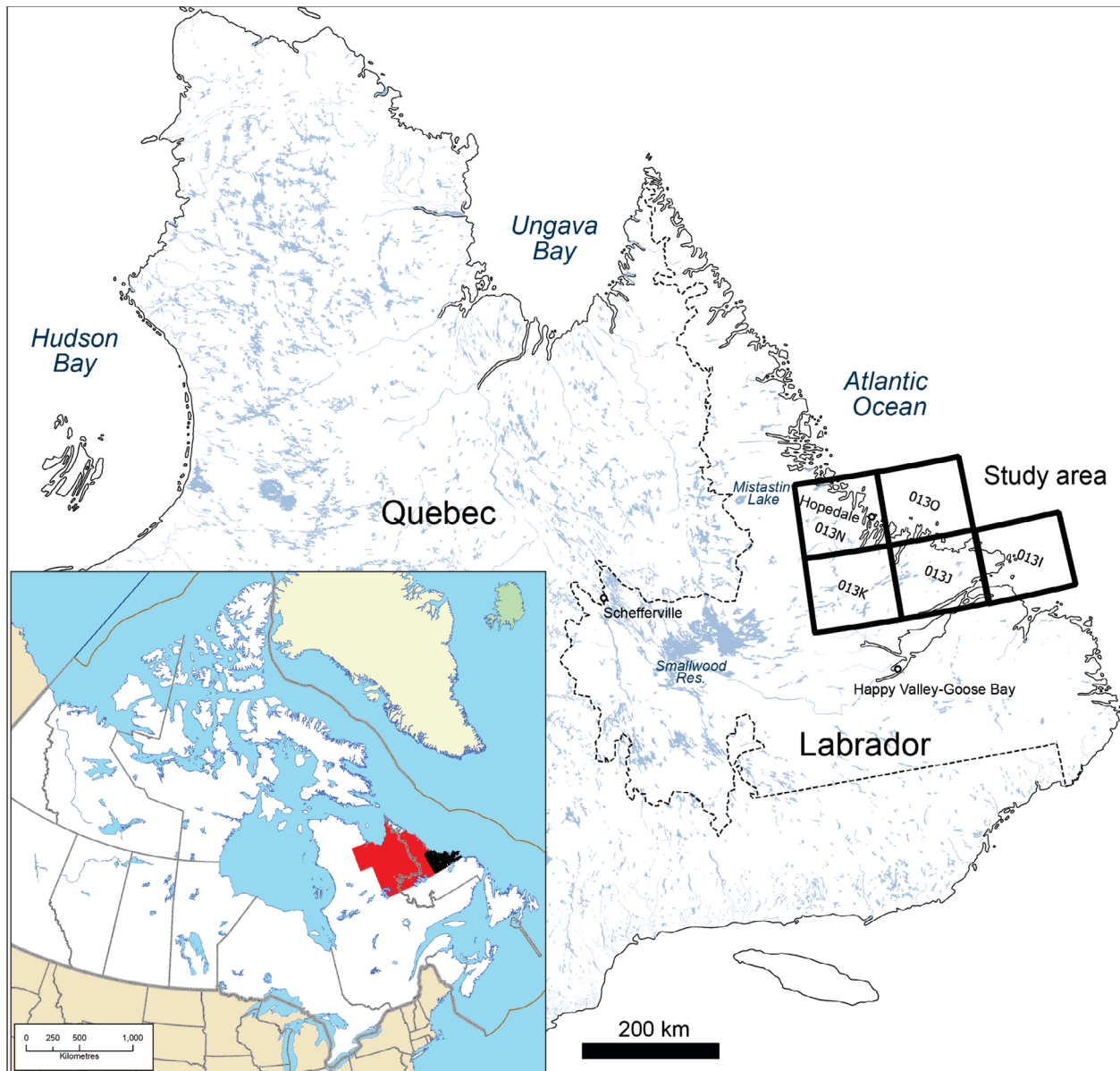


Figure 1. Location of the NTS sheets where the lake sediments were originally collected and reanalyzed. Inset shows the lake sediment sites reanalyzed for this report (black) and for a previous study of the Core zone in northern Labrador and northeastern Quebec (red; McCurdy et al., 2018; McCurdy et al., 2022).

The study area covers over 44 000 km² within the National Topographic System (NTS) map sheets 13-I, 13-J, 13-K, 13-N, and 13-O (Fig. 1). This region is of specific interest due to its bedrock geology and ample archived lake sediment coverage. Reanalysis using modern analytical techniques will provide vital data for critical and other mineral potential and assist bedrock geology research as the region's bedrock is buried beneath extensive glacial cover (e.g., Amor et al., 2019). Once completed, these data will contribute to a broad geochemical understanding of the region, which can be the foundation of future surficial mapping, bedrock mapping, and mineral exploration activities planned for GEM-GeoNorth activities around the Hopedale Region.

This open file report presents reanalysis data and QA/QC results for 65 elements from a total of 2 451 lake sediment sample sites. We quantify the accuracy, precision, fitness-for-purpose for regional mapping of the analytical data using certified reference materials (CRMs), and analytical and field duplicate samples. With the publication of this QA/QC report, we are making available high quality geochemical data to provide information for northern communities shown in Figure 2 to make informed decisions about their land, economy, society, and to highlight areas with potential for critical metals such as copper, nickel, and rare earth elements used for building renewable energy sources. Evaluation of geochemical data using adequate quality assurance and quality control (QA/QC) procedures is essential before interpreting the data (Reimann et al., 2008). The QA/QC process is designed to identify and, where possible, remediate quality issues so that potential users of geochemical data can be fully informed regarding the data quality. This QA/QC report follows the methodology presented in McCurdy and Garrett (2016) to evaluate the accuracy and precision of geochemical data.

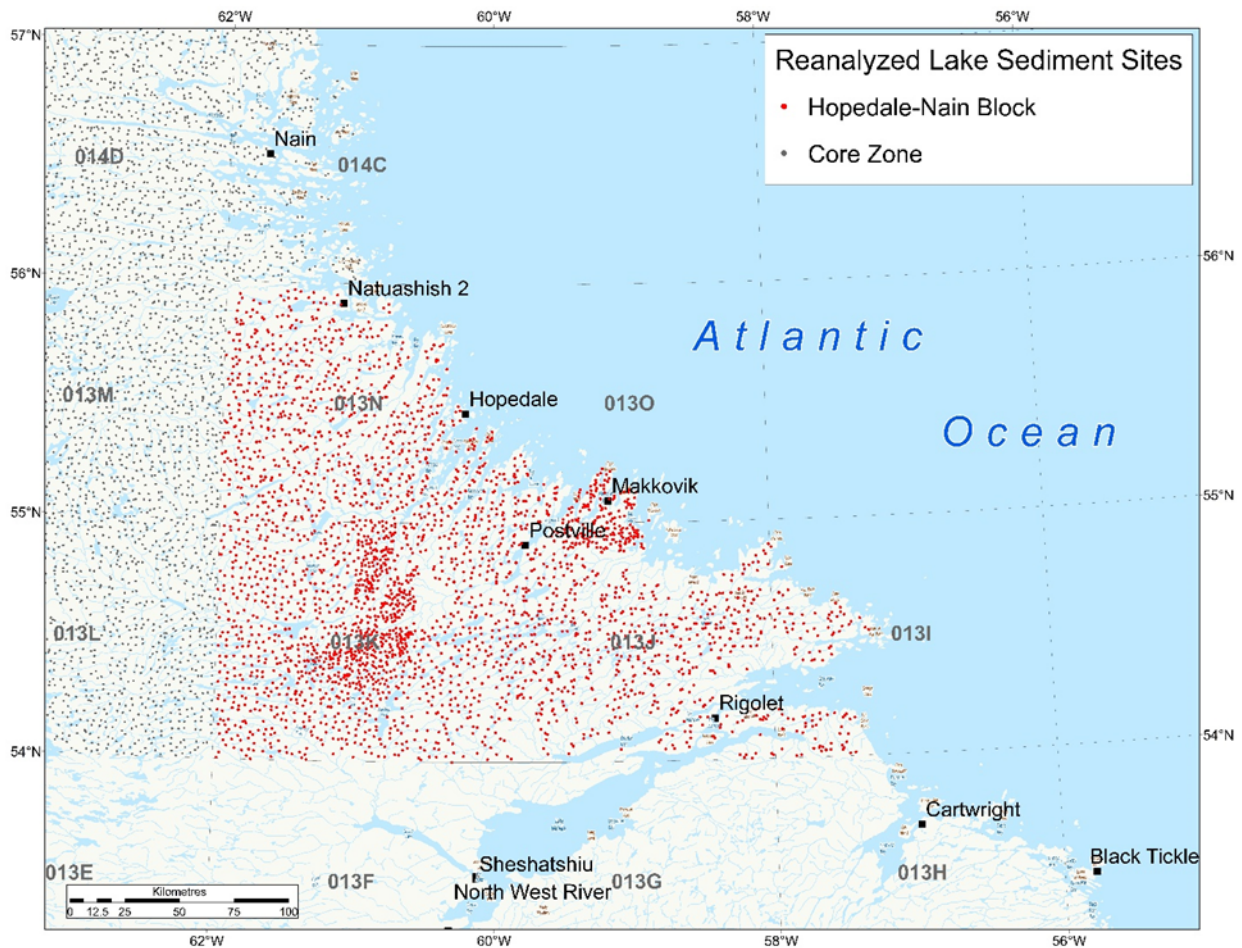


Figure 2. Sample location map showing lake sediment sites in east-central Labrador reanalyzed for this report (red dots) with contiguous lake sediment sites previously reanalyzed using the same method of sample digestion and ICP-MS analysis (black dots).

This work augments the previous reanalysis of lake sediments from the Quebec and Labrador Paleoproterozoic ‘Labrador Trough’, within the region termed the New Quebec Orogen (McCurdy et al., 2018; Amor et al., 2019). Reanalysis of 5 510 lake sediment samples from northern and western

Labrador, by ICP-MS after a modified aqua-regia digestion, permitted their combination with 26 727 samples from adjacent Québec that were digested and analyzed in the same way. The resulting composite database covers an area of almost 300 000 km² in northeastern Canada and created the largest contiguous geochemical map in Canada much of which is of current or historical interest for mineral exploration.

2 Bedrock geology of the Hopedale Block

The Hopedale Block (3.3-2.8 Ga) and Makkovik Province (1.88-1.74 Ga) are two of five regional tectonic domains that define the bedrock geology of the study area (Figure 3). These two bedrock domains, on the eastern coast of Labrador (form the Nain Province and are part of the larger North Atlantic Craton. These two bedrock domains surrounded by the Saglek Block (4.0-3.2 Ga) and Torngat Orogen (1.9-1.8 Ga) to the north, the Core Zone (2.8-2.3 Ga) to the west and is truncated to the south by the Grenville Province (Wardle et al., 2002, James et al., 2002, Ketchum et al., 2002, Corrigan et al., 2018, Hinchey et al., 2020, Godet et al., 2021).

The Hopedale Block contains two greenstone belts at its east/southeast extent that are oriented south-southwest/north-northeast just south of Natuashish: Florence Lake (3.0-2.98 Ga) and Hunt River (3.1 Ga; James et al. 2002). These belts are older than most gold-bearing Archean greenstone belts that can found around the world but are currently under further investigation (Hinchey et al., 2023; Diekrup et al., 2023).

Additionally, the west/northwest extent of the Hopedale Block is intruded by anorthosite-mangerite-charnokite-granite bodies that make up the Nain Plutonic suite, in the same suite of rocks that host the Voisey's Bay Ni-Cu-Co deposit (Ryan, 1997; Ryan and James, 2004). The Nain Plutonic Suite welds the North Atlantic Craton to the Core Zone, New Quebec Orogen, and the Torngat Orogen (collectively referred to as the Southeastern Churchill Province) (Hinchey et al., 2023). Detailed bedrock mapping has been ongoing as part of this GEM-GeoNorth activity; however, the thick cover of glacial sediments and heavily forested regions make investigations difficult. Therefore, the results of this lake sediment reanalysis study will provide important geochemical data for larger bedrock geology investigations.

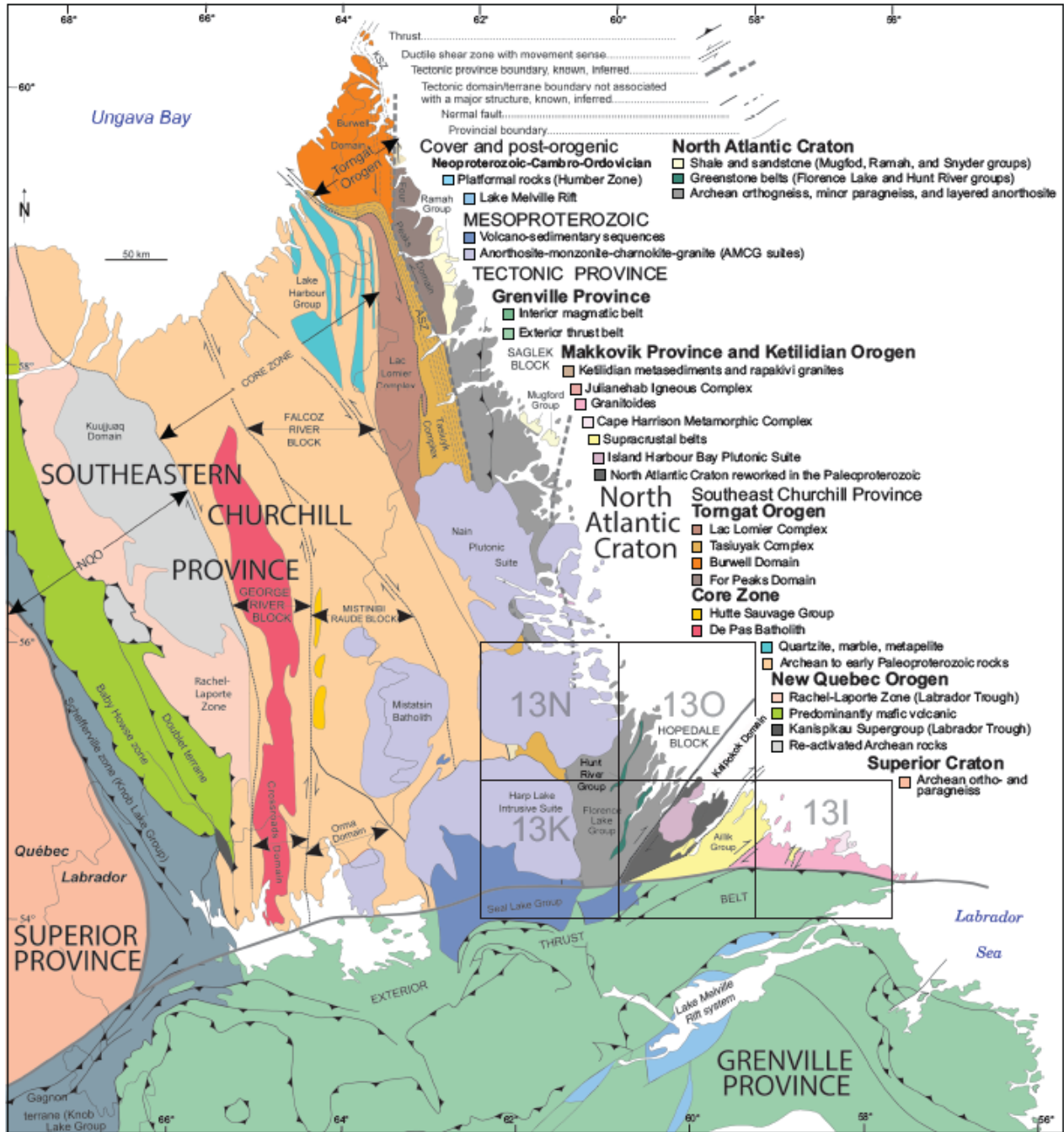


Figure 3. Generalized bedrock geology of eastern Quebec and Labrador. The study area is in east-central Labrador within NTS sheet 13-I, 13-J, 13-K, 13-N, and 13-O. Modified from Hinchey et al. (2022).

3 Sampling and analytical techniques

3.1 Description of surveys and sample management

A total of 3 736 samples, including samples used to evaluate data quality (control reference samples, analytical, field duplicate samples, and one silica blank), were shipped to a commercial laboratory for geochemical analysis. From the submitted samples, there was insufficient material in 786 samples for analysis, so analytical results were returned for 2 451 site samples (Fig. 2) and 499 QA/QC samples.

Survey samples were collected using a hollow-pipe, bottom-valved sampler, a tool developed by the GSC (Friske and Hornbrook, 1991). During retrieval of the sample, the top few centimeters of sediment were washed out while the remainder, the organic-rich gyttja ('mud'), was retained. Approximately 1 kg of wet lake sediment was collected and placed into high wet-strength paper bags. Samples were then labelled, and field observations for each site were recorded on field cards used by the GSC (Garrett, 1974). Next, samples were air-dried and sieved through a -80 mesh (177 µm) screen before being milled using a ceramic mill with ceramic balls. Typically, 1 kg of organic-rich gyttja yielded about 50 g of suitable material for analysis. After initial analysis, the unused sample material was placed in plastic containers and archived.

During the original survey, samples were numbered consecutively in blocks of 20. Within each block of 20 samples, one site duplicate pair (two samples from the same site) was collected. Each block also contained an empty slot to place an analytical duplicate split comprising a sample split from a routine site. Additionally, a control reference standard sample was added at a random pre-selected position into each block. For this report, new control reference standards (LKSD-1 and LKSD-3) replace the original standards used during the previous analysis (Lynch, 1990, 1999; Hechler, 2013). Samples selected for reanalysis were retrieved from the GSC archival facility in Ottawa and shipped to a commercial laboratory for reanalysis. The samples were already sieved and milled from sample processing conducted during the original survey. The samples' group (or block) structure and quality control measures described in the above paragraph were kept during reanalysis.

Before publication, a thorough inspection of the field and analytical data was made to check for any missing or mislabeled samples, as well as for any analytical errors. These checks were done both at the laboratory and upon receipt of the data at the GSC.

3.2 Analytical procedures 2022

Samples selected and prepared for reanalysis were analyzed at Bureau Veritas in Vancouver (British Columbia) using a modified aqua regia digestion followed by inductively-coupled plasma-mass spectroscopy (ICP-MS) analysis. A total of 65 trace elements were determined via ICP-MS (Table 1). A small portion (0.5 g) of the sample was taken and digested using a modified aqua regia solution (1:1:1 HNO₃:HCl:H₂O) for one hour on a heating block. Afterwards, the sample was brought up to volume with dilute HCl. The solution was then aspirated into a Perkin ELAN 9000 ICP mass spectrometer for the determination of elements. The commercial laboratory QA/QC protocol included the addition of CRMs (OREAS262, DS11, and BVGEO01) and total procedural blanks. Total procedural blank samples do not contain any sample material (i.e., empty vials), but are brought through the entire digestion and analysis process in the same manner as the remainder of the samples. Analytical results were verified by a British Columbia Certified Assayer prior to being delivered to the GSC.

Table 1. Lower detection limits published by Bureau Veritas for ‘partial’ aqua regia digestion followed by ICP-MS analysis.

Element Lower Detection Limits					
Ag	2 ppb	Hf	0.02 ppm	S	0.02 %
Al	0.01 %	Hg	5 ppb	Sb	0.02 ppm
As	0.1 ppm	Ho	0.02 ppm	Sc	0.1 ppm
Au	0.2 ppb	In	0.02 ppm	Se	0.1 ppm
B	20 ppm	K	0.01 %	Sm	0.02 ppm
Ba	0.5 ppm	La	0.5 ppm	Sn	0.1 ppm
Be	0.1 ppm	Li	0.1 ppm	Sr	0.5 ppm
Bi	0.02 ppm	Lu	0.02 ppm	Ta	0.05 ppm
Ca	0.01 %	Mg	0.01 %	Tb	0.02 ppm
Cd	0.01 ppm	Mn	1 ppm	Te	0.02 ppm
Ce	0.1 ppm	Mo	0.01 ppm	Th	0.1 ppm
Co	0.1 ppm	Na	0.001 %	Ti	0.001 %
Cr	0.5 ppm	Nb	0.02 ppm	Tl	0.02 ppm
Cs	0.02 ppm	Nd	0.02 ppm	Tm	0.02 ppm
Cu	0.01 ppm	Ni	0.1 ppm	U	0.1 ppm
Dy	0.02 ppm	P	0.001 %	V	1 ppm
Er	0.02 ppm	Pb	0.01 ppm	W	0.1 ppm
Eu	0.02 ppm	Pd	10 ppb	Y	0.01 ppm
Fe	0.01 %	Pr	0.02 ppm	Yb	0.02 ppm
Ga	0.1 ppm	Pt	2 ppb	Zn	0.1 ppm
Gd	0.02 ppm	Rb	0.1 ppm	Zr	0.1 ppm
Ge	0.1 ppm	Re	1 ppb		

4 QA/QC of geochemical data

Lake sediment control reference standards are used to quantify accuracy, while analytical duplicates are used to quantify precision. The fitness-for-purpose for mapping is determined using variance analyses of in-site versus between-site variability using the analysis of variance (ANOVA) of field duplicate samples. Project samples and laboratory metadata are presented in Appendix A. Data resulting from the reanalysis of lake sediment samples by the commercial laboratory, including original Certificates of Analysis, are presented in Appendix B. Elements in Appendix B are listed in the order that they were reported in the laboratory certificates and can be used to independently verify the results presented in Appendix C. Results for accuracy, precision, and fitness-for-purpose are presented in Tables C1-1, C1-2, C1-3 and C1-4 in Appendix C. Table 2 (below) lists the contents of the Appendix C1 workbook.

Table 2. Appendix C1 workbook. The workbook contains the QA/QC results for this study.

Worksheet	Contents
C1-1 Accuracy LKSD-1	Compares accepted values for CRM LKSD-1 with results from reanalysis via ICP-MS.
C1-2 Accuracy LKSD-3	Compares accepted values for CRM LKSD-3 with results from reanalysis via ICP-MS.

C1-3 Precision	Provides an estimate of precision using analytical duplicate pairs for reanalysis via ICP-MS.
C1-4 ANOVA	Provides an estimate of fitness-for-purpose using field duplicate pairs for reanalysis via ICP-MS.

4.1 Accuracy

The accuracy of analytical data was evaluated by inserting Canadian Certified Reference Lake Sediments LKSD-1 and LKSD-3 at random locations within each block of 20 samples throughout the analytical suite (McCurdy and Garrett, 2016). LKSD-1 combines lake sediments from two lakes located in central Ontario (Brady Lake, NTS 31M and Joe Lake, NTS 31F). LKSD-3 consists of a mixture of lake sediments from Calabogie Lake and unused portions of sample material from different surveys in central Ontario (NTS 31M, 41P, 42A), eastern Quebec (NTS 31N, 32C, 32D) and northeastern Saskatchewan (NTS 64L, 64M).

The accepted values for LKSD-1 and LKSD-3 were published by Lynch (1990, 1999) and Hechler (2013). Accepted values published by Lynch (1990, 1999) were derived from analyses at several national and international participating laboratories, where samples were digested using a strong acid (concentrated HNO₃-concentrated HCl) for partial digestion but with varying fuming times, acid ratios, and sample weights. It is assumed that the resulting standard deviations of the accepted values reflect variabilities in the analytical methodology across the laboratories. Comparatively, accepted values published by Hechler (2013) were measured at the Geoscience Laboratories of the Ontario Geological Survey (Sudbury). Samples were digested using a modified (nitric acid-rich) aqua regia solution for partial digestion and analyzed via ICP-MS. Taking into account lower detection levels resulting from instrument improvements over the last decades, accepted values from Lynch (1990, 1999) and Hechler (2013) using partial digestions are in agreement with all published certificates and are considered to be comparable. Whenever possible, the most recent accepted value was compared to this study's measured value.

Equation (1) Mean

$$\bar{x}_i = \frac{\sum_{i=1}^n x_i}{n}$$

Equation (2) Standard Deviation

$$S_i = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x}_i)^2}{n}}$$

To determine accuracy, we compare the means (Equation 1) and standard deviations (Equation 2) of a CRM to that of the samples for each determined element. We also calculate the relative standard deviation (RSD; Equation 3), which indicates precision at the stated mean. As an additional measure, we also calculate the relative error (RE), which provides a semi-quantitative indication of how close the measured mean (\bar{x}_i) is to the accepted one (\bar{x}_a). Here, we report the relative error in percent (%) in Equation 4. As some of the accepted values are decades old, the relative error can only be used in a semi-quantitative manner. A value of $\pm 20\%$ indicates that, on average, 95 out of 100 analyses should fall within two standard deviations on either side of the mean (Fletcher, 1981). An RSD exceeding 20% combined with a relatively narrow range of concentrations could result in overlooked anomalies (Howarth and Martin, 1979).

Equation (3) Relative Standard Deviation

$$RSD = \frac{S_i}{\bar{x}_i} \times 100\%$$

Equation (4) Relative Error

$$RE = \frac{|\bar{x}_i - \bar{x}_a|}{\bar{x}_a} \times 100\%$$

The accuracy analysis results for LKSD-1 and LKSD-3 are presented for each element in Tables C1-1 and C1-2, Appendix C. Of 65 elements determined, 7 (B, Be, Ge, Pd, Pt, Ta, and Te) in LKSD-1 and 6 (B, Ge, Pd, Pt, Re, and Ta,) in LKSD-3 are at or below laboratory detection. Furthermore, several elements could have accuracy issues (i.e., RSD >20 %). For CRM LKSD-1, these elements include Au, Be, Bi, Hf, Se, Te, and W. For the CRM LKSD-3, the elements of concern include Au, Be, Ge, Re, Se, Te, and W.

Elements at or below laboratory detection or have a high RSD are in low abundance within the CRM (both for accepted and measured values). Low detectable concentrations and subsequent relatively high RSD values (>20 %) can be caused by elements being present within discrete, often refractory, minerals, including spinels, beryl, tourmalines, chromite, zircon, monazite, niobates, tungstates, topaz, tantalite, and cassiterite (Crock and Lamothe, 2011). The apparent low concentrations of Au, B, Be, Bi, Ge, Hf, Pd, Pt, Re, Se, Ta, Te, and W in samples may be caused by the inability of the digestion to dissolve these elements in the above minerals. Additionally, the RSD % for Au in both LKSD-1 and LKSD-3 is relatively high (>20 %) due to the difficulty of creating homogeneous standard materials (Harris, 1982; Clark, 2010; Dominy, 2014). Lastly, for element means falling outside the accepted standard deviations (RE %), it should be noted that the accepted values for these elements were measured in 1990 and may not be as accurate as current determinations of sample means. Thus, the element means falling outside the accepted standard deviations reflects improved measurements of that element by modern instrumentation.

4.2 Precision

Precision is considered in terms of the closeness of agreement between analytical duplicate samples analyzed by the same method (i.e., independent test results obtained using the same equipment within short time intervals on duplicate project samples). The estimation of the analytical precision follows the procedure of Youden (1951) for up to 180 duplicate pairs, and all results are above the respective detection limits. The resulting numerical estimate of precision for variables is listed in Table C1-3 (Precision) in Appendix C as a % Relative Standard Deviation (Standard Deviation divided by the overall mean of the samples and multiplied by 100 to obtain a percentage (Reimann et al., 2008)). Elements (or analytes) are grouped based on their position in the periodic table. Included with the element and method of analysis are the Lower Detection Limit (LDL), the percentage of samples pairs below the lower detection limit (Total % Below LDL), the number of duplicate pairs removed from the calculations because one or both values are below detection ('Duplicate Pairs Removed'), the range of the remaining sample pairs, and the mean of the data used for each calculation of precision. This information provides context for the estimates of 'Precision (RSD %)' and is presented in Table C1-3.

Elements with precisions poorer than 20 % in Table C1-3 tend towards generally low concentrations in samples, as indicated by the number of duplicate pairs removed, the range, the mean, and the

percentage of data below the detection limit. Such is the case for elements As, Au, Bi, Ge, In, Pt, Re, Sb, and Te that underwent an aqua regia ('partial') digestion. Results for Au can also be affected by the particulate nature of gold ('nugget effect') and should be considered accordingly (Harris, 1982). For the elements Pd and Ta, less than two pairs of analytical duplicates have both samples above detection, and no ANOVA results are calculated.

4.3 Analysis of Variance (ANOVA)

Field duplicate data were used to test the hypothesis that the combined sampling and analytical variability (s_{sa}^2) was equal to the 'regional' variability (s_r^2) across the areal extent of the field duplicates (i.e., $H_0: s_{sa}^2 = s_r^2$) using a one-way Analysis of Variance (ANOVA; Garrett, 1983). It is desirable that this test fails, and the sampling and analytical variability is not equal to the regional variability but smaller. Otherwise, there is as much average variability at the sample sites as there is across the survey area. If this is the case, spatial variation across the survey area cannot be reliably identified. The ANOVA procedure allows the variance components to be estimated, and thus the percentage of the variability in the field duplicate pair data that can be ascribed to sampling and analytical variability and regional variability; ideally, the latter percentage should be greater than the former, and statistical significance of the underlying F-test can be used as annotation in an abbreviated table of ANOVA results, that focuses on the key issues.

Using the 'anova2' function of the 'rgr' package in the R system, a random effects model Analysis of Variance (ANOVA) estimates the combined sampling and analytical variability between sets of duplicate field samples (Garrett, 2016). Table C1-4 'ANOVA' in Appendix C shows results from an ANOVA undertaken on up to 24 field duplicate pairs collected for the original surveys. Duplicate pairs of which one or both values of an element are below detection were removed from the calculations. Calculations were only carried out if the number of duplicate pairs with both values above detection exceeds 1. Data were logarithmically transformed (base 10) to meet homogeneity of variance considerations (i.e., severe heteroscedasticity) and to account for ranges of observations exceeding 1.5 orders of magnitude (Garrett, 2016).

The Analysis of Variance (ANOVA) of field duplicates partitions variability into two components, 'Between Sites' and 'At Sites' in Table C1-4. The variance ratio, F, is calculated in 'anova2' within the 'rgr' package to gauge whether the variance 'within' is significantly smaller than the variation 'between'. As a 'rule of thumb' this ratio should exceed 4.0 for sampling and analytical errors to be significantly smaller at the 95 % confidence level. The p-value is a measure of whether the observed F-ratio could have occurred by chance alone. Generally, an acceptable p-value is less than 0.05 (>95th percentile, i.e., there is a <5 % probability the observed F ratio could have occurred due to chance alone). It should be noted that in cases where an element is evenly distributed throughout all samples, 'F' and 'p-values' may fall below levels of confidence.

The ANOVA statistics in Table C1-4 indicate that the sampling and analytical variability is significantly lower than the field survey variability, at the $p < 0.05$ level (>95 % confidence level) for all elements except Pt and B. For the elements Pd and Ta, 100 % of one or both field duplicate sample pairs are below detection, and no ANOVA results are reported. From this evaluation, it is inferred that maps of the distribution for all other elements will display the true spatial variability of those elements.

5 Conclusions

Here we present high-quality reanalysis data from lake sediments collected between 1977 and 1992 from approximately 44 000 km² in east-central Labrador. Advances in analytical instrumentation, resulting in the availability of lower detection limits, improvements in analytical precision, and an increase in the number of elements available for analysis, have warranted this activity. This work augments the previous reanalysis of 32 237 lake sediment samples from northern Quebec and Labrador. The resulting composite database covers an area of almost 350 000 km² in northeastern Canada, much of which is of current or historical interest for mineral exploration.

Quality assurance and quality control of reanalysis data have resulted in the identification of elements that need to be monitored carefully for future analyses and applications of the dataset. Apparently low concentrations of some elements in samples may be the result of the inability of the digestion to dissolve these elements in refractory minerals. Gold is difficult to homogenize in samples and this can be reflected in relatively high RSD values. Overall, geochemical data are accurate, precise, 'and fit-for-purpose', and can be used within the context of regional geochemical exploration.

6 Acknowledgements

This work was supported by the GEM-GeoNorth program. The authors wish to thank Rick McNeil and Abeer Haji Egeh, Earth Material Collections, and Shauna Madore, Alain Grenier, and Miriam Wyergangs, Geochemistry & Sedimentology Labs for their hard work locating archived samples and preparing them for analysis. Steve Adcock and Wendy Spirito are thanked for helpful advice formatting spreadsheets. We are grateful to Chris Beckett-Brown for his careful review of this report. This work was conducted under the Nunatsiavut Government Research Advisory Committee as NGRAC-19577773.

References

- Amor, S.D., McCurdy, M.W., and Garrett, R.G., 2019. Creation of an atlas of lake-sediment geochemistry of Western Labrador and Northeastern Québec; *Geochemistry: Exploration, Environment, Analysis*, Vol. 19, pp. 369–393. <https://doi.org/10.1144/geochem2018-061>
- Clark, I., 2010. Statistics or geostatistics? Sampling error or nugget effect; *The Journal of the Southern African Institute of Mining and Metallurgy*, v. 110, p. 307–312.
- Corrigan, D., Wodicka, N., McFarlane, C., Lafrance, I., van Rooyen, D., Bandyayera, D., and Bilodeau, C., 2018. Lithotectonic Framework of the Core Zone, Southeastern Churchill Province, Canada: *Geoscience Canada*, v.45, p. 1–24. Geological Association of Canada. <https://doi:10.12789/geocanj.2018.45.128>
- Crock, J.G. and Lamothe, P.J., 2011. Inorganic chemical analysis of environmental materials - a lecture series; U.S. Geological Survey, Open File 2011-1193, 177 p. <https://doi:10.3133/ofr20111193>
- Diekrup, D., Hinchey, A.M., Campbell, H.E., Rayner, N., and Piercey, S.J., 2023. Age, depositional environment, and critical mineral potential of the Florence Lake greenstone belt, Hopedale Block,

Labrador; *in* Current Research, Newfoundland and Labrador Department of Industry, Energy and Technology, Geological Survey, Report 23—1; *in press*.

Dominy, S.C., 2014. Predicting the unpredictable - evaluating high-nugget effect gold deposits; in Monograph 30 - Mineral Resource and Ore Reserve Estimation - The AusIMM guide to good practice; Australasian Institute of Mining and Metallurgy, second edition, p. 659–678.

Fletcher, W.K., 1981. Analytical methods in geochemical prospecting. In: Govett, G.J.S. (ed.), Handbook of Exploration Geochemistry, Vol. 1; Analytical Methods in Geochemical Prospecting. Elsevier, Amsterdam, 255 p.

Friske, P.W.B. and Hornbrook, E.H.W., 1991. Canada's national geochemical reconnaissance programme; *in* Institution of Mining and Metallurgy, Transactions, Section B: Applied Earth Sciences, v. 100; p. B47–B56.

Friske, P.W.B., McCurdy, M.W., Gross, H., Day, S.J., Lynch, J.J., and Durham, C.C., 1993a. National geochemical reconnaissance lake sediment and water data, central Labrador (NTS 13K); Geological Survey of Canada, Open File 2645, 136 p. <https://doi.org/10.4095/184068>

Friske, P.W.B., McCurdy, M.W., Gross, H., Day, S.J., Lynch, J.J., and Durham, C.C., 1993b. National geochemical reconnaissance lake sediment and water data, eastern Labrador (NTS 13I, 13J, 13O); Geological Survey of Canada, Open File 2646, 126 p. <https://doi.org/10.4095/184069>

Friske, P.W.B., McCurdy, M.W., Gross, H., Day, S.J., Lynch, J.J., and Durham, C.C., 1993c. National geochemical reconnaissance lake sediment and water data, eastern Labrador (NTS 13N); Geological Survey of Canada, Open File 2648, 121 p. <https://doi.org/10.4095/184071>

Friske, P.W.B., McCurdy, M.W., Gross, H., Day, S.J., Lynch, J.J., and Durham, C.C., 1993d. A detailed lake sediment and water geochemical survey, central Labrador; Geological Survey of Canada, Open File 2650, 1993, 90 p. <https://doi.org/10.4095/184073>

Garrett, R.G., 1974. Field data acquisition methods for applied geochemical surveys at the Geological Survey of Canada; Geological Survey of Canada, Open File 74-52, 42 p.

Garrett, R.G., 1983. Sampling Methodology. *in* R.J. Howarth (ed.) Statistics and Data Analysis in Geochemical Prospecting. Handbook of Exploration Geochemistry, Vol. 2, (G.J.S. Govett, series ed). Elsevier, Amsterdam, Chapter 4, pp. 83-110.

Garrett, R.G., 2016. The GSC Applied Geochemistry EDA Package, <http://cran.r-project.org/web/packages>, 14 January 2023.

Geological Survey of Canada, 2018. Geological Survey of Canada, strategic plan 2018-2023; Government of Canada, Natural Resources Canada, 32 p. <https://doi:10.4095/313405>

Godet, A., Guilmette, C., Labrousse, L., Smit, M.A., Cutts, J.A., Davis, D.W., and Vanier, M.A. 2021. Lu–Hf garnet dating and the timing of collisions: Palaeoproterozoic accretionary tectonics revealed in the Southeastern Churchill Province, Trans-Hudson Orogen, Canada; *Journal of Metamorphic Geology*, V. 39p. 977-1007. <https://doi:10.1111/jmg.12599>

Harris, J.F., 1982. Sampling and analytical requirements for effective use of geochemistry in exploration for gold; *in* Precious metals in the Northern Cordillera, (ed.) A.A. Levinson; Association of Exploration Geochemists and the Cordilleran section of the Geological Association of Canada, p. 53–67.

Hechler, J.H., 2013. QA/QC: summary of 2012-2013 quality-control data at the Geoscience Laboratory; *in* Summary of field work and other activities 2013; Ontario Geological Survey, Open file report 6290, p. 1–7.

Hinchev, A.M., Rayner, N., and Davis, W.J. 2020. Episodic Paleoproterozoic crustal growth preserved in the Aillik Domain, Makkovik Province, Labrador; *Precambrian Research*, 337: 105526. Elsevier. <https://doi:10.1016/j.precamres.2019.105526>

Hinchev, A.M., Diekrup, D., and Rayner, N., 2023. Revisiting Mesoproterozoic magmatism in Labrador: Evaluating AMGC and Peralkaline magmatism; *in* Current Research, Newfoundland and Labrador Department of Industry, Energy and Technology, Geological Survey, Report 23—1; *in press*.

Hornbrook, E. H. W., Maurice, Y. T., and Lynch, J. J., 1977. National geochemical reconnaissance release NGR 24-1977, regional lake sediment and water geochemical reconnaissance data, eastern Labrador; Geological Survey of Canada, Open File 513, 306 pages (15 sheets) <https://doi.org/10.4095/130366>

Hornbrook, E. H. W., Maurice, Y. T., and Lynch, J. J., 1979. National geochemical reconnaissance release NGR 38-1978, regional lake sediment and water geochemical reconnaissance data, central Labrador; Geological Survey of Canada, Open File 558, 60 pages (17 sheets) <https://doi.org/10.4095/130376>

Hornbrook, E. H. W., Lund, N.G., and Lynch, J. J., 1984. Geochemical lake sediment and water surveys, Labrador (13K), maps and data; Geological Survey of Canada, Open File 997, 66 pages (20 sheets) <https://doi.org/10.4095/130395>

Hornbrook, E. H. W. and Friske, P.W.B., 1989. Regional lake sediment and water geochemical reconnaissance data, east-central Labrador; Geological Survey of Canada, Open File 1636, (ed. rev.), 175 pages (50 sheets) <https://doi.org/10.4095/308442>

Hornbrook, E. H. W. and Friske, P.W.B., 1988. Regional stream and lake sediment and water geochemical infill survey data, Province of Newfoundland, eastern Labrador (parts of 13J and 13O); Geological Survey of Canada, Open File 1637, 86 pages (55 sheets) <https://doi.org/10.4095/130512>

Howarth, R.J. and Martin, L., 1979. Computer-based techniques in the compilation, mapping, and interpretation of exploration geochemical data; *in* P.J. Hood (ed.), *Geophysics and Geochemistry in the Search for Metallic Ores*; Geological Survey of Canada, Economic Geology Report 31, p. 545-574.

James, D.T., Kamo, S., and Krogh, T., 2002. Evolution of 3.1 and 3.0 Ga volcanic belts and a new thermotectonic model for the Hopedale Block, North Atlantic craton (Canada); *Canadian Journal of Earth Sciences*, 39: 687–710. <https://doi:10.1139/e01-092>

Ketchum, J.W.F., Culshaw, N.G., and Barr, S.M., 2002. Anatomy and orogenic history of a Paleoproterozoic accretionary belt: the Makkovik Province, Labrador, Canada.; *Canadian Journal of Earth Sciences*, 39: 711–730. <https://doi:10.1139/e01-099>

Lebel, D., 2020. Geological Survey of Canada 8.0: Mapping the journey towards predictive geoscience; *in* The changing role of geological surveys, v. 499, (eds.) P.R. Hill, D. Lebel, M. Hitzman, M. Smelror and H. Thorleifson; The Geological Society, London, Special Publication, p. 49–69. <https://doi:10.1144/SP499-2019-79>

Lynch, J., 1990. Provisional elemental values for eight new geochemical lake sediment and stream sediment reference materials LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3 and STSD-4; *Geostandards Newsletter*, v. 14, no. 1, p. 153–157.

Lynch, J., 1999. Additional provisional elemental values for LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3 and STSD-4; *Geostandards Newsletter*, v. 23, no. 2, p. 251–260.

McCurdy, M.W. and Garrett, R.G., 2016. Geochemical data quality control for soil, till and lake and stream sediment samples; Geological Survey of Canada, Open File 7944, 40 p. <https://doi:10.4095/2975623>

McCurdy, M.W., Amor, S.D., Corrigan, D., Garrett, R.G., and Solgadi, F., 2018. Geochemical atlas of northeastern Quebec and adjacent areas in mainland Newfoundland and Labrador / Atlas géochimique du nord-est du Québec et des régions adjacentes dans la partie continentale de Terre-Neuve-et-Labrador; Geological Survey of Canada, Open File 8348 (*also* Geological Survey of Newfoundland and Labrador, Open File LAB/1719; Ministère de l'Énergie et des Ressources naturelles du Québec DP 2018-04),1 .zip file. <https://doi.org/10.4095/306596>

McCurdy, M.W., Paulen, R.C., Rice, J.M., and Campbell, H.E., 2022. Geochemical reanalysis of archived regional lake-sediment samples from the Hopedale Block, Newfoundland and Labrador; Geological Survey of Canada, Scientific Presentation 151. <https://doi.org/10.4095/331177>

Reimann, C., Filzmoser, P., Garrett, R.G., and Dutter, R., 2008. *Statistical Data Analysis Explained*. John Wiley & Sons, Ltd. 343 p.

Ryan, B., 1997. The 1997 Howard Street Robinson Lecture: The Mesoproterozoic Nain Plutonic Suite in Eastern Canada, and the Setting of the Voisey's Bay Ni-Cu-Co Sulphide Deposit; *Geoscience Canada*, 24(4), 173–188. https://id.erudit.org/iderudit/geocan24_4art02

Ryan, B. and James, D., 2004. The Mesoproterozoic Nain Plutonic Suite and its country rocks in the Kingurutik Lake-Fraser River area, Labrador (NTS 14D/9 and 16); *in* Current Research. Government of Newfoundland and Labrador, Department of Mines and Energy, Geological Survey, Report 04-1, pages 235-258.

Wardle, R.J., James, D.T., Scott, D.J., and Hall, J., 2002. The southeastern Churchill Province: Synthesis of a Paleoproterozoic transpressional orogen. *Canadian Journal of Earth Sciences*, 39, p.639–663. <https://doi:10.1139/e02-004>

Youden, W.J., 1951. *Statistical Methods for Chemists*. John Wiley & Sons, Inc., New York, 126 p.

Appendices

Appendix_A_Metadata

A1_GSC_OF-8962_Metadata.docx

A2_Bureau_Veritas_Fee_Schedule-2021.pdf

Appendix_B_Raw_Data

B1_GSC_OF-8962_ICP-MS_Raw_Data.xlsx

B2_GSC_OF-8962_Bureau_Veritas_Certificates_of_Analysis.pdf

Appendix_C_Edited_Data

C1_GSC_OF-8962_QAQC_Results.xlsx