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Regional lake-sediment geochemical data from northwestern Manitoba (NTS 064-F): re-analysis and QA/QC evaluation

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Canada

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Regional lake sediment geochemical data from north-western Manitoba (NTS 064-F): re-analysis data and QA/QC evaluation

Abstract

This report presents the geochemical data, quality assurance and quality control (QA/QC) results of the re-analysis of lake sediment samples collected from north-western Manitoba (NTS 064-F). The original survey was conducted in 1984 and the re-analysis in 2021. Original survey results are presented in OF 1104. A total of 1,024 lake sediment samples were re-analyzed, covering an area of 13,400 km^2, averaging a density of 1 sample per 13 km^2. Samples were analyzed for 65 elements via modified aqua-regia – ICP-MS and 35 elements via INA. To ensure high quality data, the geochemical data was evaluated for contamination, accuracy, precision and fitness-for-purpose (ANOVA). QA/QC results have identified a number of elements to be monitored carefully for future analyses. Overall, the dataset is of good quality.

Résumé

Ce rapport présente les données géochimiques, l'assurance de la qualité et les résultats du contrôle de la qualité (AQ/CQ) de la ré-analyse d'échantillons de sédiments lacustres prélevés dans le nord-ouest du Manitoba (SNRC 064-F). L'étude initiale a été réalisée en 1984 et la ré-analyse en 2021. Les résultats de l'étude originale sont présentés dans OF 1104. Un total de 1 024 échantillons de sédiments lacustres ont été ré-analysés, couvrant une superficie de 13 400 km^2, avec une moyenne densité de 1 échantillon par 13 km^2. Les échantillons ont été analysés pour 65 éléments via aqua-regia modifié - ICP-MS et 35 éléments via INA. Pour garantir des données de haute qualité, les données géochimiques ont été évaluées pour la contamination, l'exactitude, la précision et l'adéquation à l'usage (ANOVA). Les résultats de l'AQ/CQ ont identifié un certain nombre d'éléments à surveiller attentivement pour les analyses futures. Dans l'ensemble, le jeu de données est de bonne qualité.

1 Introduction

Quality assurance and quality control (QA/QC) of geochemical data is an essential process towards the use of any geochemical data. The QA/QC process is designed to identify and, where possible, remediate quality issues such that potential users of geochemical data can be fully informed regarding the implications of the quality of the data. This QA/QC report adheres to the methodology presented in McCurdy and Garrett (2016), investigating for contamination and estimating the accuracy, precision and fitness-for-purpose of the data.

In 1984, lake sediment samples were collected in north-western Manitoba and the geochemical data was published in a Geological Survey of Canada (GSC) Open File 1104 by Hornbrook and Friske (1984). With recent improvements in analytical instrumentation, particularly the availability of lower detection limits, the increase in analytical precision and the diversity of elements for analysis, all original survey samples were re-analyzed. Furthermore, the original survey samples are located in the Athabasca-Wollaston area, a region with known resource potential and thus 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 re-analysis was provided by the GEM-GeoNorth Program. Among other objectives, the GEM-GeoNorth Program aims to advance regional geo-mapping of Canada's North in order 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 Manitoba Geological Survey (MGS).

The survey area is located in north-western Manitoba (NTS 064-F), encompassing a total area of 13,400 km^2 (Hornbrook and Friske, 1984). The area includes the south-eastern portion of the Proterozoic Trans-Hudson Orogen, an area known for gold (Lynn Lake gold mine), base and potential rare metals (e.g., Be, Nb,

Ta and Cs) mineralization (Martins and Kremer, 2013). However, as a whole, the survey area remains largely unexplored and undeveloped.

This report presents the re-analysis data and QA/QC results for a total of 1,024 lake sediment samples. In comparison with the original survey, which included 16 determined elements (including loss on ignition [LOI]), this report contains the results for 65 determined elements, measured at higher precision than the original analysis. I quantify the contamination, accuracy, precision and fitness-for-purpose for regional mapping of the analytical data using blanks, certified reference materials (CRMs), as well as analytical and field duplicate samples. I also highlight elements of concern. With the publication of this QA/QC report, I hope to make available high quality exploration geochemical data, to facilitate its use in regional exploration.

2 Sampling and analytical techniques

### 2.1 Description of surveys and sample management

The original lake sediment survey was conducted in the summer of 1984 in north-western Manitoba (Fig. 1). A total of 1,024 (excluding CRMs, analytical duplicates and one of the field duplicates) samples were collected covering an area of 13,400 km^2, averaging a density of 1 sample per 13 km^2 (Hornbrook and Friske, 1984). Samples were chemically analyzed for 16 elements and the results were released in 1984 as Geological Survey of Canada (GSC) Open File 1104.

Survey samples were collected using a hollow-pipe, bottom-valved sampler that was developed by the GSC (Friske and Hornbrook, 1991; Bourdeau and Dyer, 2023). During retrieval of the sample, the top few centimetres of sediment were washed out while the remainder, the organic-rich gyttja was retained. Approximately 1 kg of wet lake sediment was collected and placed into high wet-strength paper bags. Samples were then labelled and marked in a National Topographic System (NTS) 064-F field map. Field observations for each site were recorded on field cards used by the GSC (Garrett, 1974). Samples were air-dried in the field and then delivered to a commercial laboratory in Ottawa, Golders & Associates, where they were further air dried, broken into smaller fragments and sieved through a -80 mesh (177 μm) screen before being milled using a ceramic ball mill. Typically, 1 kg of organic-rich gyttja yielded about 50 g of material for analysis. After initial analysis, unused sample material was stored in plastic containers and archived.

To ensure the quality and reproducibility of the data, CRMs and analytical duplicates were added to the survey samples by the GSC. During the survey, samples were numbered consecutively and arranged into blocks (or groups) of 20. Each block of 20 samples contains one site duplicate pair; that is, 2 samples from the same site. A block also contains an analytical duplicate sample pair, where one sample from a single site was split and assigned 2 non-consecutive numbers. In this survey, the analytical duplicate was routinely split from one of the field duplicates. The analytical duplicate sample is always the first in the block of 20 samples. Additionally, a CRM was added, at random, into each block.

Samples selected for re-analysis were retrieved from the GSC archival facility in Ottawa and shipped to a commercial laboratory for re-analysis. 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 re-analysis. The only exception was the addition of new CRMs to replace the original ones from the previous analysis. Both lake sediment reference material 2 and 4 (LKSD-2 and LKSD-4) served as the CRMs for this study (Lynch, 1990, 1999; Hechler, 2013). Because of a shortage of LKSD-2, CRM LKSD-4 served as the main CRM for this study.

Before publication, a thorough inspection of the field and analytical data was made to check for any missing and/or mislabelled samples, as well as for any analytical errors. These checks were undertaken both at the laboratory and upon receipt of the data at the GSC.
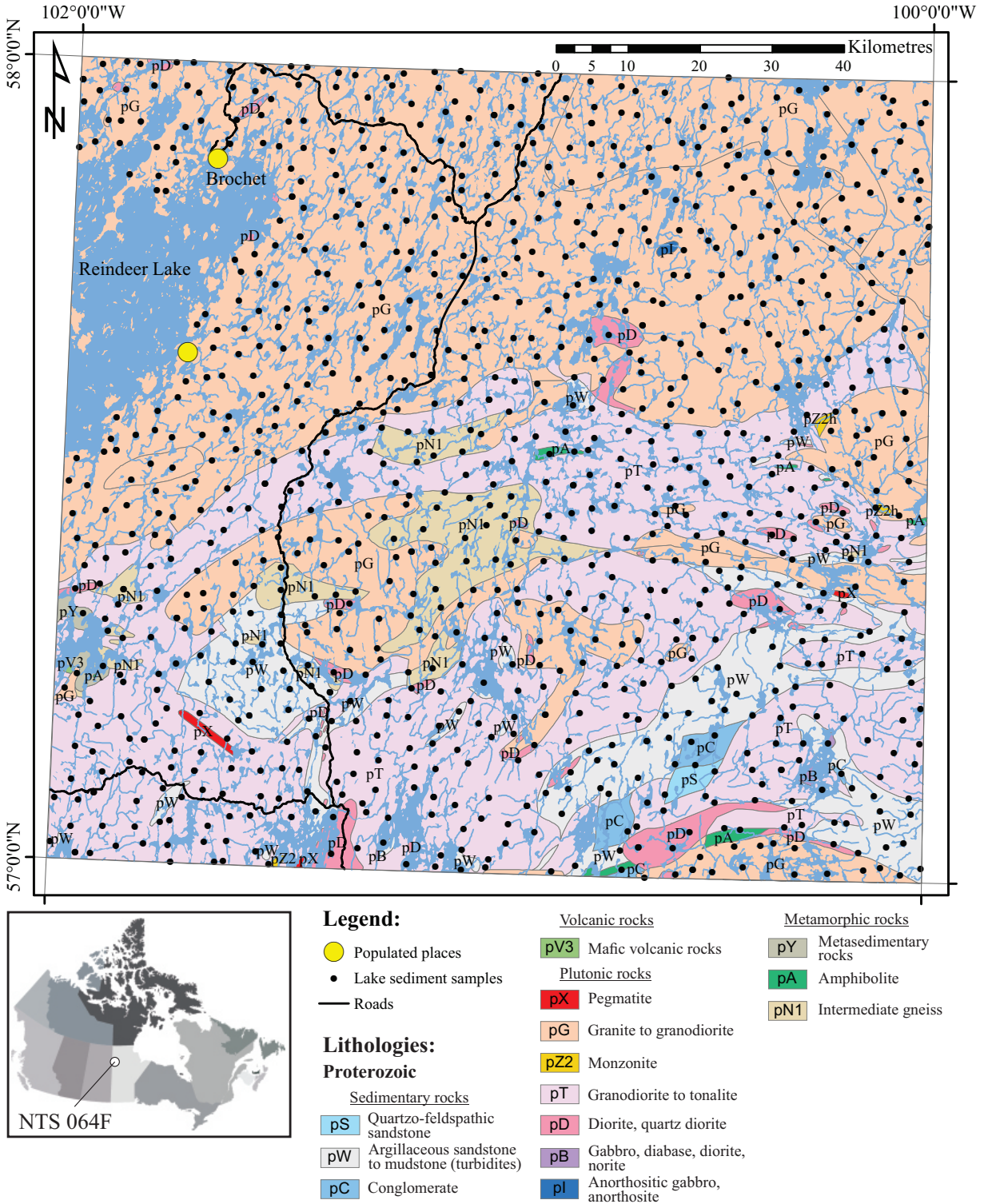
Figure 1. *Bedrock geological map of NTS 064-F, provided by the Manitoba Geological Survey. The updated geological data provided by the Manitoba Geological Survey is in preparation for release to the public. The locations of lake sediment samples collected in 1984 and re-analyzed in this study are shown on the map as black dots.*

2.2 Analytical procedures 2021

Samples selected and prepared for re-analysis were analyzed at Bureau Veritas. Samples were split and analyzed using: 1) modified aqua-regia digestion followed by inductively-coupled plasma-mass spectroscopy (ICP-MS), and 2) instrumental neutron activation (INA).

Modified aqua-regia - ICP-MS analysis A total of 65 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 HNO_3:HCl:H_2O) for 1 hour in a heating block. Afterwards, the sample was made 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 a modified aqua-regia digestion followed by ICP-MS analysis.*

Element	Lower detection limit		Element	Lower detection limit		Element	Lower detection limit	
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			

INA analysis A total of 35 trace elements were determined via INA (Table 2). In contrast with the ICP-MS analytical procedures, INA required no further sample preparation at the laboratory. Samples were weighed and placed into plastic vials with a flux monitor affixed to each vial. Samples were then stacked into a 'bundle' and exposed to neutron flux. Samples were then placed in front of a detector coupled to a multi-channel analyzer for element 'counting'. The amounts of various isotopes, and hence, elements present were determined by comparison of the spectrum energies versus the number of counts at each energy state for the samples and standards. Laboratory QA/QC protocol included the changing of vials (using feedstock) between each sample and the addition of CRMs. Analytical results were verified by a senior analyst prior to being delivered to the GSC.

Table 2. *Lower detection limits published by Bureau Veritas for INA analysis.*

Element	Lower detection limit		Element	Lower detection limit	
Ag	2	ppm	Ni	10	ppm
As	0.5	ppm	Rb	5	ppm
Au	0.002	ppm	Sb	0.1	ppm
B	0.5	ppm	Sc	0.2	ppm
Ba	50	ppm	Se	5	ppm
Cd	5	ppm	Sm	0.1	ppm
Ce	5	ppm	Sn	100	ppm
Co	5	ppm	Ta	0.1	ppm
Cr	20	ppm	Tb	0.5	ppm
Cs	0.5	ppm	Te	10	ppm
Eu	1	ppm	Th	0.2	ppm
Fe	2000	ppm	Ti	500	ppm
Hf	1	ppm	U	0.2	ppm
Ir	0.05	ppm	W	1	ppm
La	2	ppm	Yb	2	ppm
Lu	0.2	ppm	Zn	100	ppm
Mo	1	ppm	Zr	200	ppm
Na	200	ppm			

3 QA/QC of geochemical data

Blank samples are used to monitor and estimate laboratory contamination. CRMs 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 is presented in Appendix A. Lake sediment re-analysis data is presented in Appendix B in a workbook. Elements in Appendix B are listed in the order that they were reported in the laboratory certificates. Data presented in Appendix B can be used to independently verify the results presented here. QA/QC results for contamination, accuracy, precision and fitness-for-purpose are presented in Appendix C. Table 3 presents the contents of the Appendix C1 workbook. Elements in Appendix C are arranged alphabetically for ease of reading.

Table 3. *Appendix C1 workbook. The workbook contains the QA/QC results for this study.*

Worksheet	Contents
C1-1_Contamination	Compares laboratory lower detection limits with results from blank analyses.
C1-2_Accuracy LKSD-4 ICP-MS	Compares accepted values for CRM LKSD-4 with results from re-analysis via ICP-MS.
C1-3_Accuracy LKSD-2 INA	Compares accepted values for CRM LKSD-2 with results from re-analysis via INA.
C1-4_Accuracy LKSD-4 INA	Compares accepted values for CRM LKSD-4 with results from re-analysis via INA.
C1-5_Precision ICP-MS	Provides an estimate of precision using analytical duplicate pairs for re-analysis via ICP-MS.
C1-6_Precision INA	Provides an estimate of precision using analytical duplicate pairs for re-analysis via INA.
C1-7_ANOVA ICP-MS	Provides an estimate of fitness-for-purpose using field duplicate pairs for re-analysis via ICP-MS.
C1-8_ANOVA INA	Provides an estimate of fitness-for-purpose using field duplicate pairs for re-analysis via INA.

3.1 Contamination

Blank samples are typically used to quantify contamination and can be introduced at various stages during sampling, sample preparation and analysis. For this study, blanks were used to monitor for any possible contamination stemming from sample preparation (digestion) and analysis during ICP-MS analysis.

To quantify contamination, analyses of blanks can be compared to the lowest detection limit results published by the laboratory (Table 1). Since a number of blank analyses were published along with the survey samples, this report calculates the mean ($\overline{x_i}$; Equation 1) and standard deviation (s_i; Equation 2), respectively, of blank analyses for each determined element (x_i):

$$\overline{x_i} = \frac{\sum_{i=1}^{n} x_i}{n} \tag{1}$$

$$s_i = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x_i})^2}{n - 1}} \tag{2}$$

As an additional measure, the relative standard deviation (RSD), which provides an indication of the precision of the data can also be calculated. Here, I report the RSD in percent (%). For this study, a RSD $<20\%$ is an indication of reliable data, whereas a high ($>20\%$) RSD could indicate contamination issues. The RSD can be calculated via:

$$RSD = \frac{s_i}{\overline{x_i}} \times 100\% \tag{3}$$

The majority of elements published for blank samples have values below the laboratory lower detection limit (e.g., censored). Censored values are denoted by '$<$' followed by the detection limit appropriate for the element. In accordance with best practices (Grunsky et al., 2014; McCurdy and Garrett, 2016), censored values were replaced by half of their respective lower detection limits (e.g., <2 will be 1).

The contamination results for ICP-MS analysis are presented for each element in Appendix C. Of the 65 elements determined, none has a mean that is above the lower detection limit. However, 9 elements (As, Cu, Hg, Nd, Pb, Pt, Th, Zn and Zr) have a high RSD ($\leq20\%$). A detailed analysis of these elements reveals between 0 to 4 data points at or above the detection limit. All 9 elements have at least 1 data point that plots above their detection limit. There are 2 hypotheses that could explain these results: 1) there was an intermittent source of contamination, and/or 2) laboratory detection limits are not as robust as published, on average. It is well known that estimations of lower detection limits are plagued by large random variations as well as other issues (Bernal, 2013). Therefore, some leniency might be required when comparing results to published laboratory detection limits. Additionally, given that the data above the detection limit per element are not substantial outliers (e.g., $\leq3s_i$), contamination was not considered a significant factor overall.

3.2 Accuracy

In the context of QA/QC, accuracy is defined as how close a measured value is to a known or accepted value (Piercey, 2014). The known or accepted value in this study consists of a CRM inserted at random within each batch of 20 samples. The CRMs used in this study are lake sediment LKSD-2 and LKSD-4. Specifically, LKSD-2 was prepared using lake sediment from Calabogie Lake in central Ontario combined with lake sediment collected in the east arm of the Great Bear Lake in the Northwest Territories (NTS map sheets 86K and 86L; Lynch, 1990). LKSD-4 was prepared from a mixture of lake sediments from Big Gull Lake (NTS 31C) in Ontario, Key and Seahorse lakes (NTS 74H) in Saskatchewan (Lynch, 1990).

The accepted values for LKSD-2 and LKSD-4 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 HNO_3-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. Since accepted values from Lynch (1990, 1999) and Hechler (2013) were measured from partial digestions and the values are generally in agreement (with the exception for some elements caused by instrument improvements over the last decades), I consider all published certificates to be comparable. Whenever possible, the most recent accepted value was taken for comparison to this study's measured value.

To determine accuracy, this report compares the means (Equation 1) and standard deviations (Equation 2) of a CRM to that of the samples for each determined element. This report also calculates the RSD (Equation 3), which provides an indication of precision at the stated mean. As an additional measure, this report calculates the relative error (RE) which provides a semi-quantitative indication of how close the measured mean ($\overline{x_i}$) is to the accepted one ($\overline{x_a}$). Here, I report the relative error in percent (%) in Equation 4. Since some of the accepted values are decades old, the relative error can only be used in a semi-quantitative manner. For this study, a RSD <20% is an indication of good precision at the stated mean, whereas elements with a high (>20%) RSD could indicate accuracy issues.

$$RE = \frac{|\overline{x_i} - \overline{x_a}|}{\overline{x_a}} \times 100\% \tag{4}$$

The accuracy analysis results for ICP-MS are presented for each element in Appendix C for CRM LKSD-4. Of 65 elements determined, 5 (B, Ge, Pd, Pt and Ta) of these elements are at or below the laboratory lower detection limit for analyzed CRM sample LKSD-4. Furthermore, a number of elements could have accuracy issues (i.e. RSD >20%). For the CRM LKSD-4, these elements include: Au, Be, Hf, Re, W and Zr.

The accuracy analysis results for INA are presented for each element in Appendix C for CRMs LKSD-2 and LKSD-4, respectively. Of 35 elements determined, 10 (Ag, Au, Cd, Ir, Mo, Se, Sn, Te, W and Zr) and 10 (Ag, Au, Cd, Eu, Ir, Se, Sn, Te, W and Zr) of these elements are at or below the laboratory lower detection limit for analyzed samples LKSD-2 and LKSD-4, respectively. Furthermore, a number of elements could have accuracy issues (i.e. RSD >20%). For the CRM LKSD-4, these elements include: Lu, Mo, Ta and Yb.

It should be noted that all elements that are at or below laboratory detection and/or have a high RSD are in low abundance within the CRM (both for accepted and measured values) and are therefore very close to the lower detection limit. This could be caused by these elements being present within insoluble minerals that cannot be digested by aqua-regia (Crock and Lamothe, 2011). Similarly to Au, the high RSD could be caused by the difficulty in creating a perfectly homogeneous sample, also known as the 'nugget effect' (Harris, 1982; Clark, 2010; Dominy, 2014). Lastly, it should be noted that a number of elements deviate (substantially outside the published standard deviation; i.e. RE >20%) from the accepted value. For the CRM LKSD-4 using ICP-MS analysis, this is limited to the elements Au, Hf and Zr. For the CRM LKSD-4 using INA analysis, this includes the elements Lu, Mo and Ta. It should be noted that the accepted values for these elements were measured in 1990, and hence, substantial improvements in analytical accuracy since then could be the cause for these deviations.

3.3 Precision

Precision is defined as a measure of the reproducibility of a measurement (Piercey, 2014). Analytical duplicate samples were used to provide an estimate of precision. Essentially, a sample, preferably one of the field duplicates, was split into 2 (a pair), with elemental compositions analyzed in one sample (x_i) and the other sample (x_i'). To determine precision, this report calculates the mean ($\overline{x_p}$) and standard deviation (s_p) of each elemental composition of all n samples as:

$$\overline{x_p} = \frac{1}{n} \sum_{i=1}^{n} \frac{(x_i + x_i')}{2} \tag{5}$$

$$s_p = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_i')^2}{2n}} \tag{6}$$

With the mean and standard deviation calculated, I can now calculate the RSD for precision (RSD_p). For this study, a RSD <20% is an indication of good precision, whereas elements with a high (>20%) RSD could indicate precision issues. The RSD can be calculated via:

$$RSD_p = \frac{s_p}{x_p} \times 100\% \tag{7}$$

In circumstances where one or both values for an elemental composition from a pair were below the lower detection limit or above the upper detection limit, the pair was removed before calculations were made for that elemental composition. In cases (not in this study) where there is a significant deviation between pairs of analyses, an entire block (20) of samples may require re-analysis.

The precision analysis results for ICP-MS are presented for each element in Appendix C. Of 65 elements determined, Ta had measured values that were consistently below the detection limit. Thus, no result could be calculated for this element. Furthermore, elements Au, B, Ge, In, Pd, Pt, Re, Ta and Te have <30 pairs remaining. Of these elements, Au, Bi, Ge, Pt and Re also have a high RSD (>20%). Element Bi has >30 pairs remaining combined with a high RSD.

The precision analysis results for INA analysis are presented for each element in Appendix C. Of 35 elements, all had <30 pairs remaining. I therefore urge caution when interpreting the presented results. Determined elements Ag, Au, Cd, Ir, Se, Sn and Te had measured values that were consistently below their detection limits. Thus, no results could be calculated for these elements. Furthermore, elements Co, Eu, Mo, Sb and Zr also have a high RSD (>20%). Extra caution is recommended for these elements.

A closer inspection of elements with a high RSD reveal that, on average, a large number of pairs were removed from the calculations. This indicates that the elements with a high RSD had a large number of pairs with concentrations at or slightly above the lower detection limit. As previously mentioned, measurements at or near the detection limit could be caused by these elements being present in the samples at extremely low levels, and are therefore unable to be measured using current analytical techniques, and/or exist within insoluble minerals that cannot be dissolved by aqua-regia, in the case of ICP-MS analysis (Crock and Lamothe, 2011). Specifically for Au, the low precision results could be caused by the difficulty obtaining a perfectly homogeneous sample (nugget effect) (Harris, 1982; Clark, 2010; Dominy, 2014). Elements that have both a high RSD combined with <30 pairs remaining are deemed less reliable and therefore less precise (McCurdy and Garrett, 2016).

3.4 Testing if the data is fit-for-purpose using ANOVA

In the context of a geochemical survey that is intended for single element mapping, it is important to understand the significance of regional geochemical variability relative to that at a local scale. One-way ANOVA can be used to quantify the significance of the regional geochemical variability (Garrett, 1983; McKillup and Dyar, 2012; Garrett, 2013; McCurdy and Garrett, 2016). During a regional-scale survey, field duplicate samples are collected within a few meters of each other to characterize the local variability at a sample site ('within' site). The variability at the survey scale is captured by samples that are taken between sites ('between' sites). Any statistical analysis program (e.g., Statistica, SAS University edition, GNU PSPP, Statistical lab, Perl Data Language, Python) can be used to perform the ANOVA, which typically presents a summary of results that includes the F-statistic and a p-value. Additionally, an R (R Code Team, 2022) package, called 'rgr', was

developed by Garrett (2013) to perform the ANOVA and additional steps presented below. The F-statistic (F_i), or variance ratio, is calculated as the ratio of 'between' site mean squares ($(ms_i^b)^2$) and the 'within' sites mean square ($(ms_i^w)^2$) for each element i:

$$F_i = \frac{(ms_i^b)^2}{(ms_i^w)^2} \tag{8}$$

Typically, the >95 confidence level is chosen (which implies p=0.05) with degrees of freedom $n-1$ and n, where n is the number of duplicate pairs. To calculate the percentage of variance 'between' sites (bpct), this report uses the F-statistic:

$$bpct = 100 \times \left(\frac{F-1}{F+1} \right). \tag{9}$$

Finally, the percentage of variance 'within' sites (wpct) can be given as:

$$wpct = 100 - bpct \tag{10}$$

A log-transformation ($\log_{10}$) of the data is often carried out prior to ANOVA to ensure homogeneity of variance (homoscedasticity), a requirement of ANOVA (Bartlett, 1947). For each element, if one or both values from a field duplicate pair fall below the lower detection limit or above the upper detection limit, the pair is typically removed before calculations. Results derived from elements with few pairs remaining (≤ 30 pairs) are typically less reliable and could warrant further investigation (McCurdy and Garrett, 2016). Essentially, elements with a low F-statistic combined with a p$\geq$0.05 are deemed suspect and should be investigated further. However, no assumptions should be made about the nature of the cause of the low F-statistic. Furthermore, such elements will typically have a greater percentage variation within sites as compared to between sites, indicating that this element could be problematic when used for mapping purposes.

The ANOVA results for ICP-MS analysis are presented for each element in Appendix C. Of 65 elements determined, 3 elements (B, Pd and Ta) have analytical values that are consistently below their detection limits. Thus, no results could be calculated for these elements. Additionally, 5 elements (Ge, In, Pt, Re and Te) have <30 pairs remaining and 1 element (Au) has a low (<4) F-value, combined with a p-value over 0.05.

The ANOVA results for INA analysis are presented for each element in Appendix C. Of 35 elements determined, 8 elements (Ag, Au, Cd, Ir, Se, Sn, Te and Zr) have analytical values that are consistently below their detection limits. Thus, no results could be calculated for these elements. Additionally, 8 elements (Cr, Eu, Ni, Sb, Ta, Tb, W and Yb) have <30 pairs remaining. Element Zn has >30 pairs remaining combined with a low (<4) F-value and a p-value near 0.05.

Elements with a F-value smaller than 4 combined with a p-value near or above 0.05 had a large number of field duplicate pairs removed. In many cases, less than 30 pairs remain for analyses, indicating that the results derived from these elements are less reliable. Values at or near the detection limits could be caused by these elements being present in the sample at extremely low concentrations, such that they cannot be measured using current analytical techniques, and/or are present within insoluble minerals that cannot be digested by aqua-regia, in the case of ICP-MS analysis (Crock and Lamothe, 2011). The low precision results for Au are typically the result of the difficulty in homogenizing this element in a sample (nugget effect) (Dominy, 2014).

4 Conclusion

Conducting a QA/QC program for geochemical data is important prior to the use of the dataset. QA/QC results allow an informed application of geochemical data and a preliminary understanding of the root causes of data quality issues. In this study I investigated the contamination, accuracy, precision and fitness-for-purpose for prospectivity mapping of a suite of re-analyzed lake sediment samples that were collected in northwestern Manitoba (NTS 064-F). Samples were re-analyzed in large part because of a high potential for the area to host

gold, base and rare metals mineralization, as well as recent and significant advances in analytical instrumentation, which allows more elements to be determined, and overall, at a higher precision with lower detection limits than the previous analyses. QA/QC results have identified several elements that need to be monitored carefully for future analyses and for applications of the dataset. Overall, the data is of good quality and can be used within the context of regional geochemical exploration.

Acknowledgements

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Appendix A   Metadata

A.1   Metadata

Title of file: A1_GSC_OF_8948_Metadata.docx

A.2   Bureau Veritas fee schedule

Title of file: A2_Bureau_Veritas_Fee_Schedule-2021.pdf

A.3   Bureau Veritas fee schedule web link

Title of file: A3_Web_Link.txt

Appendix B   Raw Data

B.1   ICP-MS Raw Data

Title of file: B1_GSC_OF-8948_ICP-MS_Raw-Data.xlsx

B.2   INA Raw Data

Title of file: B2_GSC_OF-8948_INA_Raw-Data.xlsx

Appendix C   Edited Data

C.1   QA/QC Results

Title of file: C1_GSC_OF-8948_QAQC-Results.xlsx