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RE-ANALYSIS OF ARCHIVED TILL SAMPLES FOR MERCURY AND OTHER ELEMENTS ASSOCIATED WITH SELECTED EPITHERMAL OCCURRENCES IN EASTERN NEWFOUNDLAND

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INTRODUCTION

Epithermal mineral occurrences on the Burin and Avalon peninsulas contain mica-rich alteration zones that include anomalous trace elements, such as Ag, Bi, Cu, Mo, As, Sb, Hg and Zn (O'Brien *et al.*, 1999; Sparkes, 2012; Sparkes and Dunning, 2014). The mica from alteration zones are susceptible to erosion; and during subglacial entrainment they mix with non-metallic or non-indicative whole-rock elements. Archived till samples, collected between 2000 and 2011 from the Avalon and Burin peninsulas, were analyzed at a fine-sand fraction (<0.180 mm / 80 mesh) using “near-total” analytical methods (*e.g.*, 4-acid digestion, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Instrumental Neutron Activation Analysis (INAA)). These analytical methods measure both metallic and non-metallic minerals. However, the elements detected using “near-total” methods for the silicate-rich, fine-sand fraction of till may dilute and mask the metallic signature of finer, micaceous mineral particles entrained in till (DiLabio and Shilts, 1979) and derived from alteration zones around epithermal occurrences. In addition, some of the elements associated with epithermal occurrences (Mo, Cd, Sb, Ag) are in concentrations that are at or only slightly more than the detection limits of the ICP-OES and INAA methods. The Inductively Coupled Plasma-Mass Spectrometer (ICP-MS; Finch, 2022), is sensitive at low elemental concentrations (Tyler and Yvon, 2003) and can detect additional elements such as Mo, Cd, Sb, Ag, Sn, Ge, Ga, Tl and Bi.

This contribution presents new geochemical results from previously collected archived till samples. Re-analyses were undertaken to determine the suitability of using a fine sieve fraction and less rigorous digestion (*aqua regia*) to target base-metal content in tills, overlying, and dispersed from, several known occurrences on the Avalon and Burin peninsulas (Figure 1). The *aqua regia* digestion targets base metals and micas but does not digest oxides, quartz and feldspars that comprise most of the minerals in till samples (Haldorsen, 1983; Kauranne *et al.*, 1992). The mass spectrometer (ICP-MS) finish was used to measure elements that were previously close to or below the detection limit of the ICP-OES detector. Samples were also analyzed using Cold Vapour-Atomic Absorption Spectrometry (CV-AAS) at a commercial lab to detect mercury, which typically occurs in very small concentrations (ppb) and is volatilized with the higher temperatures used in traditional analytical preparation. The analytical results and their quality assurance data are presented in Appendix A. Results of the re-analyzed samples are presented in Appendix B; it includes the new geochemical results along with the lab and field sample numbers, the original open file numbers, the NTS map sheet, the collection year, the general site location (*e.g.*, north Avalon, central Burin) and the type of epithermal occurrence (high or low sulphidation) located near and up-ice of the till samples. Tables summarizing quality assurance data are presented along with a preliminary discussion on the differences between results from the historical “near-total” analyses of the coarse fraction and those from the new *aqua regia* digestion of the finer fraction. A report (forthcoming) will compare the effectiveness of each method in highlighting anomalies in till near or down-ice of epithermal-related mineral occurrences.

METHODS

The study encompasses till samples collected (from earlier studies) overlying and down-ice of several epithermal-related occurrences across the Avalon and Burin peninsulas (Figure 1). The

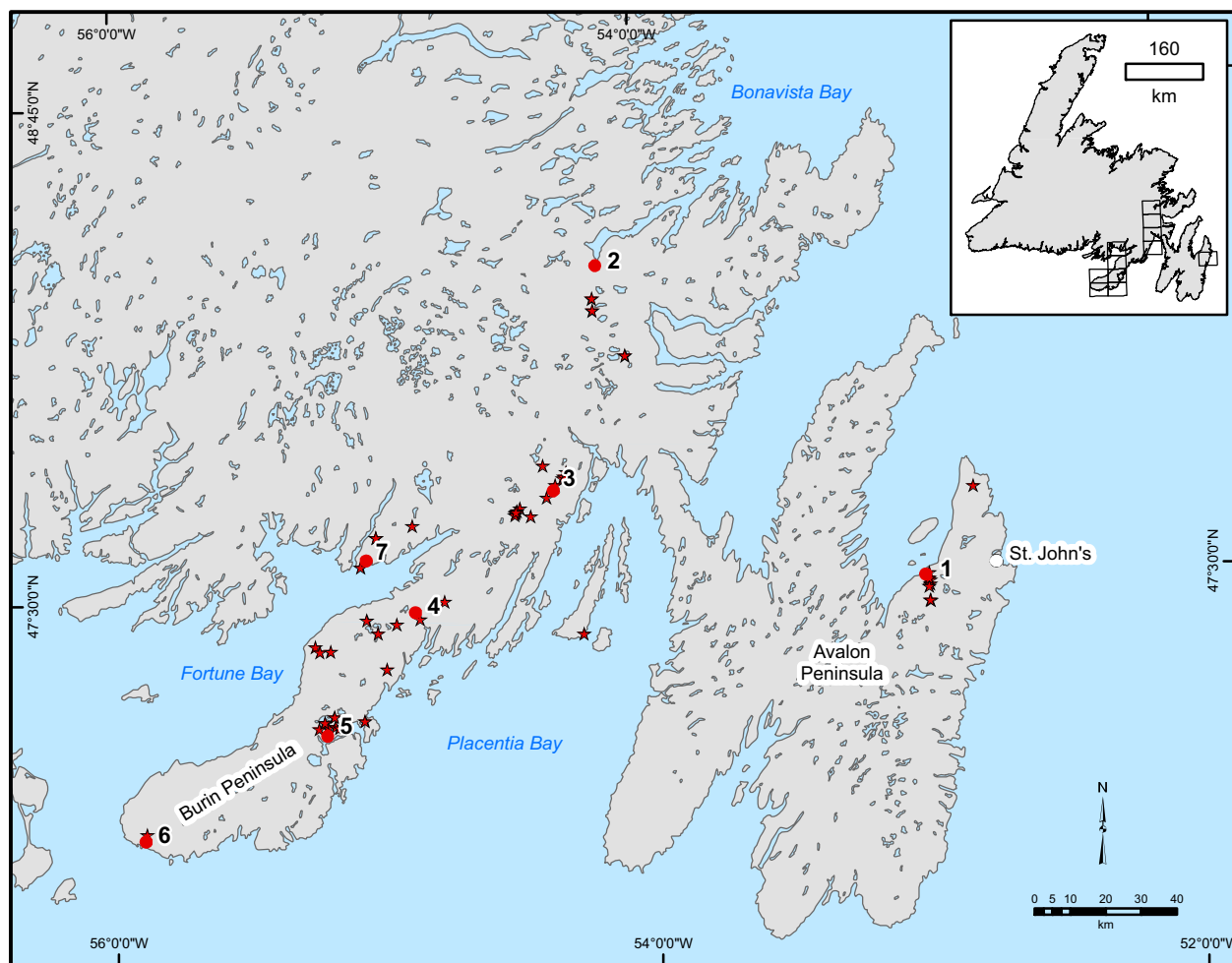


Figure 1. Location map showing the study area and sample sites chosen for re-analysis (red dots); red stars represent known epithermal mineral occurrences. The re-analysis included 31 samples from the Avalon Peninsula, near Holyrood (1), 19 samples south of Bonavista Bay (2), 13 samples northwest of Placentia Bay (3), 15 samples from the north-central Burin Peninsula (4), 39 samples from the south-central Burin Peninsula (5), 14 samples from the southern Burin Peninsula (6), and five samples from the Long Harbour area (7).

collection, analytical methods, detection limits and interpretation of the element distribution in tills are indicated in the original data open-file reports (Batterson and Taylor, 2001, 2004, 2006, 2009), and the analytical methods are detailed in Finch *et al.* (2018). Briefly, samples were collected from hand-dug pits using a shovel at the B/C to C horizons and placed in 500 g Kraft paper bags. They were dried on low heat in the oven and sieved to the <0.180 mm fine-sand fraction (except for five samples northwest of Placentia Bay that were sieved to the <0.063 mm very fine-sand fraction). They were then analyzed for 31 elements using 4-acid digestion (HCl, HNO₃, HClO₄, HF) with an ICP-OES finish. A sample split was also analyzed for 36 elements using INAA at Activation Laboratories Ltd. The quality assurance data for these samples are presented in the earlier reports (Batterson and Taylor, *op. cit.*).

For re-analysis, the samples were sieved to the fine fraction (<0.063 mm) that includes mostly silt- and clay-sized particles. Samples were digested using *aqua regia* (HCl-HNO₃) and then ana-

lyzed using ICP-MS for trace elements, and ICP-OES for major elements. A sample split was sent to Actlabs in Ancaster, Ontario, for CV-AAS (Cold Vapour FIMS in Actlabs brochure) for mercury analysis. The results are presented in Appendix A.

Seven certified and provisional reference materials were inserted into the batch to determine accuracy or recovery, which is the similarity of the lab measurements to the certified and provisional values. Three blind lab duplicates were inserted in the batch to determine the precision or closeness of measurements to each other. Three blanks were inserted by the external lab for the mercury analysis to monitor possible contamination in the analytical equipment (Appendix A).

RESULTS

The compiled results are presented in Appendix B. In Table 1, the suffix 22, represents samples analyzed using *aqua regia* digestion with an ICP-OES finish, the suffix 31, for samples analyzed using *aqua regia* digestion with ICP-MS finish, and the suffix 18, for mercury analysis using CV-AAS. Table 2 summarizes the new and previous elemental analyses using other GSNL protocols to allow the reader to compare the parameters for each method. The suffixes denoting the analytical methods used in previous years are also listed in Table 1 (*see Finch et al., 2018*).

QUALITY ASSURANCE

Quality assurance data of the reference standards for the major and trace elements are included in the tabs in Appendix A, and are summarized in Tables 3–7. Measurements of the external lab blanks were all below the detection limit. For certified reference materials, the samples include OREAS 46 (3 measurements), OREAS 47 (2 measurements) and TILL-4 (2 measurements). The OREAS reference material concentrations are certified for *aqua regia* ICP-OES/MS measurements, (<https://www.oreas.com/>) along with provisional values for some of the TILL-4 standards (https://natural-resources.canada.ca/sites/nrcan/files/mineralsmetals/pdf/mms-smm/tect-tech/ccrmp/cer-cer/TILL_CERT-eng.pdf; Lynch, 1996). Other provisional values for TILL-4 are

Table 1. Suffixes denote the analytical digestions and methods for the geochemical analysis of each element in this report

| Method Code | Analytical Method | Suffix Code |
|-------------|---|-------------|
| INAA | Instrumental Neutron Activation Analysis | 1 |
| 4A ICP-OES | Four-acid digestion, Inductively Coupled Plasma-Optical Emission Spectrometry Finish | 2 |
| AR-ICP-OES | Aqua regia digestion (HNO ₃ -HCl 3:1), Inductively Coupled Plasma-Optical Emission Spectrometry finish | 22 |
| AAS | HNO ₃ digestion, Flame Atomic Absorption Spectrometry | 6 |
| CV-AAS | Cold Vapour-Atomic Absorption Spectrometry (4M HNO ₃ -1M HCl 3:1 (Aqua Regia) + Cold Vapour AA for Mercury only) | 18 |
| AR-ICP-MS | Aqua regia digestion (HNO ₃ -HCl 3:1), Inductively Coupled Plasma-Mass Spectrometry finish | 31 |
| ISE | Ion Selective Electrode | 9 |

Table 2. The elements analyzed, detection limits, maximum and minimum values, the number of samples not analyzed and samples above detection limits for the previous till geochemical analyses (suffixes 1, 2 and 6) and till geochemical re-analysis (suffixes 22 = *aqua regia* ICP-OES, 31 = *aqua regia* ICP-MS and 18 = CV-AAS)

| Element and Analytical Suffix | Detection Limit | Maximum Value | Minimum Value | Below Detection Limit | Not Analyzed | Total Analyzed | % Above Detection Limit |
|-------------------------------|-----------------|---------------|---------------|-----------------------|--------------|----------------|-------------------------|
| AG1_PPM | 5 | <5 | <5 | 44 | 92 | 44 | 0 |
| AG6_PPM | 0.1 | 0.195 | <0.1 | 40 | 86 | 50 | 7 |
| AG31_PPM | 0.02 | 0.32 | <0.02 | 42 | 0 | 136 | 69 |
| AL2_PCT | 0.01 | 9.84 | 0.01 | 0 | 0 | 136 | 100 |
| AL22_PCT | 0.01 | 5.79 | 0.14 | 0 | 0 | 136 | 100 |
| AS1_PPM | 0.5 | 100 | <0.5 | 9 | 0 | 136 | 93 |
| AS2_PPM | 1 | 94.68 | 1 | 0 | 0 | 136 | 100 |
| AS31_PPM | 0.1 | 89.5 | 0.5 | 0 | 0 | 136 | 100 |
| AU1_PPb | 1 | 61 | <1 | 83 | 0 | 136 | 39 |
| BA1_PPM | 50 | 1900 | 95 | 0 | 0 | 136 | 100 |
| BA2_PPM | 50 | 1981 | 87 | 0 | 0 | 136 | 100 |
| BA31_PPM | 0.04 | 2099.75 | 4.06 | 0 | 0 | 136 | 100 |
| BE2_PPM | 0.2 | 24.41 | 0.33 | 0 | 0 | 136 | 100 |
| BI31_PPM | 0.01 | 2.11 | 0.03 | 0 | 0 | 136 | 100 |
| BR1_PPM | 0.5 | 287 | 2 | 0 | 1 | 135 | 99 |
| CA1_PCT | 1 | 3 | <1 | 37 | 92 | 44 | 5 |
| CA2_PCT | 0.01 | 5.539 | 0.035 | 0 | 0 | 136 | 100 |
| CA22_PCT | 0.01 | 1.72 | <0.01 | 1 | 0 | 136 | 99 |
| CD2_PPM | 0.1 | 2.39 | <0.1 | 53 | 0 | 136 | 61 |
| CD31_PPM | 0.02 | 3.53 | 0.02 | 28 | 0 | 136 | 79 |
| CE1_PPM | 3 | 525 | 17 | 0 | 0 | 136 | 100 |
| CE2_PPM | 2 | 557.2 | 20.3 | 0 | 0 | 136 | 100 |
| CE31_PPM | 0.02 | 655.65 | 10.89 | 0 | 0 | 136 | 100 |
| CO1_PPM | 1 | 54 | <1 | 1 | 2 | 134 | 98 |
| CO2_PPM | 2 | 52.1 | 2.5 | 0 | 0 | 136 | 100 |
| CO31_PPM | 0.03 | 69.62 | 0.42 | 0 | 0 | 136 | 100 |
| CR1_PPM | 5 | 260 | 0.5 | 0 | 0 | 136 | 100 |
| CR2_PPM | 2 | 226.8 | 2.7 | 0 | 0 | 136 | 100 |
| CR31_PPM | 0.2 | 177.9 | 0.6 | 0 | 0 | 136 | 100 |
| CS1_PPM | 1 | 22 | <1 | 4 | 0 | 136 | 97 |
| CS31_PPM | 0.01 | 10.65 | 0.19 | 0 | 0 | 136 | 100 |
| CU2_PPM | 2 | 271.3 | <2 | 0 | 0 | 136 | 100 |
| CU31_PPM | 1 | 272 | <1 | 6 | 0 | 136 | 96 |
| DY2_PPM | 0.2 | 18.84 | 1.18 | 0 | 0 | 136 | 100 |
| DY31_PPM | 0.01 | 21.16 | 0.44 | 0 | 0 | 136 | 100 |
| ER31_PPM | 0.01 | 3.89 | 0.23 | 0 | 0 | 136 | 100 |
| EU1_PPM | 0.5 | 5.3 | 0.1 | 0 | 0 | 136 | 100 |
| EU31_PPM | 0.01 | 6.12 | 0.15 | 0 | 0 | 136 | 100 |
| F9_PPM | 50 | 537 | 44 | 0 | 0 | 136 | 100 |
| FE1_PCT | 0.1 | 8.9 | 1.15 | 0 | 0 | 136 | 100 |
| FE2_PCT | 0.01 | 8.385 | 1.274 | 0 | 0 | 136 | 100 |
| FE22_PCT | 0.01 | 7.58 | 0.38 | 0 | 0 | 136 | 100 |
| GA2_PPM | 1 | 1 | <1 | 0 | 135 | 1 | 1 |
| GA31_PPM | 0.01 | 32.14 | 1.74 | 0 | 0 | 136 | 100 |
| GD31_PPM | 0.01 | 36.34 | 0.6 | 0 | 0 | 136 | 100 |
| GE31_PPM | 0.02 | 0.45 | <0.02 | 5 | 0 | 136 | 96 |

Table 2. Continued

| Element and Analytical Suffix | Detection Limit | Maximum Value | Minimum Value | Below Detection Limit | Not Analyzed | Total Analyzed | % Above Detection Limit |
|-------------------------------|-----------------|---------------|---------------|-----------------------|--------------|----------------|-------------------------|
| HF1_PPM | 1 | 18 | 3 | 0 | 1 | 135 | 99 |
| HF31_PPM | 0.01 | 0.58 | 0.05 | 0 | 0 | 136 | 100 |
| HG1_PPM | 1 | 1 | <1 | 43 | 92 | 44 | 1 |
| HG18_PPb | 5 | 194 | <5 | 2 | 0 | 136 | 99 |
| HO31_PPM | 0.01 | 2.27 | 0.08 | 0 | 0 | 136 | 100 |
| K2_PCT | 0.01 | 4.04 | 0.51 | 0 | 0 | 136 | 100 |
| K22_PCT | 0.01 | 0.15 | 0.02 | 0 | 0 | 136 | 100 |
| LA1_PPM | 1 | 55 | 9 | 0 | 0 | 136 | 100 |
| LA2_PPM | 1 | 47.7 | 12 | 0 | 0 | 136 | 100 |
| LA31_PPM | 0.01 | 45.1 | 5.42 | 0 | 0 | 136 | 100 |
| LI2_PPM | 0.2 | 68 | 6.2 | 0 | 0 | 136 | 100 |
| LI22_PPM | 0.1 | 31.8 | <0.1 | 1 | 0 | 136 | 99 |
| LOI_PCT | 0.01 | 26.74 | 0.6 | 0 | 0 | 136 | 100 |
| LU1_PPM | 0.05 | 1.2 | 0.14 | 0 | 0 | 136 | 100 |
| LU31_PPM | 0.01 | 0.33 | 0.03 | 0 | 0 | 136 | 100 |
| MG2_PCT | 0.01 | 3.69 | 0.16 | 0 | 0 | 136 | 100 |
| MG22_PCT | 0.01 | 4.02 | 0.02 | 0 | 0 | 136 | 100 |
| MN2_PPM | 2 | 2856 | 68 | 0 | 0 | 136 | 100 |
| MN22_PPM | 1 | 3648 | 51 | 0 | 0 | 136 | 100 |
| MO1_PPM | 1 | 50 | <1 | 61 | 0 | 136 | 55 |
| MO2_PPM | 1 | 44.5 | <1 | 108 | 0 | 136 | 21 |
| MO31_PPM | 0.03 | 41.59 | 0.04 | 3 | 0 | 136 | 98 |
| NA1_PCT | 0.1 | 3.9 | 0.52 | 0 | 0 | 136 | 100 |
| NA2_PCT | 0.01 | 4.178 | 0.471 | 0 | 0 | 136 | 100 |
| NA22_PCT | 0.01 | 0.15 | <0.01 | 30 | 0 | 136 | 78 |
| NB2_PPM | 2 | 32.3 | 8 | 0 | 0 | 136 | 100 |
| NB31_PPM | 0.03 | 8.18 | 0.27 | 0 | 0 | 136 | 100 |
| ND1_PPM | 5 | 26 | <5 | 3 | 92 | 44 | 30 |
| ND31_PPM | 0.01 | 111.5 | 4.07 | 0 | 0 | 136 | 100 |
| NI1_PPM | 2 | 110 | 10 | 0 | 92 | 44 | 32 |
| NI2_PPM | 2 | 83.7 | 0.5 | 0 | 0 | 136 | 100 |
| NI31_PPM | 0.2 | 77.9 | 0.5 | 0 | 0 | 136 | 100 |
| P2_PPM | 5 | 1997 | 78.7 | 0 | 0 | 136 | 100 |
| P22_PPM | 1 | 2029 | 7 | 0 | 0 | 136 | 100 |
| PB2_PPM | 2 | 127.2 | 2.4 | 0 | 0 | 136 | 100 |
| PB31_PPM | 0.03 | 131.68 | 3.98 | 0 | 0 | 136 | 100 |
| PR31_PPM | 0.01 | 21.51 | 1.16 | 0 | 0 | 136 | 100 |
| RB1_PPM | 15 | 160 | 2.5 | 0 | 0 | 136 | 100 |
| RB2_PPM | 10 | 209.5 | 27.5 | 0 | 19 | 117 | 86 |
| RB6_PPM | 10 | 82 | 41 | 0 | 116 | 20 | 15 |
| RB31_PPM | 0.1 | 13.9 | 1.7 | 0 | 0 | 136 | 100 |
| S22_PPM | 100 | 1809 | <100 | 60 | 0 | 136 | 56 |
| SB1_PPM | 0.1 | 2.4 | <0.1 | 5 | 0 | 136 | 96 |
| SB31_PPM | 0.02 | 0.91 | 0.05 | 0 | 0 | 136 | 100 |
| SC1_PPM | 0.1 | 34.4 | 3.7 | 0 | 0 | 136 | 100 |
| SC2_PPM | 2 | 36.35 | 4.34 | 0 | 0 | 136 | 100 |
| SC22_PPM | 0.1 | 23.4 | 0.2 | 0 | 0 | 136 | 100 |
| SE1_PPM | 1 | 3 | <1 | 134 | 0 | 136 | 1 |

Table 2. Continued

| Element and Analytical Suffix | Detection Limit | Maximum Value | Minimum Value | Below Detection Limit | Not Analyzed | Total Analyzed | % Above Detection Limit |
|-------------------------------|-----------------|---------------|---------------|-----------------------|--------------|----------------|-------------------------|
| SM1_PPM | 0.1 | 36.2 | 1.2 | 0 | 0 | 136 | 100 |
| SM31_PPM | 0.01 | 39.54 | 0.66 | 0 | 0 | 136 | 100 |
| SN1_PCT | 1 | 1 | <1 | 44 | 92 | 44 | 0 |
| SN31_PPM | 0.03 | 9.82 | 0.28 | 0 | 0 | 136 | 100 |
| SR1_PCT | 0.05 | 0.07 | <0.05 | 42 | 92 | 44 | 1 |
| SR2_PPM | 2 | 639.5 | 51.6 | 0 | 0 | 136 | 100 |
| SR31_PPM | 0.1 | 91.6 | 2.6 | 0 | 0 | 136 | 100 |
| TA1_PPM | 0.2 | 3.1 | <0.2 | 17 | 0 | 136 | 88 |
| TA31_PPM | 0.01 | 0.24 | <0.01 | 11 | 0 | 136 | 92 |
| TB1_PPM | 0.5 | 5.6 | <0.5 | 34 | 0 | 136 | 75 |
| TB31_PPM | 0.01 | 4.99 | 0.08 | 0 | 0 | 136 | 100 |
| TH1_PPM | 0.2 | 25.4 | 2.1 | 0 | 0 | 136 | 100 |
| TH31_PPM | 0.01 | 17.43 | 0.55 | 0 | 0 | 136 | 100 |
| TI2_PPM | 5 | 9033 | 2271 | 0 | 0 | 136 | 100 |
| TI22_PPM | 5 | 4771 | 38 | 0 | 0 | 136 | 100 |
| TL31_PPM | 0.01 | 0.37 | 0.01 | 0 | 0 | 136 | 100 |
| TM31_PPM | 0.01 | 0.44 | 0.03 | 0 | 0 | 136 | 100 |
| U1_PPM | 0.5 | 8.5 | <0.5 | 3 | 0 | 136 | 98 |
| U31_PPM | 0.01 | 4.24 | 0.33 | 0 | 0 | 136 | 100 |
| V2_PPM | 5 | 272.8 | 21.9 | 0 | 0 | 136 | 100 |
| V31_PPM | 0.1 | 171.5 | 7.8 | 0 | 0 | 136 | 100 |
| W1_PPM | 1 | 4 | <1 | 83 | 0 | 136 | 39 |
| W31_PPM | 0.01 | 1.8 | <0.01 | 1 | 0 | 136 | 99 |
| Y2_PPM | 2 | 50.8 | 8.4 | 0 | 0 | 136 | 100 |
| Y31_PPM | 0.03 | 36.9 | 1.9 | 0 | 0 | 136 | 100 |
| YB1_PPM | 0.2 | 10 | 1.3 | 0 | 0 | 136 | 100 |
| YB31_PPM | 0.01 | 2.25 | 0.2 | 0 | 0 | 136 | 100 |
| ZN1_PPM | 5 | 85 | <5 | 10 | 92 | 44 | 25 |
| ZN2_PPM | 2 | 404.2 | 17 | 0 | 0 | 136 | 100 |
| ZN31_PPM | 1 | 516 | 9 | 0 | 0 | 136 | 100 |
| ZR2_PPM | 2 | 181.1 | 49.2 | 0 | 0 | 136 | 100 |

derived from Burnham and Schweyer (2004) and the Geological Survey of Canada (GSC – *see* OF8808, Campbell *et al.*, 2021). The accuracies (recovery or closeness to the certified or provisional values of the measurements for different methods) are indicated in Tables 3–6. The relative standard deviations (RSD) used to ascertain the precision of the measurements (RSD – *see* McCurdy and Garrett, 2016) are also included in the tables. The lab duplicate sample precision is presented in Table 7 and graphically in the Thompson-Howarth plots in Appendix A.

The elements Er, Eu, Hf, Nb, Dy, Tm, Ge and Ta, were below the detection limits for the OREAS standards (Tables 3 and 4). The below-detection limits for these elements were expected because all (except Dy) had certified or provisional mean values below detection limits. The element Ge was below the detection limit for the provisional value of TILL-4, and no comparison was made for Cd and Ag in TILL-4, because the provisional values are below the detection limit

Table 3. Elements, measurement averages from the GSNL lab and the current study, and the recovery and relative standard deviation for measurements for OREAS 46 by *aqua regia* digestion and ICP-OES/MS finish. Bold indicates elements for which an ICP-OES finish was used

| OREAS 46 <i>Aqua Regia</i> ICP-OES MS Finish | Certified Mean | GSNL Average (n=2) | Batch Average (n=2) | Recovery % | Relative Standard Deviation % |
|--|----------------|--------------------|---------------------|------------|-------------------------------|
| Al % | 0.76 | 0.99 | 0.99 | 130 | 2 |
| Ca % | 0.61 | 0.79 | 0.79 | 130 | 5 |
| Fe % | 1.47 | 1.61 | 1.61 | 109 | 2 |
| K % | 0.11 | 0.12 | 0.12 | 108 | 1 |
| Li ppm | 6.8 | 7.0 | 7.0 | 102 | 1 |
| Mg % | 0.48 | 0.54 | 0.54 | 113 | 5 |
| Mn ppm | 250 | 291 | 291 | 117 | 2 |
| Na % | 0.08 | 0.16 | 0.15 | 189 | 9 |
| P ppm | 540 | 526 | 526 | 97 | 4 |
| S ppm | - | 27 | -100 | - | - |
| Sc ppm | 2.8 | 2.9 | 2.9 | 106 | 9 |
| Ti ppm | 640 | 855 | 855 | 134 | 10 |
| Ag ppm | 0.03 | 0.01 | 0.03 | 120 | 326 |
| As ppm | 0.7 | 1.2 | 1.2 | 167 | 28 |
| Ba ppm | 55 | 53.48 | 52.94 | 96 | 7 |
| Bi ppm | 0.03 | 0.04 | 0.04 | 143 | 80 |
| Cd ppm | 0.04 | 0.02 | 0.03 | 86 | 299 |
| Ce ppm | 27.5 | 27.67 | 27.42 | 100 | 6 |
| Co ppm | 5.67 | 5.93 | 5.96 | 105 | 3 |
| Cr ppm | 24.3 | 25.8 | 25.3 | 104 | 16 |
| Cs ppm | 0.35 | 0.33 | 0.33 | 95 | 10 |
| Cu ppm | 23 | 20 | 19 | 81 | 39 |
| Dy ppm | 2.03 | 1.05 | 1.07 | 53 | 8 |
| Er ppm | - | 0.54 | 0.55 | | 8 |
| Eu ppm | 0.00 | 0.47 | 0.47 | | 5 |
| Ga ppm | 2.99 | 2.76 | 2.77 | 93 | 8 |
| Gd ppm | 1.64 | 1.69 | 1.67 | 102 | 6 |
| Ge ppm | 0.06 | 0.09 | 0.09 | 148 | 34 |
| Hf ppm | - | 0.19 | 0.20 | | 26 |
| Ho ppm | 0.20 | 0.19 | 0.19 | 97 | 11 |
| La ppm | 15.6 | 15.56 | 15.47 | 99 | 4 |
| Lu ppm | 0.07 | 0.07 | 0.07 | 100 | 30 |
| Mo ppm | 0.65 | 0.61 | 0.59 | 91 | 20 |
| Nb ppm | - | 0.35 | 0.37 | | 100 |
| Nd ppm | 13.2 | 12.70 | 12.68 | 96 | 4 |
| Ni ppm | 16.2 | 16.0 | 16.0 | 99 | 10 |
| Pb ppm | 2.02 | 2.08 | 2.03 | 100 | 23 |
| Pr ppm | 3.75 | 3.50 | 3.43 | 92 | 8 |
| Rb ppm | 6.1 | 6.1 | 6.0 | 98 | 7 |
| Sb ppm | 0.07 | 0.07 | 0.07 | 108 | 41 |
| Sm ppm | 2.11 | 2.06 | 2.03 | 96 | 4 |
| Sn ppm | 0.38 | 0.33 | 0.32 | 83 | 17 |
| Sr ppm | 27.8 | 25.5 | 25.5 | 92 | 8 |
| Ta ppm | | 0.02 | 0.01 | | 203 |
| Tb ppm | 0.2 | 0.21 | 0.21 | 103 | 11 |
| Th ppm | 2.84 | 2.55 | 2.53 | 89 | 6 |
| Tl ppm | 0.06 | 0.07 | 0.07 | 115 | 43 |
| Tm ppm | | 0.08 | 0.08 | | 31 |
| U ppm | 0.43 | 0.40 | 0.41 | 95 | 4 |
| V ppm | 23.1 | 23.4 | 23.3 | 101 | 6 |
| W ppm | 0.07 | 0.09 | 0.09 | 128 | 41 |
| Y ppm | 5.00 | 4.89 | 4.94 | 99 | 5 |
| Yb ppm | | 0.46 | 0.47 | | 6 |
| Zn ppm | 20 | 20 | 20 | 98 | 11 |
| Zr ppm | 5.2 | 5.6 | 5.6 | 108 | 16 |

Table 4. Elements, measurement averages from the GSNL lab and the current study, and the recovery and relative standard deviation measurements for OREAS 47 by *aqua regia* digestion and ICP-OES/MS finish. Bold indicates elements for which an ICP-OES finish was used

| OREAS 47 <i>Aqua Regia</i> ICP-OES MS Finish | Certified Mean | GSNL Average (n=2) | Batch Average (n=2) | Recovery % | Relative Standard Deviation % |
|--|----------------|--------------------|---------------------|------------|-------------------------------|
| Al % | 0.82 | 1.05 | 1.05 | 127 | 7 |
| Ca % | 0.55 | 0.71 | 0.71 | 128 | 5 |
| Fe % | 1.67 | 1.76 | 1.77 | 106 | 4 |
| K % | 0.12 | 0.13 | 0.13 | 111 | 5 |
| Li ppm | 8.6 | 9.0 | 9.1 | 106 | 7 |
| Mg % | 0.50 | 0.55 | 0.55 | 110 | 5 |
| Mn ppm | 280 | 308 | 309 | 110 | 4 |
| Na % | 0.09 | 0.17 | 0.17 | 187 | 14 |
| P ppm | 550 | 557 | 557 | 101 | 6 |
| S ppm | 450 | 449 | 449 | 10 | 1 |
| Sc ppm | 3.0 | 3.2 | 3.2 | 108 | 3 |
| Ti ppm | 690 | 842 | 842 | 122 | 3 |
| Ag ppm | 0.11 | 0.10 | 0.10 | 94 | 59 |
| As ppm | 9.6 | 9.7 | 10.2 | 105 | 19 |
| Ba ppm | 62 | 61.16 | 61.56 | 99 | 3 |
| Bi ppm | 0.15 | 0.15 | 0.15 | 100 | 11 |
| Cd ppm | 0.51 | 0.47 | 0.48 | 93 | 14 |
| Ce ppm | 44.9 | 44.37 | 44.06 | 98 | 4 |
| Co ppm | 48.8 | 48.04 | 48.53 | 99 | 4 |
| Cr ppm | 29.8 | 30.6 | 30.4 | 102 | 6 |
| Cs ppm | 1.19 | 1.07 | 1.09 | 91 | 5 |
| Cu ppm | 157 | 157 | 153 | 97 | 10 |
| Dy ppm | - | 1.15 | 1.18 | | 11 |
| Er ppm | - | 0.56 | 0.58 | | 9 |
| Eu ppm | 0.59 | 0.58 | 0.58 | 98 | 6 |
| Ga ppm | 3.28 | 2.99 | 3.03 | 92 | 5 |
| Gd ppm | 1.92 | 2.03 | 2.01 | 105 | 4 |
| Ge ppm | 0.08 | 0.09 | 0.09 | 120 | 23 |
| Hf ppm | - | 0.17 | 0.18 | | 12 |
| Ho ppm | 0.21 | 0.20 | 0.20 | 95 | 3 |
| La ppm | 25.0 | 25.58 | 25.73 | 103 | 3 |
| Lu ppm | 0.07 | 0.07 | 0.06 | 91 | 15 |
| Mo ppm | 12.6 | 12.37 | 12.25 | 97 | 5 |
| Nb ppm | - | 0.64 | 0.67 | | 83 |
| Nd ppm | 17.8 | 17.12 | 17.24 | 97 | 2 |
| Ni ppm | 77 | 75.0 | 75.1 | 98 | 1 |
| Pb ppm | 282 | 246.82 | 240.59 | 85 | 9 |
| Pr ppm | 5.30 | 5.01 | 4.95 | 93 | 5 |
| Rb ppm | 7.2 | 6.8 | 6.8 | 94 | 4 |
| Sb ppm | 0.21 | 0.20 | 0.20 | 93 | 6 |
| Sm ppm | 2.66 | 2.58 | 2.57 | 97 | 2 |
| Sn ppm | 2.54 | 2.28 | 2.25 | 89 | 5 |
| Sr ppm | 32.3 | 28.0 | 28.1 | 87 | 2 |
| Ta ppm | - | 0.01 | 0.00 | | |
| Tb ppm | 0.23 | 0.23 | 0.23 | 100 | 5 |
| Th ppm | 3.25 | 3.06 | 3.06 | 94 | 5 |
| Tl ppm | 0.08 | 0.08 | 0.09 | 102 | 10 |
| Tm ppm | - | 0.07 | 0.08 | | 4 |
| U ppm | 0.47 | 0.43 | 0.43 | 91 | 5 |
| V ppm | 25.7 | 24.7 | 24.9 | 97 | 3 |
| W ppm | 0.11 | 0.11 | 0.11 | 100 | 14 |
| Y ppm | 5.69 | 5.11 | 5.13 | 90 | 3 |
| Yb ppm | 0.50 | 0.47 | 0.48 | 96 | 8 |
| Zn ppm | 207 | 202 | 202 | 98 | 1 |
| Zr ppm | 6.2 | 5.4 | 5.6 | 90 | 11 |

Table 5. Elements, measurement averages from the GSNL lab and the current study. Recovery and relative standard deviation measurements for TILL-4 by *aqua regia* digestion and ICP-MS finish. Elements in blue are provisional values from GSC Open File 8808 (Campbell *et al.*, 2021), elements in red are provisional values from Lynch (1996), and elements in green are provisional values from Burham and Schweyer (2004). Bold indicates elements for which an ICP-OES finish was used

| Till-4 <i>Aqua Regia</i> ICP-OES MS Finish | Certified Mean | GSNL Average (n=2) | Batch Average (n=2) | Recovery % | Relative Standard Deviation % |
|--|----------------|--------------------|---------------------|------------|-------------------------------|
| Al % | 1.85 | 2.09 | 2.09 | 113 | 2 |
| Ca % | 0.11 | 0.17 | 0.17 | 155 | 4 |
| Fe % | 3.3 | 3.56 | 3.56 | 108 | 3 |
| K % | 0.29 | 0.31 | 0.31 | 107 | 1 |
| Li ppm | 19.5 | 20.0 | 20.0 | 102 | 2 |
| Mg % | 0.49 | 0.53 | 0.54 | 109 | 2 |
| Mn ppm | 260 | 317 | 317 | 122 | 0 |
| Na % | 0.026 | 0.08 | 0.08 | 308 | 5 |
| P ppm | 730 | 745 | 745 | 102 | 1 |
| S ppm | 600 | 698 | 698 | 116 | 2 |
| Sc ppm | 4.42 | 4.5 | 4.5 | 102 | 0 |
| Ti ppm | 1070 | 1293 | 1294 | 121 | 3 |
| Ag ppm | <0.2 | 0.16 | 0.17 | | 33 |
| As ppm | 102 | 102.9 | 104.1 | 102 | 6 |
| Ba ppm | 71 | 69.12 | 69.21 | 97 | 5 |
| Bi ppm | 44 | 46.78 | 46.97 | 107 | 4 |
| Cd ppm | <0.2 | 0.15 | 0.15 | | 10 |
| Ce ppm | 48.6 | 53.03 | 52.33 | 108 | 5 |
| Co ppm | 6 | 6.29 | 6.14 | 102 | 9 |
| Cr ppm | 26 | 23.5 | 22.7 | 87 | 15 |
| Cs ppm | 8.51 | 7.28 | 7.31 | 86 | 5 |
| Cu ppm | 254 | 236 | 227 | 89 | 18 |
| Dy ppm | 1.97 | 2.20 | 2.25 | 114 | 14 |
| Er ppm | 0.85 | 0.94 | 0.96 | 113 | 11 |
| Eu ppm | 0.48 | 0.54 | 0.53 | 111 | 9 |
| Ga ppm | 6.10 | 6.01 | 6.01 | 99 | 1 |
| Gd ppm | 3.07 | 3.27 | 3.25 | 106 | 9 |
| Ge ppm | <0.1 | 0.11 | 0.11 | | 40 |
| Hf ppm | 0.09 | 0.10 | 0.10 | 114 | 3 |
| Ho ppm | 0.33 | 0.35 | 0.35 | 106 | 7 |
| La ppm | 26 | 28.01 | 27.98 | 108 | 7 |
| Lu ppm | 0.10 | 0.10 | 0.10 | 99 | 16 |
| Mo ppm | 14 | 14.38 | 14.34 | 102 | 3 |
| Nb ppm | 2.39 | 2.37 | 2.41 | 101 | 6 |
| Nd ppm | 19.2 | 20.04 | 20.02 | 104 | 6 |
| Ni ppm | 15 | 14.1 | 14.2 | 94 | 3 |
| Pb ppm | 36 | 33.99 | 33.12 | 92 | 10 |
| Pr ppm | 5.4 | 5.67 | 5.55 | 103 | 10 |
| Rb ppm | 36.4 | 34.0 | 34.2 | 94 | 2 |
| Sb ppm | 0.74 | 0.53 | 0.52 | 70 | 13 |
| Sm ppm | 3.6 | 3.93 | 3.86 | 107 | 9 |
| Sn ppm | 5.27 | 5.09 | 5.01 | 95 | 9 |
| Sr ppm | 9.3 | 9.6 | 9.5 | 102 | 7 |
| Ta ppm | 0.01 | 0.01 | 0.01 | 38 | 133 |
| Tb ppm | 0.43 | 0.43 | 0.43 | 99 | 10 |
| Th ppm | 11.5 | 10.54 | 10.54 | 92 | 9 |
| Tl ppm | 0.43 | 0.39 | 0.38 | 89 | 9 |
| Tm ppm | 0.12 | 0.12 | 0.12 | 104 | 8 |
| U ppm | 2.57 | 2.42 | 2.43 | 95 | 4 |
| V ppm | 38 | 39.0 | 38.7 | 102 | 4 |
| W ppm | 157.80 | 156.50 | 160.57 | 102 | 10 |
| Y ppm | 7.7 | 7.94 | 7.89 | 102 | 5 |
| Yb ppm | 0.71 | 0.77 | 0.79 | 111 | 11 |
| Zn ppm | 63 | 59 | 55 | 87 | 26 |
| Zr ppm | 4.3 | 4.0 | 4.1 | 94 | 13 |

Table 6. Mercury measurement averages from the GSNL lab and the current study. Recovery and relative standard deviation measurements for OREAS 46, 47 and TILL-4 by CV-AAS

| OREAS 46 HG CV-AAS In-house | Indicated Mean | GSNL Average (n=2) | Batch Average (n=2) | Recovery % | Relative Standard Deviation % |
|--------------------------------|-------------------|-----------------------|------------------------|---------------|----------------------------------|
| Hg ppb | 7 | 8 | 8 | 91 | 8 |
| OREAS 47 HG CV-AAS In-house | Indicated Mean | GSNL Average (n=2) | Batch Average (n=2) | Recovery % | Relative Standard Deviation % |
| Hg ppb | 14 | 16 | 16 | 90 | 5 |
| TILL-4 HG CV-AAS In-house | Indicated Mean | GSNL Average (n=2) | Batch Average (n=2) | Recovery % | Relative Standard Deviation % |
| Hg ppb | 39 | 24 | 24 | 62 | 0 |

for this standard. Recoveries for the other trace elements range from 80–120% except for Al, Ca, Na, Mn, Sb, Ti, As and Bi. The major elements Al, Ca, Na and Ti, and Ca, Mn, Na and Ti were greater than certified values from the OREAS and TILL-4 standards, respectively. The higher recoveries relative to other standards may reflect the *aqua regia* digestion used (3HCl: HNO₃) and may have been more aggressive than that used for the certified and provisional values. The element Sb was poorly recovered in TILL-4 (70%), whereas Ag and Bi were higher than the certified values provided for the OREAS 47 standard. Mercury analysis indicates good recovery from the in-house and external OREAS standards (Table 6) but poor recovery for TILL-4.

All the internal and external lab recoveries for mercury (Hg) in the OREAS standards (Table 6) were below 10% precision (*i.e.*, good precision). The lab duplicates include five elements, Na, Cd, Cu, Mo and Ta, with poor precision (*e.g.*, greater than 20% RSD). These are highlighted in red in Table 7.

DISCUSSION

CORRELATIONS BETWEEN ANALYTICAL METHODS

The results vary in concentration, analytical range and elemental proportions between the new and the historical results due to the differences in the analytical methods and sample preparation. Correlation coefficients were derived from a Spearman rank correlation matrix of symmetrical balances of trace elements to quantify this variance. This correlation method is similar to a traditional Spearman rank correlation; however, the symmetrical balances account for the “closure effect” in closed compositional data (*see* Kynčlova *et al.*, 2017; Garrett *et al.*, 2017). The correlation coefficients are presented in Table 8 with the element and method symbol code and the element class on the periodic table. For this study, a correlation coefficient of <0.5 is considered poor to medium, 0.50–0.69 moderate and 0.70 or larger is strong.

Table 7. The averages, standard deviations and relative standard deviations for duplicate measurements of three samples from the re-analysis by *aqua regia* digestion, ICP-MS finish and CV-AAS. Values in red are above 20%

| Element | Average (n=3) | Standard Deviation | Relative Standard Deviation % | Element | Average (n=3) | Standard Deviation | Relative Standard Deviation % |
|---------|------------------|-----------------------|-------------------------------------|---------|------------------|-----------------------|-------------------------------------|
| Al % | 1.19 | 0.01 | 1 | Hf ppm | 0.33 | 0.03 | 9 |
| Ca % | 0.18 | 0.02 | 9 | Hg ppm | 55 | 3.00 | 5 |
| Fe % | 1.94 | 0.01 | 1 | Ho ppm | 0.56 | 0.02 | 3 |
| K % | 0.08 | 0.00 | 5 | La ppm | 17.52 | 0.26 | 1 |
| Li ppm | 11.4 | 0.2 | 2 | Lu ppm | 0.09 | 0.01 | 12 |
| Mg % | 0.17 | 0.00 | 2 | Mo ppm | 0.66 | 0.20 | 31 |
| Mn ppm | 298 | 8 | 3 | Nb ppm | 3.92 | 0.17 | 4 |
| Na % | 0.01 | 0.00 | 35 | Nd ppm | 28.59 | 0.33 | 1 |
| P ppm | 162 | 1 | 1 | Ni ppm | 3.8 | 0.3 | 8 |
| S ppm | 157 | 1 | 1 | Pb ppm | 26.51 | 0.20 | 1 |
| Sc ppm | 2.4 | 0.1 | 5 | Pr ppm | 6.59 | 0.08 | 1 |
| Ti ppm | 2195 | 89 | 4 | Rb ppm | 7.2 | 0.2 | 3 |
| Ag ppm | 0.07 | 0.01 | 17 | Sb ppm | 0.22 | 0.01 | 5 |
| As ppm | 7.0 | 0.4 | 6 | Sm ppm | 6.89 | 0.09 | 1 |
| Ba ppm | 12.57 | 0.41 | 3 | Sn ppm | 2.19 | 0.01 | 0 |
| Bi ppm | 0.38 | 0.01 | 4 | Sr ppm | 11.6 | 0.4 | 4 |
| Cd ppm | 0.07 | 0.01 | 22 | Ta ppm | 0.03 | 0.01 | 49 |
| Ce ppm | 116.14 | 1.24 | 1 | Tb ppm | 0.86 | 0.01 | 1 |
| Co ppm | 2.58 | 0.07 | 3 | Th ppm | 2.67 | 0.03 | 1 |
| Cr ppm | 7.3 | 1.1 | 15 | Tl ppm | 0.15 | 0.02 | 13 |
| Cs ppm | 1.64 | 0.01 | 0 | Tm ppm | 0.14 | 0.01 | 8 |
| Cu ppm | 2 | 1 | 22 | U ppm | 0.78 | 0.03 | 4 |
| Dy ppm | 4.17 | 0.04 | 1 | V ppm | 27.7 | 0.3 | 1 |
| Er ppm | 1.29 | 0.03 | 2 | W ppm | 0.26 | 0.02 | 9 |
| Eu ppm | 1.12 | 0.02 | 2 | Y ppm | 12.06 | 0.18 | 1 |
| Ga ppm | 10.07 | 0.16 | 2 | Yb ppm | 0.79 | 0.02 | 3 |
| Gd ppm | 6.44 | 0.06 | 1 | Zn ppm | 65 | 1 | 1 |
| Ge ppm | 0.13 | 0.01 | 8 | Zr ppm | 11.0 | 0.7 | 6 |

For some of the elements in the re-analyzed sample suite including Zn (2), Li (2), Nb (2), Co (1,2), Ca (2), As(1), Cs(1), Cu (2), Sr (2), V (2), P(2) and Cr (2), the *aqua regia* values were similar to those obtained through 4-acid digestion and INAA methods (Spearman rank correlation = 0.70–0.92). Other elements that were moderately correlated between the methods (Spearman rank 0.50–0.69) include As (2), U (1), Ce (1,2), Sb (1), Rb (1), Sc (1, 2), Y (2), La (1, 2), Ti (2), Dy (2), Ni (2), Pb (2), Cr (1), Mn (2) and Th (1). Elements that were poorly correlated between the methods (0.09–0.47) are W (1), Ta (1), Tb (1), Zr (2), Ba (1,2), Cd (2), Mo (1,2), Nd (1), Hf (1), Sm (1), Lu (1), Rb (2), Eu (1), Yb (1) and As (2). Poor correlation between the methods for the elements Cd (2), Mo (1, 2), Nd (1) and W (1) is attributed largely to the difference in instrument sensitivities, as 40–100% more of these elements are detected in the re-analyses as opposed to the original results (Table 2). For the rest of the elements that have low intra-method correlations, the differences could reflect the sieve sizes used between the methods, where samples sieved at a coarser mesh size (<0.180 mm) could include fine sands comprising different mineral phases to the finer (<0.063 mm) mesh used for in the sample re-run. The proportions of feldspar and quartz and their associated elemental contents in the coarse fraction relative to the fine fraction would

Table 8. Spearman rank correlation coefficients of symmetrical balances between previous trace-element analytical measurements (1,2) and the same elements analyzed with *aqua regia* digestion ICP-MS/ICP-OES finish

| Low Correlation | | | Medium Correlation | | | High Correlation | | |
|-----------------|--------------|----------------------|--------------------|--------------|------------------|------------------|--------------|----------------------|
| Element | Coefficients | Element Class | Element | Coefficients | Element Class | Element | Coefficients | Element Class |
| W1_PPM | 0.09 | Transition Metal | CE1_PPM | 0.50 | Lanthanide | ZN2_PPM | 0.70 | Transition Metal |
| TA1_PPM | 0.14 | Transition Metal | LA1_PPM | 0.51 | Lanthanide | LI2_PPM | 0.72 | Alkali Metal |
| TB1_PPM | 0.15 | Lanthanide | SB1_PPM | 0.53 | Metalloid | NB2_PPM | 0.73 | Transition Metal |
| ZR2_PPM | 0.18 | Transition Metal | U1_PPM | 0.56 | Actinides | CO2_PPM | 0.75 | Transition Metal |
| BA2_PPM | 0.23 | Alkaline Earth Metal | RB1_PPM | 0.58 | Alkali Metal | CS1_PPM | 0.78 | Alkali Metal |
| BA1_PPM | 0.25 | Alkaline Earth Metal | CE2_PPM | 0.60 | Lanthanide | AS1_PPM | 0.82 | Metalloid |
| CD2_PPM | 0.28 | Transition Metal | SC1_PPM | 0.60 | Transition Metal | CU2_PPM | 0.83 | Transition Metal |
| MO2_PPM | 0.28 | Transition Metal | Y2_PPM | 0.60 | Transition Metal | SR2_PPM | 0.84 | Alkaline Earth Metal |
| ND1_PPM | 0.30 | Lanthanide | TI2_PPM | 0.61 | Transition Metal | V2_PPM | 0.85 | Transition Metal |
| MO1_PPM | 0.32 | Transition Metal | DY2_PPM | 0.63 | Lanthanide | P2_PPM | 0.88 | Non-metal |
| HF1_PPM | 0.33 | Transition Metal | NI2_PPM | 0.64 | Transition Metal | CR2_PPM | 0.89 | Transition Metal |
| SM1_PPM | 0.34 | Lanthanide | PB2_PPM | 0.64 | Transition Metal | CO1_PPM | 0.92 | Transition Metal |
| LU1_PPM | 0.35 | Lanthanide | SC2_PPM | 0.64 | Transition Metal | | | |
| RB2_PPM | 0.41 | Alkali Metal | CR1_PPM | 0.67 | Transition Metal | | | |
| EU1_PPM | 0.42 | Lanthanide | LA2_PPM | 0.67 | Lanthanide | | | |
| YB1_PPM | 0.46 | Lanthanide | MN2_PPM | 0.67 | Transition Metal | | | |
| AS2_PPM | 0.47 | Metalloid | TH1_PPM | 0.68 | Actinides | | | |

contribute to variance in the correlations. It is also possible that different mineral species hosting the elements in the till may respond differently to the digestion methods (*e.g.*, an oxide *vs.* sulphate), or the digestions may be unequally effective at higher or lower concentrations.

Boxplots display the similarities and dissimilarities between trace-element, log-transformed concentrations of samples analyzed using *aqua regia* and the “near total” methods. In Figure 2, the log concentrations of the *aqua regia* digestion analysis of Hf and Zr are much lower than those analyzed by the “near total” (Hf1, Zr 2) methods. This is displayed by the differences in medians (line in the box), the absence of overlap in the ranges (lines leading from the box from 2 to 98%), the difference in the anomalous (>98%) samples (signified by the + sign) and the interquartile ranges (length of the box) between the analytical methods. The lower concentrations from the re-analyzed samples is expected, as; 1) these elements commonly occur in silicates and oxides that comprise a high proportion of the coarser grain size (<0.180 mm) analyzed from the archived samples, and 2) the elements reside in resistant minerals that would not be decomposed through *aqua regia* digestion, but partially digested or analyzed by a “near total” digestion or INAA. The log-transformed concentrations of Ba1 and Ba2 (“near-total” digestions) have similar median (line in box) and data spread, including the interquartile range and total range, and the anomalies are also similar. In contrast, the median of Ba31 (analyzed by *aqua regia*) is lower, the range is more extensive, overlapping lower concentrations of Ba1 and Ba2, and the outliers are slightly higher than in Ba1 and Ba2. The dissimilarity between the “near total” and *aqua regia* digestions highlighted in the boxplots is not unexpected. The “near total” and *aqua regia* digestions may target different minerals in till. Kauranne *et al.* (1991) report contrasting barium anomalies in till geochemistry from “near total” and *aqua regia* digestions where till was collected over a mica schist and rapikivi granite bedrock units (Kauranne *et al.*, 1992, Figure 3). The barium anomalies from the “near total” digestion are derived from the rapakivi granites (most likely from feldspars), and the barium anomalies highlighted by *aqua regia* digestion occurred over the mica schists and are most likely from biotite (Kauranne *et al.*, 1992). The comparisons between the boxplots for rubid-

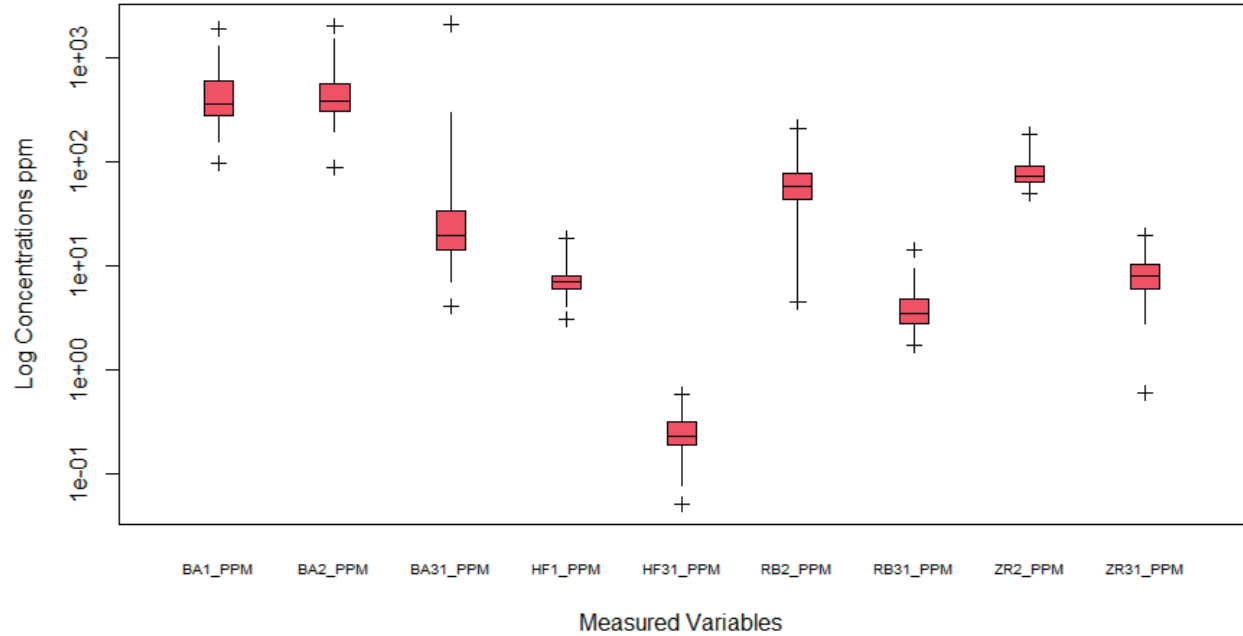


Figure 2. Simple boxplots of elements that show weak correlation between the original analytical methods and the aqua regia digestion ICP-MS finish.

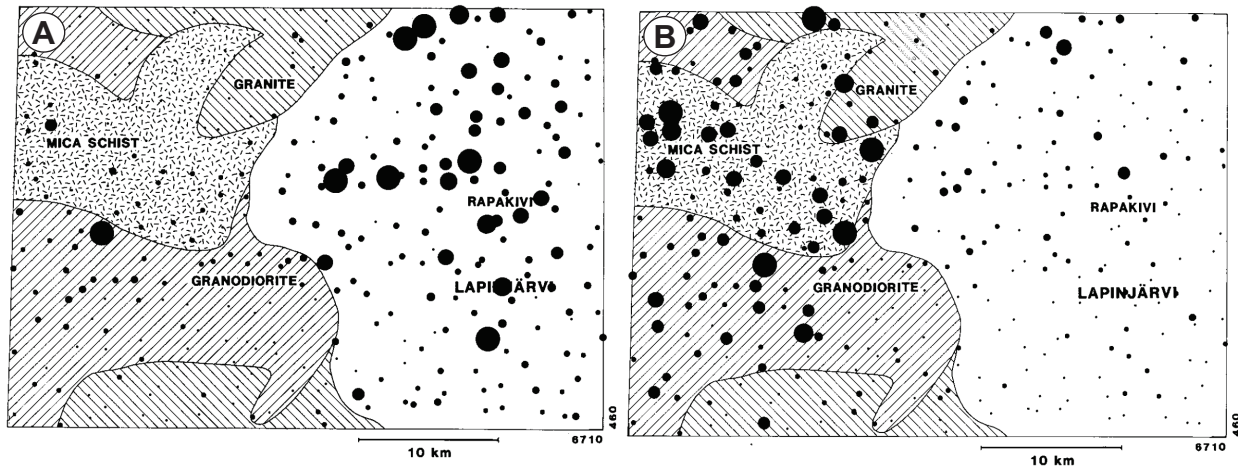


Figure 3. Dotplots of Ba analyzed by “near total” (A) and aqua regia (B) digestions in the silt plus clay fraction of till samples in the Askola region of southeastern Finland. The “near total” digestion highlights barium in the K-feldspar-rich rapakivi granites (A); the aqua regia digestions highlights barium in the mica schist (after Kauranne et al., 1992, Chapter 9).

ium in this study are similar to those of barium and may also indicate that the digestions are targeting rubidium from different minerals (*e.g.*, in feldspars *vs.* micas?).

Strong correlations between the analytical methods are also indicated by similar shapes between the boxplots (Figure 4). For the elements Co, Cu and P, the median values, the interquartile ranges and the outliers are similar. The medians are different for Cr, Sr and V, but the interquartile range is similar, as is the position of the outliers relative to the interquartile range. In

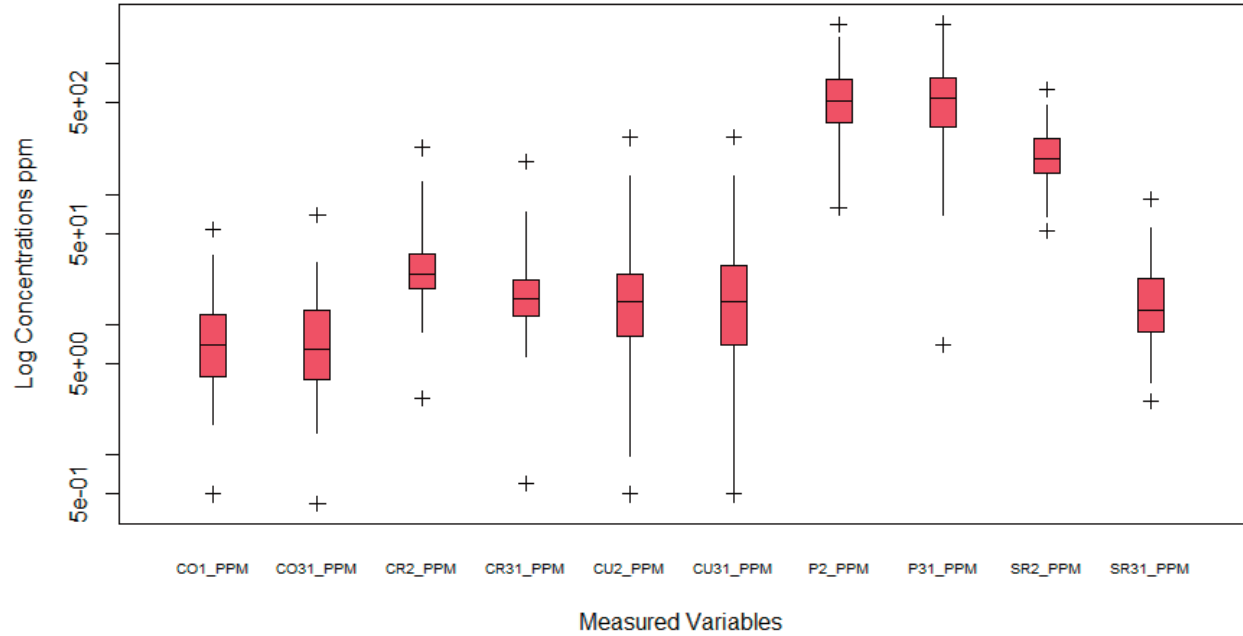


Figure 4. Simple boxplots of some elements that are strongly correlated between the original methods and the aqua regia digestion ICP-MS finish.

contrast to the boxplots of the poorly correlative elements, it suggests the methods are targeting the same minerals in till, in equal or relatively equal proportions between sieve sizes, and with *aqua regia* often recovering similar (Co, Cu, P) and lower (Cr, V, Sr) concentrations of the elements from the mineral in the sample.

INTER-ELEMENT CORRELATIONS

Inter-element correlations of symmetrical balances for the trace element geochemical results of the *aqua regia* digestion are displayed in a correlation plot in Figure 5, where blue indicates a high correlation. Red shows a low correlation, and the size of the circle is proportional to the correlation coefficients (Wei and Simko, 2021). The results of this plot are summarized in Table 9.

Elements associated with epithermal deposits in Newfoundland (Ag, Bi, Cu, As, Mo, Sb, Hg and Zn (O'Brien *et al.*, 1999; Sparkes, 2012; Sparkes and Dunning, 2014)) are correlated, which is expected as the samples were collected overlying and dispersed from known occurrences. The sensitivity of the ICP-MS finish ensures that lower concentrations of elements such as Bi, Ag, Sn, Ga, Gd and Tl are also detected, which may assist in tracing till anomalies to source. Many of the trace elements associated with high and low sulphidation epithermal occurrences are correlated in our data, but there are also notable differences in affinities (*e.g.*, As and Sb are correlated with Zn, but not with Bi and Mo (Figure 5, Table 9). Nickel, Co, Zn, Li and Cu are all correlated; however, the correlation may reflect the combined contributions of mafic bedrock and alteration minerals in till. More re-analyses and multivariate analysis of the geochemical results will assist in unravelling the relative geochemical contributions of mineralized and unmineralized bedrock in till, and provide till geochemical indices to aid in exploration for mineralization under cover.

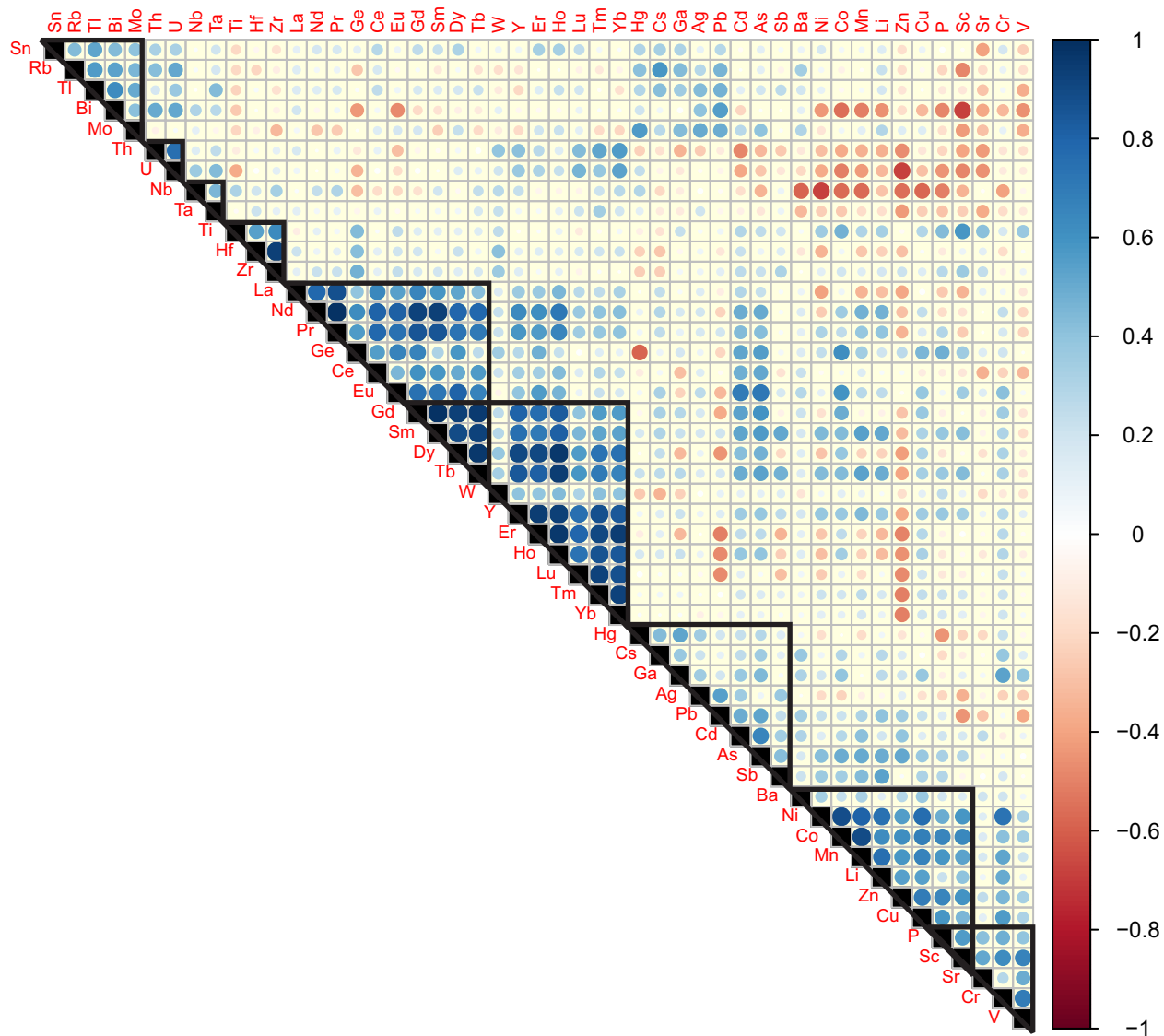


Figure 5. Spearman rank correlation matrix of symmetrical balances (Kynčlova et al., 2017; Garrett et al., 2017) showing inter-element correlations between trace elements measured using aqua regia digestion ICP-MS finish shaded from red (low correlation) to blue (high correlation). The circles' size and darkness indicate the correlation's magnitude, and the correlations are grouped (black borders) using hierarchical clustering (Wei and Simko, 2021).

CONCLUSIONS

The results for elements associated with epithermal deposits (Cu, As, Mo, Sb and Zn) show low to high correlations (0.28 and 0.83) between “near-total” (INAA and 4-acid digestion ICP-OES) and *aqua regia* digestions. The variation in the correlations between the analytical methods suggests that although many elements are identified through the “near total” analyses, the *aqua regia* digestion ICP-MS results can provide a similar or more complete element suite (Ag, Sb, Mo, Sn, Bi, Cd, Tl, Ga), particularly at low concentrations in till. Because this analysis can be done in-house, it can offer a low-cost solution to increase the elemental footprint of till samples in the

Table 9. Summary of inter-element correlations from Figure 5, presenting the clustered strongly correlated elements (blue dots on on the left side bordered in black) and their other element correlations to the right of the figure

| Clustered Intercorrelated Elements | Other Highly or Moderately Correlated Elements |
|---|--|
| Sn, Rb, Tl, Bi, Mo | Ta (Tl only), Hg, Cs, Ga, Ag, Pb |
| Th, U | Sn, Rb, Tl, Bi, Lu, Tm, Yb |
| Nb, Ta | - |
| Ti, Hf, Zr | Ge and W (all); Ni, Co, Mn, Li, Cu, P, Sc, Sr, V (Ti only) |
| La, Nd, Pr, Ge, Ce, Eu, Gd, Sm, Dy, Tb, W | Cd, As, \pm Y, Er, Ho, Lu, Tm, Y; Co, Mn, Li (Nd, Pr and Ge only) |
| Hg, Cs, Ga, Ag, Pb, Cd, As, Sb \pm Ba | La, Nd, Pr, Ge, Ce, Eu, Gd, Sm, Dy, Tb (As and Sb only), Sn, Rb, Tl, Bi, Mo (Hg, Cs, Ga, Ag and Pb only); Ni, Co, Mn, Li, Zn, Cu (As and \pm Sb) |
| Ni, Co, Mn, Li, Zn, Cu, P, Sc, Sr | Ge, Eu, Gd, Sm, Dy, Tb; Nd, Pr and Ge (Co, Mn and Li only) |
| P, Sc, Sr, V, Cr | Ga, (V, Cr) |

GSNL archive. The extra elements may assist in uncovering mineralization in regions covered by till. Although the mercury analysis is performed at a commercial lab, it could be a viable and low-cost option (\$12–\$15 per sample) for till samples that may not contain anomalous concentrations of traditional base metals such as Cu, Zn and Pb (*e.g.*, samples overlying and dispersed from low-sulphidation deposits). Future studies comparing the two different sieve fractions analyzed by the same method will help determine the total variance to the results caused by grain size differences. Additional work, comparing the distribution of mercury and the other elements in till detected using the *aqua regia* ICP-MS analysis to epithermal occurrences, will validate the utility of using these geochemical signatures in till to detect underlying and dispersed mineral content.

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APPENDICES

Appendices A and B are included in the OF_NFLD_3441 zip folder as Microsoft Excel (.xlsx) or Comma Delimited Value (.csv) files.

APPENDIX A: Analyses and Quality Assurance Reports for Geochemical Re-analysis of Till Samples Overlying and Dispersed from Select Epithermal Occurrences in Eastern Newfoundland

APPENDIX B: Re-analyzed Samples and Locations