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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

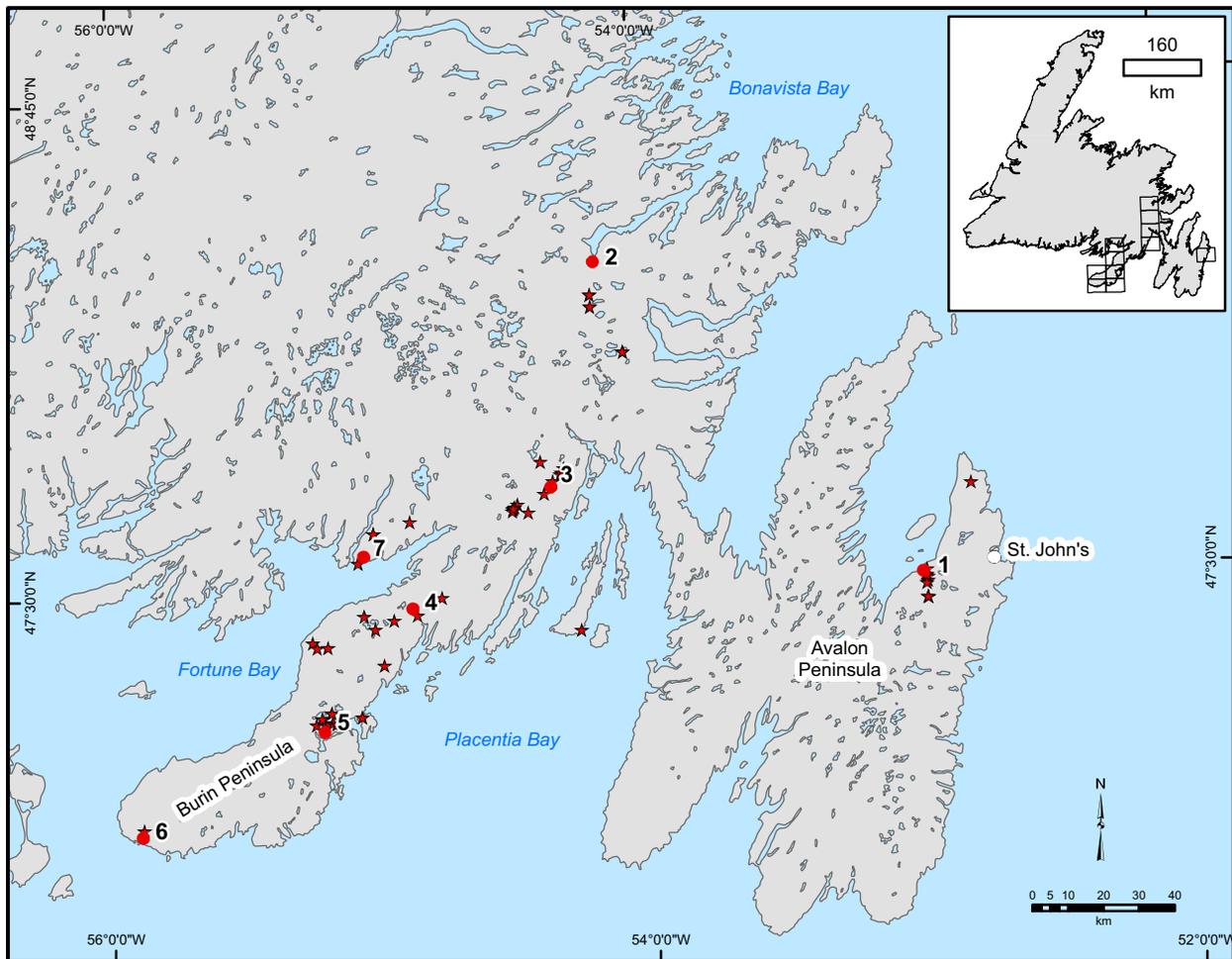


Figure 1. Location map showing the study area and sample sites chosen for re-analysis (red dots); red stars represent known epithermal mineral occurrences. The re-analysis included 31 samples from the Avalon Peninsula, near Holyrood (1), 19 samples south of Bonavista Bay (2), 13 samples northwest of 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-

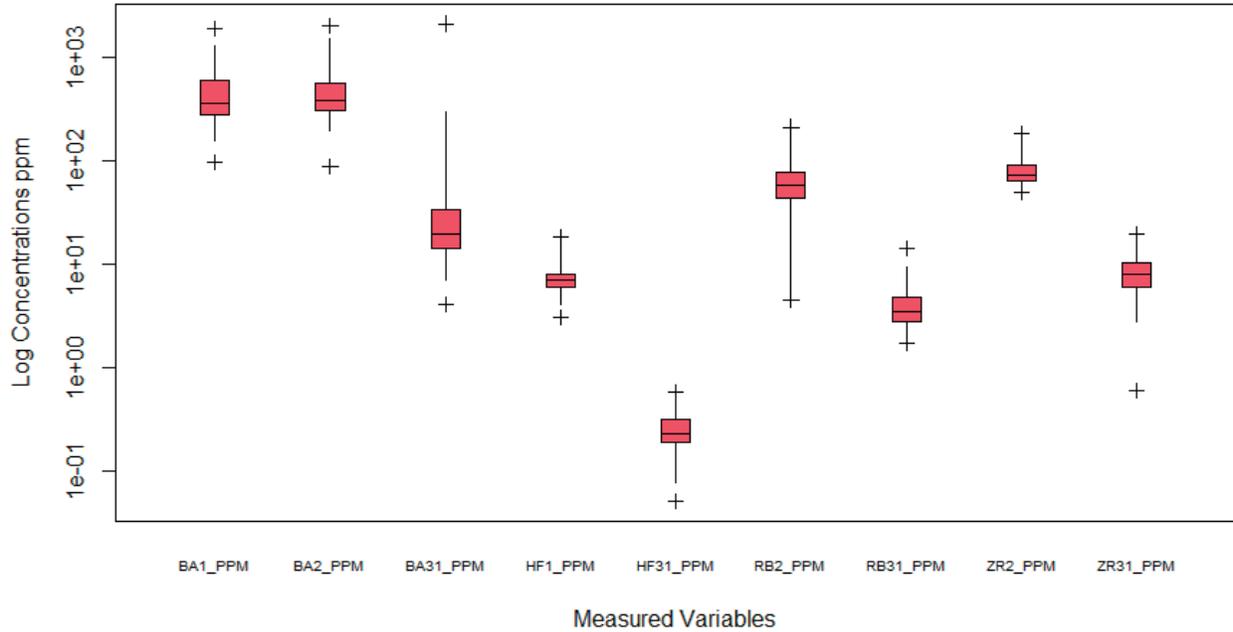


Figure 2. Simple boxplots of elements that show weak correlation between the original analytical methods and the aqua regia digestion ICP-MS finish.

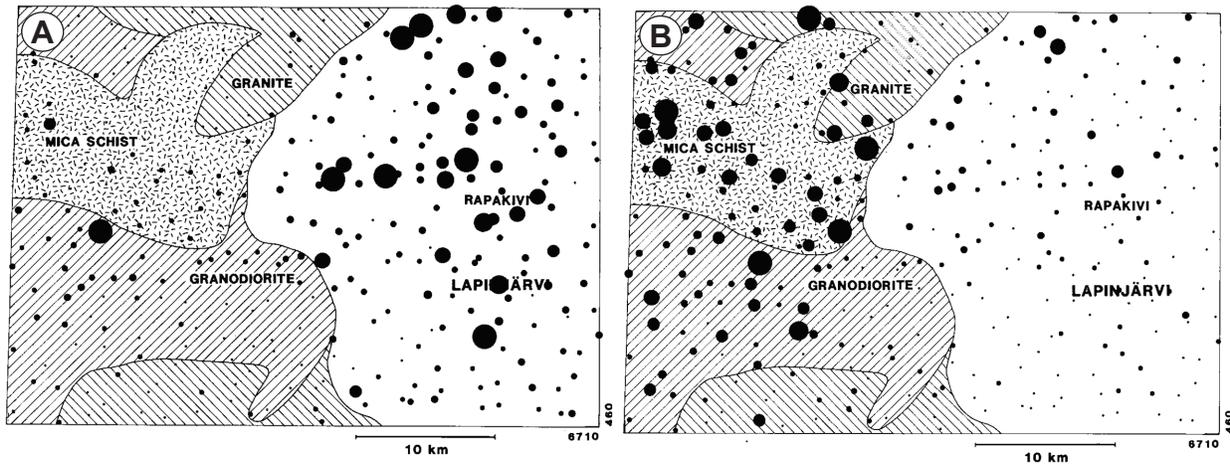


Figure 3. Dotplots of Ba analyzed by “near total” (A) and aqua regia (B) digestions in the silt plus clay fraction of till samples in the Askola region of southeastern Finland. The “near total” digestion highlights barium in the K-feldspar-rich rapakivi granites (A); the aqua regia digestions highlights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

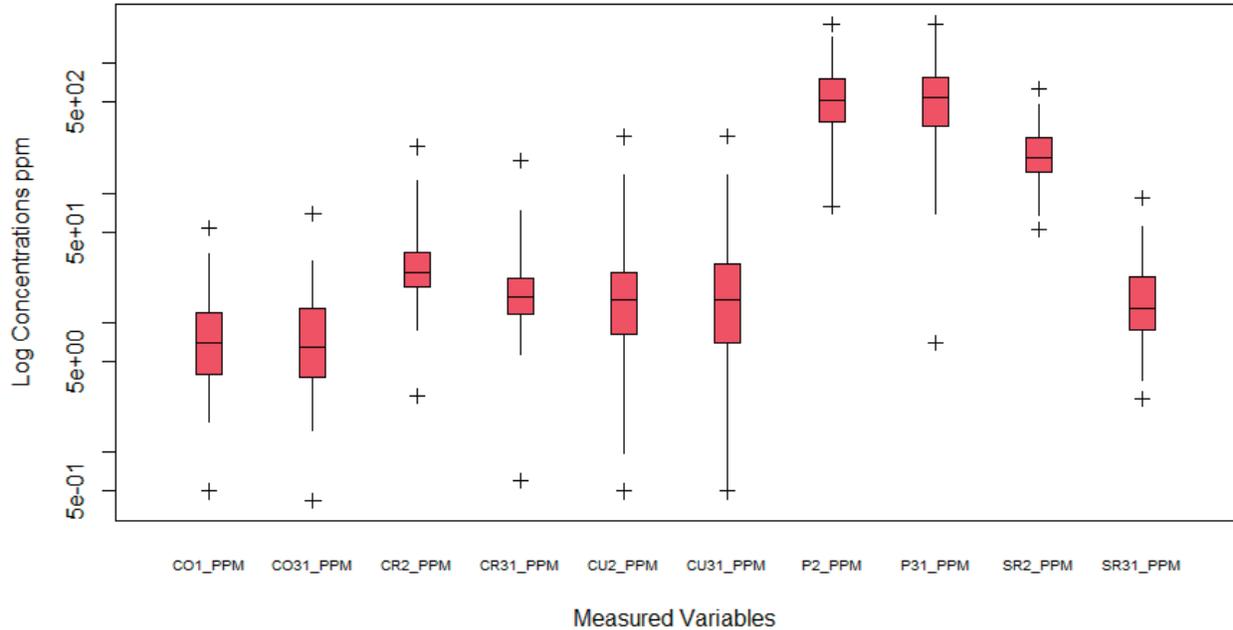


Figure 4. Simple boxplots of some elements that are strongly correlated between the original methods and the aqua regia digestion ICP-MS finish.

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.

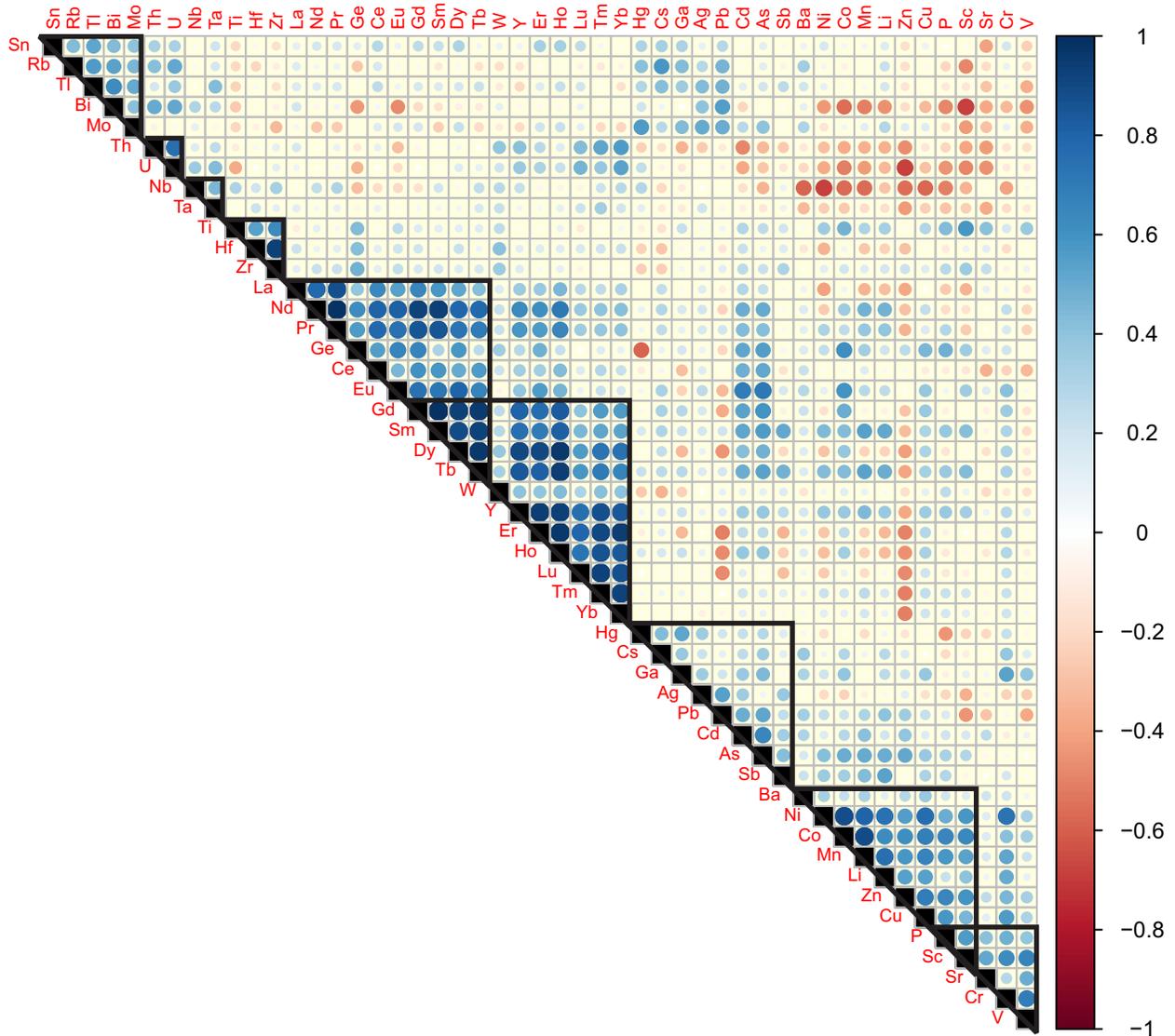


Figure 5. Spearman rank correlation matrix of symmetrical balances (Kynčlova et al., 2017; Garrett et al., 2017) showing inter-element correlations between trace elements measured using aqua regia digestion ICP-MS finish shaded from red (low correlation) to blue (high correlation). The circles' size 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 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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REFERENCES

Batterson, M.J. and Taylor, D.M.

2001: Till geochemistry of the Bonavista area, Newfoundland. Government of Newfoundland and Labrador, Department of Mines and Energy, Geological Survey, Open File NFLD 2734, 181 pages.

2004: Till geochemistry of the central Avalon and Bay de Verde peninsulas, Newfoundland (NTS map sheets 1N/5, 1N/6, 1N/11, 1N/12, 1N/14, 2C/2 and 2C/3). Government of Newfoundland and Labrador, Department of Mines and Energy, Geological Survey, Open File NFLD 2869, 189 pages.

2006: Till geochemistry of the northern Burin Peninsula and adjacent areas, Newfoundland (NTS map areas 1M/7, 1M/8, 1M/9, 1M/10, 1M/15 and 1M/16). Government of Newfoundland and Labrador, Department of Natural Resources, Geological Survey, Open File 1M/0573, 145 pages.

2009: Till geochemistry of the Burin Peninsula, Newfoundland (NTS map areas 1L/13, 1L/14, 1M/2, 1M/3, 1M/4, 1M/6, 1M/7, 1M/10 and 1M/11). Government of Newfoundland and Labrador, Department of Natural Resources, Geological Survey, Open File NFLD/3043, 155 pages.

Burnham, O.M. and Schweyer, J.

2004: Trace element analysis of geological samples by inductively coupled plasma mass spectrometry at the Geoscience Laboratories: Revised capabilities due to improvements to instrumentation. *In* Summary of Field Work and Other Activities 2004. Ontario Geological Survey, Open File Report 6145, pages 54-1 to 54-20.

Campbell, J.E., McMartin I., McCurdy, M.W., Godbout, P.-M., Tremblay, T. and Normandeau, P.X.

2021: Field data and till composition in the GEM-2 Rae Glacial Synthesis Activity field areas, Nunavut and Northwest Territories. Geological Survey of Canada, Open File 8808, 21 pages. <https://doi.org/10.4095/328454>

DiLabio, R.N.W. and Shilts, W.W.

1979: Compositional variation of debris in glaciers, Bylot Island, District of Franklin. *In* Current Research, Part B. Geological Survey of Canada, Paper 78-1B, pages 91-94.

Finch, C.

2022: Replacement and commissioning of the new Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at the Geochemical Laboratory, Geological Survey of Newfoundland and Labrador. *In* Current Research. Government of Newfoundland and Labrador, Department of Industry, Energy and Technology, Geological Survey, Report 22-1, pages 183-187.

- Finch, C., Roldan, R., Walsh, L., Kelly, J. and Amor, S.
2018: Analytical methods for chemical analysis of geological materials. Government of Newfoundland and Labrador, Department of Natural Resources, Geological Survey, Open File NFLD/3316, 67 pages.
- Garrett, R.G., Reimann, C., Hron, K., Kynčlova, P. and Filmoser, P.
2017: Finally, a correlation coefficient that tells the geochemical truth. Explore-Newsletter for the Association of Applied Geochemists, Number 176.
- Haldorsen, S.
1983: The enrichment of quartz in tills. *In* Tills and Related Deposits: Genesis, Petrology, Application, Stratigraphy. *Edited by* E.B. Evenson, Ch. Schlucter and J. Rabassa. Proceedings of the INQUA Symposia on the Genesis and Lithology of Quaternary Deposits, USA 1981, Argentina 1982. A.A. Balkema, Rotterdam. 454 pages.
- Kauranne, K., Salminen, R. and Eriksson, K.
1992: Regolith exploration geochemistry in arctic and temperate terrains. Handbook of Exploration Geochemistry, Volume 5, Elsevier, Amsterdam, 443 pages.
- Kynčlova, P., Hron, K. and Filmoser, P.
2017: Correlation between compositional parts based on symmetric balances. *Mathematical Geosciences*, Volume 49, pages 777-796.
- Lynch, J.
1996: Provisional elemental values for four new geochemical soil and till reference materials TILL-1, TILL-2, TILL-3 and TILL-4. *Geostandards Newsletter*, Volume 20, pages 277-287.
- O'Brien, S.J., Dubé, B. and O'Driscoll, C.F.
1999: High-sulphidation, epithermal-style hydrothermal systems in late Neoproterozoic Avalonian rocks on the Burin Peninsula, Newfoundland: Implications for gold exploration. *In* Current Research. Government of Newfoundland and Labrador, Department of Mines and Energy, Geological Survey, Report 99-1, pages 275-296.
- Sparkes, G.W.
2012: New developments concerning epithermal alteration and related mineralization along the western margin of the Avalon Zone, Newfoundland. *In* Current Research. Newfoundland and Labrador, Department of Natural Resources, Geological Survey, Report 12-1, pages 103-120.
- Sparkes, G.W. and Dunning, G.R.
2014: Late Neoproterozoic epithermal alteration and mineralization in the western Avalon Zone: A summary of mineralogical investigations and new U–Pb geochronological results. *In* Current Research. Government of Newfoundland and Labrador, Department of Natural Resources, Geological Survey, Report 14-1, pages 99-128.

Tyler, G. and Yvon, J.

2003: ICP-OES, ICP-MS and AAS techniques compared. ICP Optical Emission Spectroscopy, Technical Note 05, Jobin Yvon Horiba, pages 1-11.

Wei, T. and Simko, V.

2021: R package 'corrplot': Visualization of a Correlation Matrix. (Version 0.92), <https://github.com/taiyun/corrplot>

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