

# PROVISIONAL ELEMENTAL VALUES FOR FOUR NEW GEOCHEMICAL SOIL AND TILL REFERENCE MATERIALS, TILL-1, TILL-2, TILL-3 AND TILL-4\*

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The collection and preparation of two soil reference samples and two till reference samples are described. Like their predecessors the LKSD series and the STSD series, the TILL series are characterized for total elements and for elements derived by partial extractions. Provisional data are presented for major, minor and trace elements. In addition, information data from a single source are provided for a number of elements derived by EPA digestions 3050 and 3051; these data allow a comparison with other partial extractions reported herein.

Information values from single sources were reported by Lynch (1) for TILL-1, TILL-2, TILL-3 and TILL-4. These four samples, two soils and two tills, complete a series of reference samples of surficial material originally intended for quality control in geochemical exploration studies. Lake sediment and stream sediment samples have been described previously (1).

The number of laboratories providing data for the TILL series has been below expectation and hence the number of determinations for some of the elements in the TILL series is less than for the LKSD and STSD series.

Guidelines for collection and preparation of the TILL series were as follows:

- Samples were to represent different geological areas of Canada.
- The concentration gradients for Ag, As, Au, Co, Cu, Mo, Ni, Rb, W and Zr were to be broadened beyond those of the LKSD and STSD series. In most cases this represented a modest increase in concentration levels for the TILL series.

Highly anomalous samples were to be avoided, if possible.

- Like the sediment series, the TILL samples were to be characterized for major element oxides, total elements and elements by the analysis of partial extractions. The partial extractions would be concentrated hydrochloric-concentrated nitric acids and dilute hydrochloric-dilute nitric acids.

## SOIL AND TILL COLLECTION

For the two soil samples (TILL-1 and TILL-3), the combined B and C horizons were collected using shovels. TILL-1 was collected 25 kilometres north-west of Lanark, Ontario; TILL-3 was collected 8 kilometres east of Cobalt, Ontario. The two till samples (TILL-2 and TILL-4) were collected near Scission's Brook, New Brunswick. At this location, extensive trenching had been done by the mining company that owned the property in order to expose the till. The company had obtained preliminary analyses of till samples collected at various sites within the trenched areas. These analyses were used as guidelines to sampling. The sampling was done by shovelling. No effort was made to collect any particular horizon. In order to augment the molybdenum levels in one of the samples, a small quantity of a molybdenite-bearing soil was collected near an old test pit. Approximately 50 kg of this material were collected. Sample collection locations are shown in Table A.

## SOIL AND TILL PREPARATION

Each sample was dried and prepared separately. For each sample, all of the collected material was spread to a depth of 7.5 to 10 cm over a 6 mil (6/1000") polyethylene sheet and allowed to dry for several weeks at room temperature. Moist air was continually removed by the use of fans. During the drying period, each sample was mixed and agitated with a garden rake in order to speed up drying

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\* Geological Survey of Canada Contribution number 1996701

Table A. Sample collection locations

Sample	NTS Designations	Location	Enriched Elements
TILL-1	31F	Joe Lake, Ontario	Au, Sb
TILL-2	21C	5 km West Scisson's Brook, New Brunswick	As, Cs, Cu, Li, Mo, Sn, W
TILL-3	31M	O'Brien Mine, near Cobalt Ontario	Ag, As, Au
TILL-4	21C	Scisson's Brook, New Brunswick	As, Cs, Cu, Mo, Pb, W
	31C	Molybdenite occurrence near Hull, Québec	

and to remove rocks, twigs and leaves. When dry, each sample was sieved through an 80-mesh (177  $\mu\text{m}$ ) screen. The +80 mesh fraction was discarded. The -80 mesh fraction was ball milled and sieved through a 200 mesh screen (74  $\mu\text{m}$ ). The oversize material from this sieving was retained, ball milled and sieved a second time through the 200 mesh screen. At this point, any oversize fraction (+200 mesh) was discarded. The two -200 mesh fractions were combined and tumbled as a single batch in a conical blender for eight hours.

#### Homogeneity testing

A method described previously by Lynch (1) was employed for homogeneity testing. No changes in the methodology were made.

#### CHEMICAL CHARACTERIZATION

TILL-1, TILL-2, TILL-3 and TILL-4 were characterized by the same method used for the LKSD and STSD samples. Like the sediment series, only a limited number of laboratories, in all 31 laboratories, submitted data for the TILL series, and, hence, the assignment of certified values for the elements is beyond the scope of this work.

The calculation of provisional values for the soil and till reference materials series did not justify a rigorous statistical treatment of the data. The two step trimming method described by Lynch (1) for the LKSD and STSD series was applied to the TILL series without modification.

#### COMPILED DATA

Provisional and informational values for TILL-1 to TILL-4 are contained in Tables 1 to 10 and a summary of them in Tables 11 to 14, with a page guide after each Table number:

Table 1 (page 280). Major and minor elements expressed as oxides of the element.

Table 2 (page 280). Summation of major and minor elements expressed as oxides.

Table 3 (page 280). "Total" elements.

Table 4 (page 282). Summary of "total" values in TILL series.

Table 5 (page 283). Elements derived from the analysis of a partial extraction using concentrated nitric acid and concentrated hydrochloric acid.

Table 6 (page 283). Summary of Table 5.

Table 7 (page 284). Elements derived from the analysis of a partial extraction using dilute nitric acid and dilute hydrochloric acid.

Table 8 (page 284). Summary of Table 7.

Table 9 (page 284). Elements derived by EPA method 3050. These are informational only.

Table 10 (page 285). Elements derived by EPA method 3051. These are informational only.

Table 11 (page 285). Summary of all values, both provisional and informational, for TILL-1.

Table 12 (page 285). Summary of all values, both provisional and informational, for TILL-2.

Table 13 (page 285). Summary of all values, both provisional and informational, for TILL-3.

Table 14 (page 286). Summary of all values, both provisional and informational, for TILL-4.

In Tables 1, 3, 5 and 7,

N = number of laboratories after outliers have been removed;  
n = number of determinations after outliers have been removed;  
 $\bar{x}$  = mean;  $\sigma$  = standard deviation.

Qualified = number of values reported below the detection limit. If more than 50% of the values from a laboratory were below the detection limit for a given element in a particular sample, all of the values for that element in that sample were deleted and did not appear in either of the last two columns. If the qualified values were not deleted, they were set arbitrarily to one half of the detection limit.

Outliers = values which were deleted by the two step trimming method.

## DATA EVALUATION

For the data in Tables 3, 5 and 7 there were no restrictions placed on the initial selection of data. The sources of data for the major and minor elements expressed as oxides were restricted to those laboratories who reported these elements as a package. When major and minor element data were acquired as part of a trace element package (e.g. Fe, Mn), these data were excluded from the oxide compilation. If warranted, a second compilation expressed as % or ppm element involving the combined oxide and non-oxide data was made. In Table 1, N and n appear incomplete for SiO<sub>2</sub>, MnO and LOI (1000°C). Some of the laboratories providing oxide data omitted data for the two elements and LOI (1000°C) and hence N and n are low.

Two sets of informational values are contained in Tables 9 and 10. These data are from a single source and represent single measurements, rather than averages of multiple determinations. Hence they should be treated with discretion. The data in Table 9 were obtained by decomposing the sample by EPA method 3050. The data in Table 10 were obtained by decomposing the sample by EPA method 3051.

EPA method 3050 consists of heating a 1 gm sample with 15 mL concentrated HNO<sub>3</sub> and 6 mL 30% H<sub>2</sub>O<sub>2</sub> for four hours at 100°C on a hot plate. After cooling, the resulting solution is diluted to 50 mL for analysis by inductively coupled plasma-emission spectroscopy.

EPA method 3051 consists of heating a 0.3 gm sample with 10 mL concentrated HNO<sub>3</sub> in a microwave oven at high power (600 watts) for 15 minutes. After heating, the sample solution is cooled and diluted to 50 mL and analysed by ICP-ES.

## FINAL REMARKS

### Notes on sample collection

In the section "Guidelines for Collection and Preparation of the TILL Series" it was stated that attempts would be made to broaden the concentration gradients of a number of elements. This objective was partially realized for As, Au, Cu, Mo, Rb, W and Zr. Unfortunately there was very little improvement for Ag, Co and Ni. In the case of TILL-1, a detailed survey was done on the proposed site which was adjacent to a gold occurrence. Analyses of many samples from the site suggested that a value of 25 ppb Au should be achievable. The provisional Au value for TILL-1 is 13 ppb; collection of this sample introduced considerable dilution. Attempting to target specific elemental concentrations for bulk samples can be a difficult task.

### Summary of "Total" elements methods

#### *Solution Methods*

Methods of dissolution involved HF-HNO<sub>3</sub>-HClO<sub>4</sub> or HF-HNO<sub>3</sub>-HCl acid extraction or LiBO<sub>2</sub>/Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> fusion and subsequent dissolution in dilute HNO<sub>3</sub>.

Methods of determination included

- atomic absorption spectroscopy (AAS)
- graphite furnace atomic absorption spectrometry (GF-AAS)
- hydride atomic absorption spectrometry (HY-AAS)
- inductively coupled plasma-emission spectrometry (ICP-ES)
- inductively coupled plasma-mass spectrometry (ICP-MS).

Data for some elements measured by solution methods involving HF and mineral acids exhibited a negative bias when compared to data obtained by borate fusion solution methodology or non solution methodology. Elements which

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*Text continues on page 286*

Table 1. Major and Minor Elements (%)

El./sample	N	n	$\bar{x}$	$\sigma$	Qual.	Outliers
SiO <sub>2</sub> /TILL-1	8	29	60.9	0.2	0	4
SiO <sub>2</sub> /TILL-2	7	29	60.8	0.2	0	3
SiO <sub>2</sub> /TILL-3	7	26	69.1	0.3	0	6
SiO <sub>2</sub> /TILL-4	7	31	65.0	0.4	0	1
Al <sub>2</sub> O <sub>3</sub> /TILL-1	10	40	13.7	0.1	0	9
Al <sub>2</sub> O <sub>3</sub> /TILL-2	9	39	16.0	0.1	0	9
Al <sub>2</sub> O <sub>3</sub> /TILL-3	9	41	12.2	0.1	0	8
Al <sub>2</sub> O <sub>3</sub> /TILL-4	9	41	14.4	0.2	0	8
Fe <sub>2</sub> O <sub>3</sub> (T)/TILL-1	10	40	6.82	0.20	0	0
Fe <sub>2</sub> O <sub>3</sub> (T)/TILL-2	9	37	5.39	0.19	0	3
Fe <sub>2</sub> O <sub>3</sub> (T)/TILL-3	10	48	3.92	0.12	0	2
Fe <sub>2</sub> O <sub>3</sub> (T)/TILL-4	10	49	5.63	0.21	0	1
MgO/TILL-1	9	46	2.15	0.07	0	4
MgO/TILL-2	9	47	1.83	0.06	0	3
MgO/TILL-3	9	43	1.71	0.05	0	7
MgO/TILL-4	9	44	1.26	0.04	0	6
CaO/TILL-1	10	56	2.72	0.10	0	4
CaO/TILL-2	10	58	1.27	0.07	0	2
CaO/TILL-3	10	57	2.63	0.10	0	3
CaO/TILL-4	11	59	1.25	0.05	0	1
Na <sub>2</sub> O/TILL-1	10	54	2.71	0.10	0	6
Na <sub>2</sub> O/TILL-2	10	52	2.19	0.17	0	8
Na <sub>2</sub> O/TILL-3	10	54	2.64	0.11	0	6
Na <sub>2</sub> O/TILL-4	10	53	2.46	0.11	0	7
K <sub>2</sub> O/TILL-1	11	59	2.22	0.10	0	1
K <sub>2</sub> O/TILL-2	11	58	3.07	0.12	0	2
K <sub>2</sub> O/TILL-3	11	56	2.42	0.10	0	4
K <sub>2</sub> O/TILL-4	11	57	3.25	0.12	0	3
MnO/TILL-1	7	28	0.18	0.01	0	0
MnO/TILL-2	7	26	0.10	0.00	0	2
MnO/TILL-3	7	28	0.06	0.01	0	0
MnO/TILL-4	7	28	0.06	0.00	0	0
TiO <sub>2</sub> /TILL-1	11	57	0.98	0.04	0	1
TiO <sub>2</sub> /TILL-2	10	56	0.88	0.03	0	2
TiO <sub>2</sub> /TILL-3	10	52	0.49	0.02	0	6
TiO <sub>2</sub> /TILL-4	11	58	0.81	0.03	0	0
P <sub>2</sub> O <sub>5</sub> /TILL-1	9	53	0.22	0.01	0	6
P <sub>2</sub> O <sub>5</sub> /TILL-2	9	52	0.17	0.02	0	7
P <sub>2</sub> O <sub>5</sub> /TILL-3	8	53	0.11	0.01	0	6
P <sub>2</sub> O <sub>5</sub> /TILL-4	9	53	0.20	0.01	0	6
LOI (1000°C)						
LOI/TILL-1	5	29	7.3	0.2	0	1
LOI/TILL-2	5	30	8.1	0.3	0	0
LOI/TILL-3	5	30	4.6	0.2	0	0
LOI/TILL-4	5	30	5.7	0.2	0	0

Table 2. Summation of major and minor elements expressed as oxides (%)

	TILL-1	TILL-2	TILL-3	TILL-4
SiO <sub>2</sub>	60.9	60.8	69.1	65.0
Al <sub>2</sub> O <sub>3</sub>	13.7	16.0	12.2	14.4
Fe <sub>2</sub> O <sub>3</sub> (T)	6.82	5.39	3.92	5.63
MgO	2.15	1.83	1.71	1.26
CaO	2.72	1.27	2.63	1.25
Na <sub>2</sub> O	2.71	2.19	2.64	2.46
K <sub>2</sub> O	2.22	3.07	2.42	3.25
MnO	0.18	0.10	0.06	0.06
TiO <sub>2</sub>	0.98	0.88	0.49	0.81
P <sub>2</sub> O <sub>5</sub>	0.22	0.17	0.11	0.20
LOI (1000°C)	7.3	8.1	4.6	5.7
Sum	99.90	99.80	99.88	100.02

Table 3. "Total" elements (ppm)

El./sample	N	n	$\bar{x}$	$\sigma$	Qual.	Outliers
As/TILL-1	7	58	18	1	0	0
As/TILL-2	7	59	26	2	0	1
As/TILL-3	6	49	87	4	0	3
As/TILL-4	5	59	111	6	0	4
Au (ppb)						
Au/TILL-1	9	65	13	4	0	7
Au/TILL-2	7	52	2	2	14	6
Au/TILL-3	9	65	6	4	7	4
Au/TILL-4	9	77	5	3	11	3
Ba/TILL-1	16	121	702	59	0	15
Ba/TILL-2	17	134	540	56	0	4
Ba/TILL-3	16	117	489	36	0	12
Ba/TILL-4	17	132	395	37	0	9
Be/TILL-1	4	26	2.4	0.6	0	1
Be/TILL-2	5	28	4.0	0.5	0	0
Be/TILL-3	4	27	2.0	0.5	0	0
Be/TILL-4	4	27	3.7	0.5	0	0
Bi/TILL-1	4	25	<5	-	19	-
Bi/TILL-2	4	25	<5	-	17	-
Bi/TILL-3	4	25	<5	-	20	-
Bi/TILL-4	3	23	40	3	0	2
Br/TILL-1	5	44	6.4	0.6	0	3
Br/TILL-2	5	49	12.2	1.1	0	0
Br/TILL-3	5	40	4.5	0.5	0	1
Br/TILL-4	5	51	8.6	0.9	0	1
Ce/TILL-1	11	75	71	6	0	10
Ce/TILL-2	11	79	98	7	0	8
Ce/TILL-3	11	74	42	5	0	5
Ce/TILL-4	11	81	78	7	0	9

Table 3 (cont'd). "Total" elements (ppm)

El./sample	N	n	$\bar{x}$	$\sigma$	Qual.	Outliers
Co/TILL-1	13	95	18	2	0	13
Co/TILL-2	13	96	15	2	0	10
Co/TILL-3	13	96	15	2	0	6
Co/TILL-4	13	94	8	2	3	15
Cr/TILL-1	10	58	65	6	0	7
Cr/TILL-2	10	61	74	8	0	6
Cr/TILL-3	10	56	123	14	0	4
Cr/TILL-4	10	66	53	10	0	4
Cs/TILL-1	4	36	1.0	0.2	0	1
Cs/TILL-2	7	57	12	1	0	3
Cs/TILL-3	5	41	1.7	0.4	0	1
Cs/TILL-4	7	59	12	1	0	4
Cu/TILL-1	9	48	47	4	0	5
Cu/TILL-2	9	52	150	10	0	0
Cu/TILL-3	9	49	22	5	0	4
Cu/TILL-4	9	53	237	17	0	0
Eu/TILL-1	7	50	1.3	0.5	9	1
Eu/TILL-2	7	53	1.0	0.5	20	0
Eu/TILL-3	6	35	<1.0	-	23	-
Eu/TILL-4	7	56	<1.0	-	32	-
Er/TILL-1	2	4	3.6	0.5	0	0
Er/TILL-2	2	4	3.7	0.6	0	0
Er/TILL-3	2	4	1.4	0.1	0	0
Er/TILL-4	2	4	3.2	0.1	0	0
Fe (%)						
Fe/TILL-1	17	98	4.81	0.22	0	9
Fe/TILL-2	16	97	3.84	0.17	0	12
Fe/TILL-3	17	88	2.78	0.12	0	13
Fe/TILL-4	17	105	3.97	0.19	0	7
Hf/TILL-1	8	62	13	1	0	3
Hf/TILL-2	8	66	11	1	0	1
Hf/TILL-3	8	58	8	2	0	1
Hf/TILL-4	8	69	10	1	0	1
La/TILL-1	14	100	28	2	0	8
La/TILL-2	14	101	44	4	0	9
La/TILL-3	14	96	21	2	0	6
La/TILL-4	14	108	41	4	0	5
Li/TILL-1	5	35	15	1	0	0
Li/TILL-2	5	35	47	4	0	0
Li/TILL-3	5	32	21	2	0	3
Li/TILL-4	4	34	30	3	0	1
LOI (500°C) (%)						
LOI/TILL-1	3	27	6.3	0.5	0	1
LOI/TILL-2	3	26	6.8	0.5	0	2
LOI/TILL-3	3	25	3.6	0.4	0	3
LOI/TILL-4	3	26	4.4	0.3	0	2

Table 3 (cont'd). "Total" elements (ppm)

El./sample	N	n	$\bar{x}$	$\sigma$	Qual.	Outliers
Lu/TILL-1	4	39	0.6	0.1	1	4
Lu/TILL-2	3	35	0.6	0.2	0	0
Lu/TILL-3	3	30	0.2	0.1	6	0
Lu/TILL-4	4	48	0.5	0.2	4	0
Mn/TILL-1	10	46	1420	75	0	5
Mn/TILL-2	8	42	780	28	0	8
Mn/TILL-3	9	45	520	39	0	6
Mn/TILL-4	9	45	490	30	0	6
Mo/TILL-1	6	53	2	1	9	1
Mo/TILL-2	9	74	14	2	0	1
Mo/TILL-3	5	38	2	1	6	0
Mo/TILL-4	9	77	16	2	0	1
Nb/TILL-1	6	37	10	2	0	1
Nb/TILL-2	6	36	20	2	0	2
Nb/TILL-3	6	36	7	2	1	2
Nb/TILL-4	5	35	15	2	0	1
Nd/TILL-1	3	14	26	2	0	0
Nd/TILL-2	3	14	36	3	0	0
Nd/TILL-3	3	13	16	1	0	1
Nd/TILL-4	3	14	30	2	0	0
Ni/TILL-1	9	57	24	4	0	4
Ni/TILL-2	9	53	32	3	0	7
Ni/TILL-3	9	52	39	7	0	9
Ni/TILL-4	9	57	17	3	0	4
P/TILL-1	10	60	930	60	0	9
P/TILL-2	10	62	750	80	0	7
P/TILL-3	9	62	490	40	0	7
P/TILL-4	9	60	880	50	0	9
Pb/TILL-1	9	46	22	3	0	6
Pb/TILL-2	9	50	31	3	0	2
Pb/TILL-3	8	49	26	3	0	3
Pb/TILL-4	9	48	50	4	0	4
Rb/TILL-1	10	86	44	6	0	4
Rb/TILL-2	10	81	143	12	0	11
Rb/TILL-3	10	87	55	7	0	7
Rb/TILL-4	10	86	161	15	0	9
S (%)						
S/TILL-1	3	14	<0.05	-	11	-
S/TILL-2	3	14	<0.05	-	11	-
S/TILL-3	3	14	<0.05	-	14	-
S/TILL-4	2	13	0.08	0.01	0	1
Sb/TILL-1	6	48	7.8	0.5	0	0
Sb/TILL-2	5	46	0.8	0.1	0	3
Sb/TILL-3	5	41	0.9	0.1	0	0
Sb/TILL-4	6	48	1.0	0.1	0	5

Table 3 (cont'd). "Total" elements (ppm)

El./sample	N	n	$\bar{x}$	$\sigma$	Qual.	Outliers
Sc/TILL-1	8	64	13	2	0	0
Sc/TILL-2	8	64	12	1	0	2
Sc/TILL-3	8	55	10	1	0	3
Sc/TILL-4	8	69	10	1	0	0
Sm/TILL-1	7	45	5.9	0.4	0	6
Sm/TILL-2	7	50	7.4	0.6	0	3
Sm/TILL-3	7	42	3.3	0.3	0	3
Sm/TILL-4	7	48	6.1	0.4	0	8
Sr/TILL-1	9	61	291	10	0	8
Sr/TILL-2	9	65	144	8	0	4
Sr/TILL-3	9	61	300	12	0	8
Sr/TILL-4	9	64	109	11	0	5
Ta/TILL-1	6	47	0.7	0.1	0	1
Ta/TILL-2	5	47	1.9	0.2	0	3
Ta/TILL-3	6	41	<0.5	-	19	-
Ta/TILL-4	5	52	1.6	0.2	0	1
Tb/TILL-1	6	48	1.1	0.2	0	0
Tb/TILL-2	6	48	1.2	0.2	0	2
Tb/TILL-3	6	42	<0.5	-	30	-
Tb/TILL-4	6	53	1.1	0.2	0	0
Tb/TILL-1	8	58	5.6	0.5	0	10
Tb/TILL-2	8	67	18.4	1.4	0	3
Tb/TILL-3	8	55	4.6	0.4	2	7
Tb/TILL-4	6	60	17.4	1.4	0	3
Ti/TILL-1	10	54	5990	210	0	4
Ti/TILL-2	10	56	5300	190	0	2
Ti/TILL-3	10	52	2910	90	0	6
Ti/TILL-4	10	51	4840	130	0	7
U/TILL-1	6	53	2.2	0.3	0	5
U/TILL-2	7	58	5.7	0.4	0	12
U/TILL-3	7	49	2.1	0.2	0	3
U/TILL-4	7	65	5.0	0.5	0	8
V/TILL-1	11	72	99	10	0	0
V/TILL-2	11	70	77	10	0	2
V/TILL-3	11	69	62	6	0	3
V/TILL-4	10	70	67	7	0	2
W/TILL-1	8	48	<1	-	40	0
W/TILL-2	6	49	5	1	0	1
W/TILL-3	6	42	<1	-	36	0
W/TILL-4	9	81	204	24	0	2
Y/TILL-1	6	34	38	4	0	3
Y/TILL-2	6	36	40	4	0	1
Y/TILL-3	5	36	17	3	0	0
Y/TILL-4	6	35	33	3	0	2
Yb/TILL-1	8	52	3.9	0.4	0	2

Table 3 (cont'd). "Total" elements (ppm)

El./sample	N	n	$\bar{x}$	$\sigma$	Qual.	Outliers
Yb/TILL-2	8	55	3.7	0.5	0	1
Yb/TILL-3	5	20	1.5	0.2	0	0
Yb/TILL-4	8	55	3.4	0.5	1	4
Zn/TILL-1	12	69	98	10	0	4
Zn/TILL-2	12	64	130	8	0	8
Zn/TILL-3	11	68	56	6	0	5
Zn/TILL-4	12	67	70	7	0	6
Zr/TILL-1	11	72	502	58	0	11
Zr/TILL-2	9	57	390	39	2	9
Zr/TILL-3	9	51	230	24	3	12
Zr/TILL-4	8	55	385	34	5	9

Table 4. Summary of "Total" elements in TILL series (in ppm unless otherwise noted)

	TILL-1	TILL-2	TILL-3	TILL-4
As	18	26	87	111
Au (ppb)	13	2	6	5
Ba	702	540	489	395
Be	2.4	4.0	2.0	3.7
Bi	<5	<5	<5	40
Br	6.4	12.2	4.5	8.6
Ce	71	98	42	78
Co	18	15	15	8
Cr	65	74	123	53
Cs	1.0	12.	1.7	12
Cu	47	150	22	237
Eu	1.3	1.0	<1.0	<1.0
Er	3.6	3.7	1.4	3.2
Fe (%)	4.81	3.84	2.78	3.97
Hf	13	11	8	10
La	28	44	21	41
Li	15	47	21	30
LOI (500°C) %	6.3	6.8	3.6	4.4
Lu	0.6	0.6	0.2	0.5
Mn	1420	780	520	490
Mo	2	14	2	16
Nb	10	20	7	15
Nd	26	36	16	30
Ni	24	32	39	17
P	930	750	490	880
Pb	22	31	26	50
Rb	44	143	55	161
S (%)	<0.05	<0.05	<0.05	0.08
Sb	7.8	0.8	0.9	1.0
Sc	13	12	10	10
Sm	5.9	7.4	3.3	6.1
Sr	291	144	300	109
Ta	0.7	1.9	<0.5	1.6
Tb	1.1	1.2	<0.5	1.1

Table 4 (cont'd). Summary of "Total" elements in TILL series (in ppm unless otherwise noted)

	TILL-1	TILL-2	TILL-3	TILL-4
Th	5.6	18.4	4.6	17.4
Ti	5990	5300	2910	4840
U	2.2	5.7	2.1	5.0
V	99	77	62	67
W	<1	5	<1	204
Y	38	40	17	33
Yb	3.9	3.7	1.5	3.4
Zn	98	130	56	70
Zr	502	390	230	385

Table 5. Partial extraction elements (ppm); concentrated HNO<sub>3</sub>-concentrated HCl (in ppm unless otherwise noted)

El./sample	N	n	$\bar{x}$	$\sigma$	Qual.	Outliers
Ag/TILL-1	4	28	0.2	0.1	6	0
Ag/TILL-2	5	29	0.2	0.1	10	0
Ag/TILL-3	7	47	1.6	0.2	0	4
Ag/TILL-4	4	28	<0.2	-	19	-
As/TILL-1	6	36	13	4	0	3
As/TILL-2	6	39	22	11	0	0
As/TILL-3	6	39	84	12	0	0
As/TILL-4	6	39	102	13	0	0
Ba/TILL-1	4	22	84	6	0	0
Ba/TILL-2	4	22	95	7	0	1
Ba/TILL-3	4	18	43	2	0	4
Ba/TILL-4	4	20	71	4	0	2
Bi/TILL-1	3	18	<3	-	9	-
Bi/TILL-2	4	17	4	2	3	2
Bi/TILL-3	3	18	<3	-	14	-
Bi/TILL-4	4	18	44	4	0	1
Cd/TILL-1	3	24	<0.2	-	11	-
Cd/TILL-2	3	24	0.3	0.2	7	0
Cd/TILL-3	3	24	<0.2	-	14	-
Cd/TILL-4	3	24	<0.2	-	14	-
Co/TILL-1	8	53	12	1	0	6
Co/TILL-2	8	53	13	1	0	7
Co/TILL-3	8	55	11	1	0	4
Co/TILL-4	8	57	6	2	0	2
Cr/TILL-1	4	17	30	3	0	0
Cr/TILL-2	4	18	40	3	0	0
Cr/TILL-3	4	17	73	8	0	0
Cr/TILL-4	4	17	26	2	0	0
Cu/TILL-1	7	52	48	2	0	6
Cu/TILL-2	7	56	149	8	0	3
Cu/TILL-3	7	56	23	1	0	2
Cu/TILL-4	7	56	254	15	0	2

Table 5 (cont'd). Partial extraction elements; concentrated HNO<sub>3</sub>-concentrated HCl (in ppm unless otherwise noted)

El./sample	N	n	$\bar{x}$	$\sigma$	Qual.	Outliers
Fe (%)						
Fe/TILL-1	5	43	3.1	0.2	0	1
Fe/TILL-2	5	45	3.2	0.2	0	0
Fe/TILL-3	5	39	2.0	0.1	0	5
Fe/TILL-4	5	43	3.3	0.2	0	1
Hg (ppb)						
Hg/TILL-1	4	31	92	11	0	3
Hg/TILL-2	4	32	74	13	0	2
Hg/TILL-3	4	33	107	15	0	1
Hg/TILL-4	4	34	39	12	0	0
Mn/TILL-1	4	35	950	70	0	5
Mn/TILL-2	4	40	530	80	0	1
Mn/TILL-3	4	40	310	40	0	0
Mn/TILL-4	4	40	260	40	0	0
Mo/TILL-1	7	60	<2	-	54	-
Mo/TILL-2	8	60	11	2	0	0
Mo/TILL-3	7	59	<2	-	45	-
Mo/TILL-4	8	58	14	1	0	3
Ni/TILL-1	9	65	18	2	0	2
Ni/TILL-2	9	66	31	3	0	2
Ni/TILL-3	9	67	32	3	0	0
Ni/TILL-4	9	66	15	2	0	1
Pb/TILL-1	7	49	12	1	0	0
Pb/TILL-2	7	49	21	2	0	1
Pb/TILL-3	7	48	16	1	0	1
Pb/TILL-4	7	49	36	3	0	0
V/TILL-1	9	68	48	8	0	0
V/TILL-2	9	65	38	4	0	4
V/TILL-3	9	68	33	5	0	1
V/TILL-4	9	64	38	4	0	5
Zn/TILL-1	7	53	70	7	0	2
Zn/TILL-2	7	51	116	6	0	5
Zn/TILL-3	7	54	43	5	0	1
Zn/TILL-4	7	55	63	6	0	0

Table 6. Summary of partial extraction elements; concentrated HNO<sub>3</sub>-concentrated HCl (in ppm unless otherwise noted)

	TILL-1	TILL-2	TILL-3	TILL-4
Ag	0.2	0.2	1.6	<0.2
As	13	22	84	102
Ba	84	95	43	71
Bi	<3	4	<3	44
Cd	<0.2	0.3	<0.2	<0.2

Table 6 (cont'd). Summary of partial extraction elements; concentrated HNO<sub>3</sub>-concentrated HCl (in ppm unless otherwise noted)

	TILL-1	TILL-2	TILL-3	TILL-4
Co	12	13	11	6
Cr	30	40	73	26
Cu	48	149	23	254
Fe (%)	3.1	3.2	2.0	3.3
Hg (ppb)	92	74	107	39
Mn	950	530	310	260
Mo	<2	11	<2	14
Ni	18	31	32	15
Pb	12	21	16	36
V	48	38	33	38
Zn	70	116	43	63

Table 7. Partial extraction elements; dilute HNO<sub>3</sub>-dilute HCl (in ppm unless otherwise noted)

El./sample	N	n	$\bar{x}$	$\sigma$	Qual.	Outliers
Ag/TILL-1	5	50	<0.2	-	5	-
Ag/TILL-2	5	50	<0.2	-	4	-
Ag/TILL-3	5	49	1.4	0.2	0	1
Ag/TILL-4	5	50	<0.2	-	7	-
Co/TILL-1	5	50	12	1	0	0
Co/TILL-2	5	50	12	2	0	0
Co/TILL-3	5	50	10	1	0	0
Co/TILL-4	5	50	6	2	0	0
Cu/TILL-1	4	37	49	2	0	3
Cu/TILL-2	4	39	152	6	0	1
Cu/TILL-3	4	40	23	1	0	0
Cu/TILL-4	4	37	252	7	0	3
Fe (%)						
Fe/TILL-1	3	30	3.4	0.4	0	0
Fe/TILL-2	3	30	3.4	0.4	0	0
Fe/TILL-3	3	30	2.2	0.2	0	0
Fe/TILL-4	3	30	3.5	0.4	0	0
Mn/TILL-1	3	29	1020	90	0	1
Mn/TILL-2	3	30	570	60	0	0
Mn/TILL-3	3	28	310	30	0	2
Mn/TILL-4	3	30	260	40	0	0
Mo/TILL-1	3	30	1	0	0	0
Mo/TILL-2	3	30	13	1	0	0
Mo/TILL-3	3	30	1	0	0	0
Mo/TILL-4	3	30	15	1	0	0
Ni /TILL-1	5	50	17	2	0	0
Ni /TILL-2	5	50	30	3	0	0
Ni /TILL-3	5	49	32	3	0	1
Ni /TILL-4	5	49	14	2	0	1

Table 7 (cont'd). Partial extraction elements; dilute HNO<sub>3</sub>-dilute HCl (in ppm unless otherwise noted)

El./sample	N	n	$\bar{x}$	$\sigma$	Qual.	Outliers
Pb /TILL-1	5	46	14	3	0	4
Pb /TILL-2	5	50	24	4	0	0
Pb /TILL-3	5	49	17	3	0	1
Pb /TILL-4	5	48	37	5	0	2
Zn/TILL-1	5	50	71	5	0	0
Zn/TILL-2	5	48	116	7	0	2
Zn/TILL-3	5	49	43	5	0	1
Zn/TILL-4	5	48	62	4	0	2

Table 8. Summary of partial extraction elements; dilute HNO<sub>3</sub>-dilute HCl (in ppm unless otherwise noted)

	TILL-1	TILL-2	TILL-3	TILL-4
Ag	<0.2	<0.2	1.4	<0.2
Co	12	12	10	6
Cu	49	152	23	252
Fe (%)	3.4	3.4	2.2	3.5
Mn	1020	570	310	260
Mo	1	13	1	15
Ni	17	30	32	14
Pb	14	24	17	37
Zn	71	116	43	62

Table 9. EPA 3050 Digestion - ICP-ES Analysis (all values in ppm)

Element	TILL - 1	TILL - 2	TILL - 3	TILL - 4
Al	18883	32600	10750	25200
Ba	84.3	104.6	46.4	75.1
Be	1.1	2.1	0.8	1.6
Cd	<0.33	<0.33	<0.33	<0.33
Ca	4145	1940	6240	1438
Cr	29.3	39.3	66.7	25.8
Cu	44.0	162	17.6	266
Fe	29167	33967	19900	32533
Pb	24.0	35.7	24.0	50.0
Mg	6250	7547	6510	5470
Mn	1060	601	294	243
Mo	8.7	18.7	5.0	20.7
Ni	14.0	27.5	28.0	11.0
P	915	856	470	1150
K	1188	4355	1220	3915
Na	530	527	336	313
V	89	107.2	71.6	82.9
Zn	65.2	111.0	42.5	59.0
Co	11.7	12.5	10.2	5.8



Table 10. EPA 3051 Digestion - ICP-ES Analysis (all values in ppm)

Element	TILL-1	TILL-2	TILL-3	TILL-4
Al	18050	27550	12000	20400
Ba	77.8	60.8	49.2	102
Be	<0.2	1.7	<0.2	<0.2
Cd	<0.35	<0.3	<0.35	<0.3
Ca	3817	1640	5660	1565
Cr	29.3	34.7	64.7	24.3
Cu	44.8	176	16.5	332
Fe	37900	38600	21000	40500
Pb	<10.0	31.5	23	42
Mg	6990	8525	7445	5570
Mn	1060	588	317	280
Mo	<2.5	<1.7	6.0	22.5
Ni	18.7	29.5	26.5	11.0
P	834	540	457	1260
K	640	3370	964	3115
Na	575	450	427	485
V	70	111.2	66.1	88.0
Zn	69.8	112.7	42.7	57.6
Co	12.3	15.5	14.8	8.1

Table 12. TILL-2. Summary of total and partial extraction values (all values are in ppm unless otherwise noted)

Element	Total	Conc. HNO <sub>3</sub> -HCl	Dilute HNO <sub>3</sub> -HCl	EPA 3050	EPA 3051
Ag	-	0.2	<0.2	-	-
Al (%)	8.5	-	-	3.26	2.76
As	26	22	-	-	-
Ba	540	95	-	104.6	60.8
Be	4.0	-	-	2.1	1.7
Bi	<5	4	-	-	-
Ca (%)	0.91	-	-	0.19	0.16
Cd	-	0.3	-	<0.33	<0.3
Co	15	13	12	12.5	15.5
Cr	74	40	-	39.3	34.7
Cu	150	149	152	162	176
Fe (%)	3.77	3.2	3.4	3.4	3.86
K (%)	2.55	-	-	0.44	0.34
Mg (%)	1.10	-	-	0.75	0.85
Mn	780	530	570	601	588
Mo	14	11	13	18.7	<1.7
Na (%)	1.62	-	-	0.05	0.04
Ni	32	31	30	27.5	29.5
P	750	-	-	856	540
Pb	31	21	24	35.7	31.5
V	77	38	-	107.2	111.2
Zn	130	116	116	111.0	112.7

Table 11. TILL-1. Summary of total and partial extraction values (all values are in ppm unless otherwise noted)

Element	Total	Conc. HNO <sub>3</sub> -HCl	Dilute HNO <sub>3</sub> -HCl	EPA 3050	EPA 3051
Ag	-	0.2	<0.2	-	-
Al (%)	7.3	-	-	1.89	1.80
As	18	13	-	-	-
Ba	702	84	-	84.3	77.8
Be	2.4	-	-	1.1	<0.2
Bi	<5	<3	-	-	-
Ca (%)	1.94	-	-	0.41	0.38
Cd	-	<0.2	-	<0.33	-
Co	18	12	12	11.7	12.3
Cr	65	30	-	29.3	29.3
Cu	47	48	49	44.0	44.8
Fe (%)	4.77	3.1	3.4	2.92	3.79
K (%)	1.84	-	-	0.12	0.06
Mg (%)	1.30	-	-	0.62	0.70
Mn	1420	950	1020	1060	-
Mo	2	<2	1	8.7	<2.5
Na (%)	2.01	-	-	0.05	0.06
Ni	24	18	17	14	18.7
P	930	-	-	915	834
Pb	22	12	14	24	<10
V	99	48	-	89	70
Zn	98	70	71	65.2	69.8

Table 13. TILL-3. Summary of total and partial extraction values (all values are in ppm unless otherwise noted)

Element	Total	Conc. HNO <sub>3</sub> -HCl	Dilute HNO <sub>3</sub> -HCl	EPA 3050	EPA 3051
Ag	-	1.6	1.4	-	-
Al (%)	6.5	-	-	1.08	1.20
As	87	84	-	-	-
Ba	489	43	-	46.4	49.2
Be	2.0	-	-	0.8	<0.2
Bi	<5	<3	-	-	-
Ca (%)	1.88	-	-	0.62	0.57
Cd	-	<0.2	-	<0.33	<0.35
Co	15	11	10	10.2	14.8
Cr	123	73	-	66.7	64.7
Cu	22	23	23	17.6	16.5
Fe (%)	2.74	2.0	2.2	1.99	2.10
K (%)	2.01	-	-	0.12	0.10
Mg (%)	1.03	-	-	0.65	0.74
Mn	520	310	310	294	317
Mo	2	<2	1	5	6.0
Na (%)	1.96	-	-	0.03	0.04
Ni	39	32	32	28.0	26.5
P	490	-	-	470	457
Pb	26	16	17	24	23
V	62	33	-	71.6	66.1
Zn	56	43	43	42.5	42.7

Table 14. TILL-4. Summary of total and partial extraction values (all values are in ppm unless otherwise noted)

Element	Total	Conc. HNO <sub>3</sub> -HCl	Dilute HNO <sub>3</sub> -HCl	EPA 3050	EPA 3051
Ag	-	<0.2	<0.2	-	-
Al (%)	7.6	-	-	2.52	2.04
As	111	102	-	-	-
Ba	395	71	-	75.1	102
Be	3.7	-	-	1.6	<0.2
Bi	40	44	-	-	-
Ca (%)	0.89	-	-	0.14	0.16
Cd	-	<0.2	-	<0.33	<0.3
Co	8	6	6	5.8	8.1
Cr	53	26	-	25.8	24.3
Cu	237	254	252	266	332
Fe (%)	3.94	3.3	3.5	3.25	4.05
K (%)	2.70	-	-	0.39	0.31
Mg (%)	0.76	-	-	0.55	0.56
Mn	490	260	260	243	280
Mo	16	14	15	20.7	22.5
Na (%)	1.83	-	-	0.03	0.05
Ni	17	15	14	11.0	11.0
P	880	-	-	1150	-
1260	-	-	-	-	-
Pb	50	36	37	50	42
V	67	38	-	82.9	88.0
Zn	70	63	62	59.0	57.6

exhibited this bias included Cr, Y, Zr and the rare earth elements Tb, Er, Yb, Lu. These types of low recovery using HF and mineral acids have been reported elsewhere by Hall and Plant (2), Reeves and Brooks (3), Dolezal et al., (4) and Fletcher (5). Hence data for these seven elements which had been obtained by solution methods involving HF and mineral acids were not included in the calculations of provisional values.

#### *Non-solution methods*

These methods included

- instrumental neutron activation analyses (INAA)
- neutron activation analysis - delayed neutron counting (INA-DNC)
- X-ray fluorescence (XRF)
- gravimetric analysis.

#### **Summary of methods for partial extraction elements**

##### *Concentrated HNO<sub>3</sub> - concentrated HCl*

In most instances, a 1 gram sample was reacted with a mixture of 3 parts HNO<sub>3</sub> and 1 part HCl. (Lefort Aqua

Regia). Three laboratories used the same sample weight with the reverse ratio of HNO<sub>3</sub> and HCl. The room temperature contact time was frequently overnight and the heating time at 90°C varied from 2 to 4 hours.

##### *Dilute HNO<sub>3</sub> - dilute HCl*

Two laboratories used a mixture consisting of 6M HCl - 2.7M HNO<sub>3</sub>. Two other laboratories used a mixture which was 4M HNO<sub>3</sub> - 1 M HCl. One laboratory used a solution which was 3M HNO<sub>3</sub> - 5M HCl. Sample weights were either 0.5 g or 1.0 g and heating times varied from 1 to 3 hours.

The methods of determination for the concentrated HNO<sub>3</sub> - HCl extractions included AAS, ICP-ES, HY AAS and cold vapour AAS (for Hg). For the dilute HNO<sub>3</sub> - HCl extractions, only AAS and ICP-ES methods were employed.

##### **EPA Digestion 3050 and 3051**

Tables 9 and 10 contain data for 19 elements obtained by these two different EPA decompositions. These data are reported mainly to illustrate the fact that different partial extractions produce different levels of efficiency when compared to total values (e.g. Al, K, V). In other instances essentially the same values are reported for the four samples regardless of what partial extraction is used (e.g. Ba, Cu, Co, Zn). In practice, different decompositions will require specific certification programmes.

##### **Future work**

Provisional data for a large number of elements in TILL-1, TILL-2, TILL-3 and TILL-4 have been calculated. These data complement similar data published previously for LKSD-1, LKSD-2, LKSD-3, LKSD-4. STSD-1, STSD-2, STSD-3 and STSD-4. Future work should be focused on the acquisition of quality data in sufficient quantity that a substantial number of elements may be certified for all three sets of reference samples. Certification related to extractions useful for environmental studies might also be considered.

#### **ACKNOWLEDGEMENT**

##### **Collection and preparation**

Dr. R.B. Lortie, Lac Minerals Ltd., Mr. Hugh Moore, Silverfields Mining Corp. Ltd.; Dr. W.B. Coker, E.H. Hornbrook, C.C. Durham, G. Gauthier, G. Lund, M.

McCurdy, J.E. Vaive, Geological Survey of Canada; Dr. H. Steger, Dr. C. Smith, P. Westra, D. MacIntosh, W. Bowman and M. Leaver, CCRMP, Canada Centre for Mineral and Energy Technology. Special thanks are due to G.E.M. Hall for reviewing this manuscript, providing both many analyses as well as encouragement for this project.

**Analyses were provided by the following laboratories:**

- Acme Analytical Laboratories, Vancouver, B.C.
- Activation Laboratories, Ancaster, Ontario
- AGAT Laboratories, Calgary, Alberta
- Becquerel Laboratories Inc., Mississauga, Ontario
- Bondar-Clegg and Company Ltd., Ottawa, Ontario
- BRGM, Orléans-La Source, France
- Can Tech Laboratories, Calgary, Alberta
- Central Physico-Chemical and Analytical Facilities, Bhubaneswar - 751 013, India
- Chemex Labs Ltd., North Vancouver, British Columbia
- Chimitek Ltee., Ste-Foy, Quebec
- Government of Canada, Geological Survey of Canada, Analytical Chemistry Section, Ottawa, Ontario
- Government of Canada, Geological Survey of Canada, Geochemical Laboratories Section, Ottawa, Ontario
- Government of Manitoba, Department of Energy and Mines, Winnipeg, Manitoba
- Government of Newfoundland and Labrador, Department of Mines and Energy, St. John's, Newfoundland
- Government of Switzerland, Swiss Federal Laboratories for Materials Testing and Research, Bern 30520, Switzerland
- Geological Institute, University of Bonn, Bonn, Germany
- Loring Laboratories, Calgary, Alberta
- The Mineral Lab, Lakewood, Colorado, USA

- Norwest Labs, Edmonton, Alberta

- Niedersächsisches Landesamt Für Immissionsschutz, Hannover, Germany.

**RESUME**

**Le prélèvement et la préparation de deux échantillons de référence de sol et de deux échantillons de référence de moraine (till) sont décrits. Comme leurs prédécesseurs, les séries LKSD et STSD, la série TILL est caractérisée pour des éléments totaux et des éléments obtenus par extraction partielle. Des valeurs provisoires sont présentées pour les éléments majeurs, mineurs et en traces. De plus, des données obtenues par une seule source sont fournies pour un certain nombre d'éléments obtenus selon les protocoles de digestion EPA 3050 et 3051; ces données permettent une comparaison avec les autres données d'extractions partielles présentées dans ce rapport.**

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