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**GEOLOGICAL SURVEY OF CANADA
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and aqua regia results from the Warden borehole,
southern Ontario**

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1.0 Introduction

Over the past 20 years the Geological Survey of Canada (GSC) and the Ontario Geological Survey (OGS) have carried out numerous studies on the glacial sediments of southeastern Ontario (Fig. 1). Much of the work carried out by the GSC and others is referenced in a field trip guidebook examining the extent, architecture, sedimentary facies and origin of buried valleys within the Oak Ridges Moraine (ORM) (Sharpe et al., 2013). Although much work has been carried out on sequence stratigraphy and basin analyses of sediments within this region there is lack of information on the regional geochemistry of sediments. Results from such studies are helpful for defining chemical and related mineralogical variations within sediments and supplements sediment description, grain size data, downhole geophysical and stratigraphic correlations. Geochemical data also provides the opportunity to establish a chemostratigraphic framework that complements other stratigraphic correlation techniques, such as lithostratigraphy and biostratigraphy.

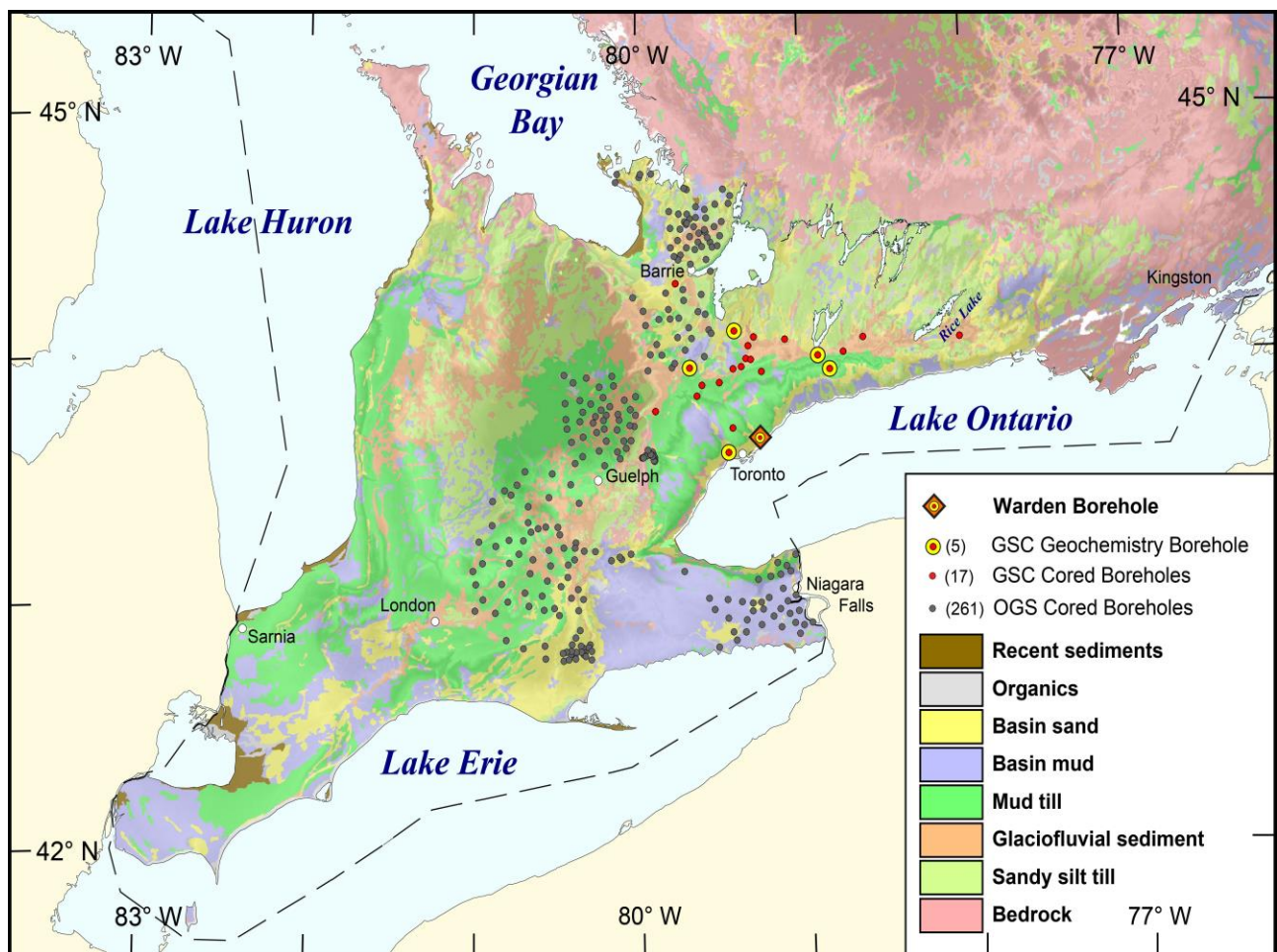


Figure 1: Location of the Warden borehole with simplified regional geology of southwestern Ontario overlying a DEM. Note the distribution of OGS and GSC stratigraphic boreholes with continuous core descriptions. Geology simplified from Barnett et al. (1991).

For groundwater studies, the collection of sediment geochemistry data is often beyond the scope, and budget of many programs, and is generally not included as a part of routine data collection. Portable X-ray fluorescent (pXRF) spectrometry has proven to be a successful tool to characterize the chemostratigraphy of glacially derived sediments (e.g. Crow et al., 2012; Knight et al., 2015a, 2015c) as well as improving the interpretation of downhole geophysics, micropaleontology results, and pore water geochemistry (Medioli et al., 2012). Data collected from this method has now become a routine part of borehole studies within the Groundwater Geoscience Program at the GSC (Knight et al., 2015a, 2015c, 2012). To eliminate nugget effects of sand size and gravel grains common in unconsolidated or crushed bedrock detritus, samples are sieved to <0.063 mm (silt and clay) size fraction (Plourde et al., 2012, Knight et al., 2012). The analysis on such normalized size fraction provides fundamental information used to define chemical and mineralogical variations within aquifers and aquitards.

The objective of this Open File is to publish geochemical data analyses of 119 samples obtained from an 80.5 m borehole and associated QA-QC data collected using a portable X-ray fluorescence spectrometer (pXRF). A sub-set of 37 samples were analysed using ICP-ES and ICP-MS after digestions by aqua-regia, multi-acid and lithium borate/tetraborate fusion methods to provide a comparison with more widely used laboratory geochemistry results and the pXRF results.

2.0 Study Area Geological Setting

The Warden borehole is located on the grounds of the Warden Avenue Junior Public School in Toronto, Ontario, at easting 638868m and northing 4840084m (UTM NAD 83 - Zone 17) and ~ 138 m a.s.l. (Fig. 2). The borehole intercepts bedrock of the Blue Mountain Formation and unconsolidated sediments from the Scarborough and Thorncliffe formations and the Newmarket Till (Fig. 3). The Scarborough and Thorncliffe formations, occur extensively throughout the area and are mapped in downhole geophysical logs (Eyles et al. 1985, Fligg and Rodrigues, 1983) and continuously cored boreholes within the Greater Toronto Region (Sharpe et al., 2013; Logan et al., 2008). The Scarborough Formation, at the Scarborough Bluffs type section, consists of a lower clay unit of ~20 m thickness overlain by an upper sand unit, averaging 15 m in thickness (Karrow, 1967). The basal clay member consists of rhythmically-bedded, stratified clay and silt to massive sandy silt beds 1- 2 meters thick with irregularly-bedded silt and sand. Disseminated fine organic detritus is present along with occasional larger pieces of wood a few centimetres long which occur more commonly upward. The clays are dark grey in color when wet, but dry to a light creamy grey, having a brownish appearance when compared to glacial varved clays, which in comparison appear almost blue-grey. The sand member is interbedded with silt near the base, and coarsens upward from fine to coarse sand. Crossbedding is common in the sands with deformation structures attributed to underwater slumping during sedimentation (Karrow, 1967).

Sediments assigned to the Sunnybrook Till that overlies and drapes the Scarborough Formation are not present in the Warden Borehole. Here the Scarborough Formation is directly overlain by sediments of the Thorncliffe Formation.

The Thorncliffe Formation (Fig. 3) consists of three units (Lower, Middle, and Upper) separated by the Seminary Till, and the Meadowcliffe Till. The Lower Thorncliffe Formation is composed



Figure 2: Location of the Warden borehole, located on the grounds of Warden Ave. Junior Public School. Image from Goggle Earth, 2015.

of single and multiple graded silt laminations with clay caps (Eyles and Clarke 1988), that are well-exposed at the Don brickyard where the sediments are referred to as, the Bloor Member (Karrow, 1967). The tops of the silt layers are bioturbated by mm diameter horizontal burrows (Eyles and Clarke 1988). Graded discrete silts were probably deposited by weak quasi-continuous density underflows, or turbidity currents with the clay cap representing later pelagic sedimentation. The Seminary Till and the Meadowcliffe Till are not present in the Warden borehole where sediments assigned to the Newmarket Till directly overlie sand, silt and clay of the Thorncliffe Formation.

Newmarket Till is a dense, 10–70 m thick, stony sandy silt diamicton with minor sand-mud interbeds and stone lines (Sharpe et al., 1997; Boyce et al., 1995) that forms a regional seismo-stratigraphic marker bed due to its high seismic velocity (Pugin et al., 1999; Pullan et al., 2002). The Newmarket Till is generally considered to be an aquitard, however, where exposed at the surface fractures may provide connectivity to inter-beds at depth and may allow recharge to underlying aquifers at a rate of 30-35 mm/year, (Gerber and Howard, 2000). East of Toronto, the Purple Woods Conservation Area borehole records the greatest thickness of Newmarket Till in the GTA at ~68 m (Knight et al., in press) To the north, the Oak Ridges Moraine rises to >300 m elevation asl and can be up to 200 metres thick, particularly over buried tunnel valleys that can locally erode to bedrock (e.g. Sharpe et al., 2002).

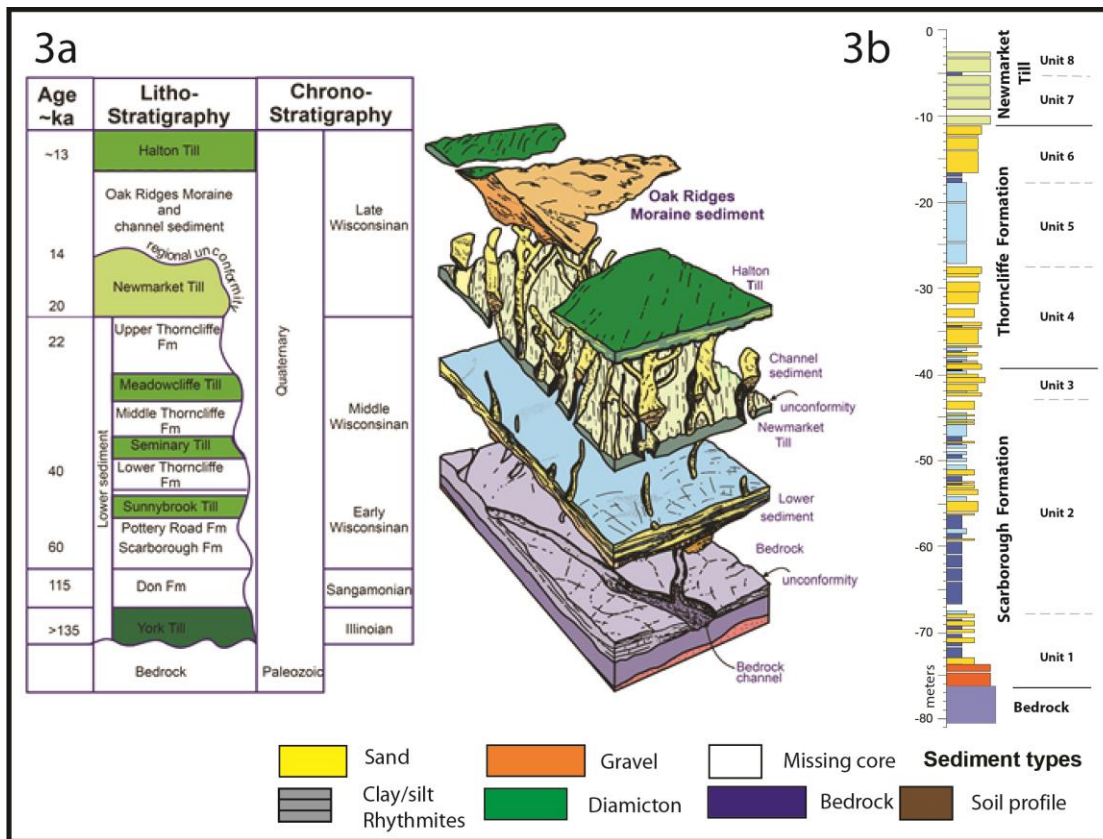


Figure 3a: Stratigraphy of the Greater Toronto Area. Modified from Sharpe et al. 2002. Key till units highlighted in green. Figure 3b: Generalized lithostratigraphy of the Warden borehole.

3.0 Sample collection, processing and analytical methods

The boreholes were drilled in January of 2010 by Golder Associates for the City of Toronto using a full-sized, truck-mounted Sonic drill. The hole was terminated four and a half meters into bedrock. Borehole core was placed in five foot PVC tubes, and sealed with tape. The sediment cores were shipped to GSC Tunney's Pasture facility in Ottawa for further logging, sampling, and storage.

Prior to pXRF analyses the sediment was disaggregated by impacting the sample, placed between brown construction paper, with a rubber mallet (Fig. 4). After disaggregation, all samples were sieved to $<63 \mu\text{m}$ (silt + clay) at the GSC Sedimentology Laboratories in Ottawa. A split of the processed samples were placed in 23 mm diameter plastic vials, to an approximate height of 30 mm, previous studies indicate that this thickness is adequate to satisfy the assumption of an infinitely thick sample (Knight et al., 2015b), and sealed with 4 μm Chemplex[®] Prolene[®] Thin-Film. Data were acquired using a handheld Thermo Scientific, Niton XL3t GOLDD XRF spectrometer equipped with Cygnit 50 kV, 2-watt Ag anode X-ray tube and a XL3 silicon drift detector (SDD) with 180,000 counts per second (cps) throughput, mounted to a test stand (Fig. 5).

Additionally, a subset of 37 samples was sent to Bureau Veritas Commodities Ltd. (formerly Acme), Vancouver for traditional laboratory geochemical analyses. These samples were selected at an interval of about one sample every two meters or where there was a noticeable increase in elemental concentration (a spike) by pXRF methods in order to provide a comparative dataset between the pXRF results and more traditional laboratory digestion.

Three mineral laboratory analytical procedures were employed: (1) aqua regia, a hot (95°C) HNO₃-HCl digestion, followed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analysis; (2) multi acid, a hot dissolution in HNO₃-HClO₄-HF, dried to a residue and then dissolved in HCl, followed by ICP-MS analysis; and (3) a lithium metaborate/ tetraborate fusion followed by dilute nitric acid digestion of the fused disc, and analysis by Inductively Coupled Plasma Emission Spectroscopy ICP-ES (major elements) and ICP-MS (trace elements). A tabulation of the elements analysed by each method is presented in Appendix A along with a second Excel (.xls) file containing data on QA-QC for duplicate sample analyses and standard reference materials that were analysed with the samples from the Warden borehole. A summary list of elements detected by these three traditional geochemical methods and the limits of detection is presented in Table 1.

Samples were analyzed in Soil Mode using Compton normalization which is recommended for elements expected to occur with < 1% concentration. In order to honor the protocol used for previous borehole studies (Knight et al., 2015a, Knight et al., 2012, Plourde et al., 2012) a dwell time of 60 seconds was used for each filter (Main, Low, and High), for a total of 180 seconds per analysis. The X-ray emission lines used to determine elemental concentrations in Soil Mode are listed in Table 2.

3.1 Reproducibility and Precision of Standards

Three standards (Till-1, Till-4, and TCA 8010) and 2 blanks (SiO₂ and Teflon) were analyzed at the beginning and at the end of each analytical session and after every 10 analyses of the borehole samples. A SiO₂ blank and Teflon blank were analysed to determine the cleanliness of the pXRF window and sample stand environment. When data for either of these blanks returned values for elements that should not be detected in greater amounts than trace, the operating environment (test stand) was purged with compressed air and wiped clean with Methanol until returned values were normal. The Chemplex[®] Prolene[®] thin-film that separates all samples except the Teflon blank from the spectrometer may contain trace amounts of Ca, P, Fe, Zn, Cu, Zr, Ti and Al. For the SiO₂ blank, Ba, Cd, K and V returned values below the recommended limits of detection (< LOD), which are not listed as known impurities and most likely represent internal detector noise. We recommend that the Chemplex Prolene thin-film be replaced on a regular bases to avoid contamination. A study into the precision, accuracy, instrument drift, dwell time optimization and calibration of pXRF spectrometry for reference materials including Till-1, Till-4, and TCA 8010 is available from Knight et al. (2013).

For each element detected in a given standard, the count, minimum value, maximum value, mean, standard deviation, relative standard deviation (%RSD), %error, and recommended values are listed in Till-1 (Table 3), Till-4 (Table 4), and TCA 8010 (Table 5). The %error column contains the difference between the mean and recommended value. Low absolute values in this column indicate that the element is measured accurately; high absolute values indicate that a calibration

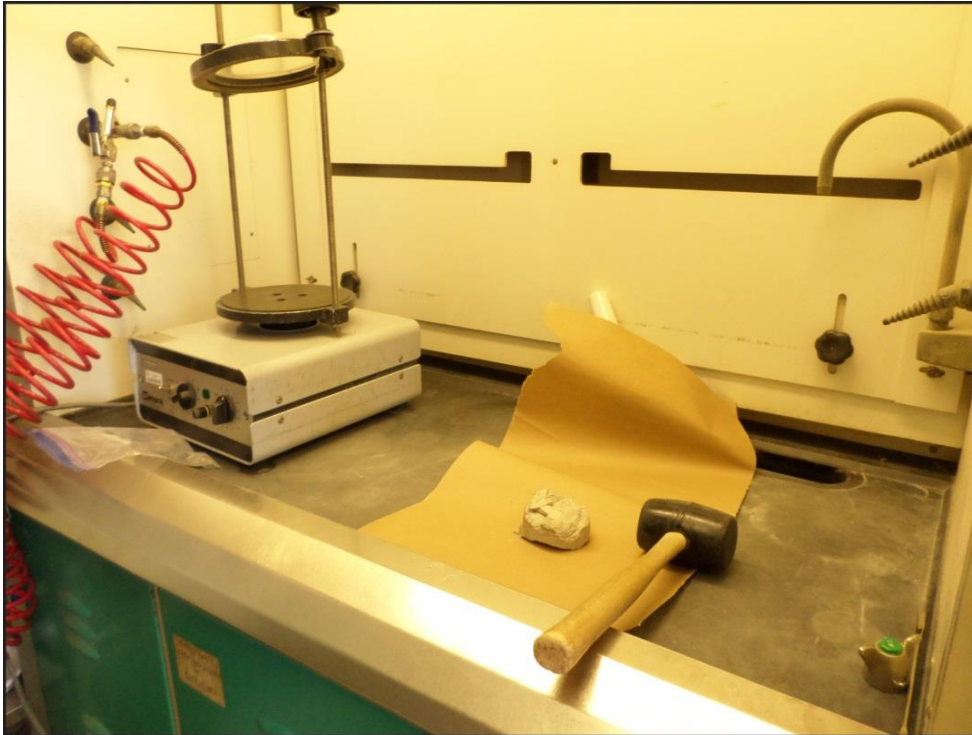


Figure 4: Prior to sieving sediment samples were disaggregated. The sample was placed between two pieces of brown construction paper and impacted with a rubber mallet.

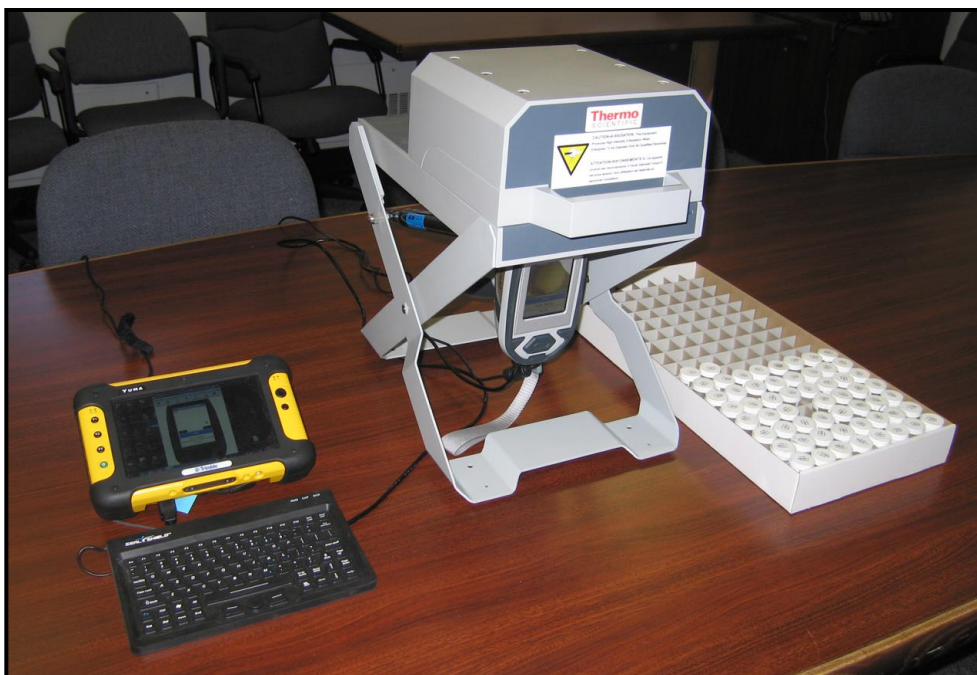


Figure 5. Example of pXRF spectrometer mounted in a test stand with microcomputer for analysis of processed sediment samples.

Table 1: Summary of elements analyses by traditional geochemical methods.
From Kjarsgaard et al. 2014. MDL = Minimum detection limit, LOI = Loss on ignition, TOT/C = Total carbon, TOT/S = Total sulphur.

FUSION			4 Acid			Aqua regia		
Element	Unit	MDL	Element	Unit	MDL	Element	Unit	MDL
SiO ₂	%	0.01	Ti	%	0.001	Ti	%	0.001
TiO ₂	%	0.01	Al	%	0.01	Al	%	0.01
Al ₂ O ₃	%	0.01	Fe	%	0.01	Fe	%	0.01
Cr ₂ O ₃	%	0.002	Ca	%	0.01	Mg	%	0.01
Fe ₂ O ₃	%	0.04	Mg	%	0.01	Ca	%	0.01
MnO	%	0.01	Na	%	0.01	Na	%	0.001
MgO	%	0.01	K	%	0.01	K	%	0.01
CaO	%	0.01	P	%	0.01	P	%	0.001
Na ₂ O	%	0.01	S	%	0.05	S	%	0.05
K ₂ O	%	0.01	Li	ppm	0.5	Sr	ppm	1
P ₂ O ₅	%	0.01	Rb	ppm	0.5	Te	ppm	0.2
LOI	%	0.10	Be	ppm	5	Zn	ppm	1
TOT/C	%	0.02	Ba	ppm	5	Cu	ppm	0.1
TOT/S	%	0.02	Ta	ppm	0.5	Zr	ppm	0.1
Ba	ppm	1	Nb	ppm	0.5	Tl	ppm	0.1
Be	ppm	1	La	ppm	0.5	Bi	ppm	0.1
Ce	ppm	0.1	Zn	ppm	5	V	ppm	2
Co	ppm	0.2	Cu	ppm	0.5	Se	ppm	0.5
Cr	ppm	14	Zr	ppm	0.5	As	ppm	0.5
Cs	ppm	0.1	Mo	ppm	0.5	Sc	ppm	0.1
Cu	ppm	5	V	ppm	10	Pb	ppm	0.1
Dy	ppm	0.05	Sn	ppm	0.5	W	ppm	0.1
Er	ppm	0.03	Sb	ppm	0.5	Ga	ppm	1
Eu	ppm	0.02	Sc	ppm	1	Ba	ppm	1
Ga	ppm	0.5	Pb	ppm	0.5	Co	ppm	0.1
Gd	ppm	0.05	As	ppm	5	Cd	ppm	0.1
Hf	ppm	0.1	Ce	ppm	5	B	ppm	20
Ho	ppm	0.02	Sr	ppm	5	Cr	ppm	1
La	ppm	0.1	Co	ppm	1	La	ppm	1
Lu	ppm	0.01	Cd	ppm	0.5	Ni	ppm	0.1
Mo	ppm	1	Hf	ppm	0.5	Sb	ppm	0.1
Nb	ppm	0.1	Cr	ppm	1	Mn	ppm	1
Nd	ppm	0.30	Th	ppm	0.5	Mo	ppm	0.1
Ni	ppm	20	Ni	ppm	0.5	Ag	ppm	0.1
Pb	ppm	1	Bi	ppm	0.5	Au	ppb	0.5
Pr	ppm	0.02	Mn	ppm	5	Hg	ppm	0.01
Rb	ppm	0.1	W	ppm	0.5			
Sc	ppm	1	Y	ppm	0.5			
Sm	ppm	0.05	U	ppm	0.5			
Sn	ppm	1	Se	ppm	5			
Sr	ppm	0.5	Ag	ppm	0.5			
Ta	ppm	0.1						
Tb	ppm	0.01						
Th	ppm	0.2						
Tm	ppm	0.01						
U	ppm	0.1						
V	ppm	8						
W	ppm	0.5						
Y	ppm	0.1						
Yb	ppm	0.05						
Zn	ppm	5						
Zr	ppm	0.1						

Table 2: X-ray energy intensities used to determine elemental concentrations in Soil Mode, as provided by Thermo Scientific (pers. comm.).

Element	Line	Energy (keV)	Window Low (keV)	Window High (keV)	Filter
Ba	K α_1	32.19	31.70	32.70	High
Ca	K α_1	3.69	3.50	3.89	Low
Cu	K α_1	8.05	7.84	8.24	Main
Fe	K α_1	6.40	6.20	6.60	Main
K	K α_1	3.31	3.10	3.49	Low
Mn	K α_1	5.90	5.70	6.10	Main
Ni	K α_1	7.48	7.35	7.67	Main
Rb	K α_1	13.39	13.18	13.60	Main
S	K α_1	2.31	2.20	2.45	Low
Sr	K α_1	14.16	13.95	14.38	Main
Ti	K α_1	4.51	4.21	4.70	Low
V	K α_1	4.95	4.80	5.10	Low
Zn	K α_1	8.64	8.49	8.83	Main
Zr	K α_1	15.77	15.53	15.98	Main

curve is required to correct the data or that the data is not reliable. As an example Ni values obtained from Till-1 have an error of 237%. Values returned by the pXRF were often greater than 3 times the recommended value. Similarly, U values obtained from Till-4 have an error of 160%. Although care must be taken when interpreting data with a high error, it may be useful to plot these elements since chemostratigraphy utilizes both absolute and relative changes in concentration, and for relative changes high precision is more important than accuracy. It is important to note that the precision and accuracy are affected by concentration. Lower concentrations, especially those near the LOD (e.g. Ni) tend to result in lower precision, and thus higher %RSD.

3.2 Limit of Detection

Thermo Scientific provides a list of the sensitivity or limits of detection for the pXRF. During analyses the pXRF provides an error of each individual measurement taken throughout the 180 second analysis. For this study the error was recorded as 2 standard deviations. Surprisingly for some elements (e.g. Ni) returned analyses were lower than the LOD. When this occurred, the point was plotted on the chemostratigraphy graph using the returned number however an arrow and title (“LOD”) was placed on the x-axis depicting the LOD value. Elements detected by each filter and the corresponding lower limits of detection are listed in Table 6.

4.0 Results and Surficial chemostratigraphy

The pXRF data are interpreted using single element trends from the base to the top of the borehole. Fourteen elements (Ba, Ca, Cu, Fe, K, Mn, Ni, Rb, S, Sr, Ti, V, Zn, and Zr) were detected in sufficient quantities to produce meaningful results using the pXRF spectrometer. Four elements (Cu, Ni, S, and V) returned some values below the limits of detection. Elemental concentrations as determined by pXRF spectrometry, as well as blank samples and standard reference materials are tabulated in Appendix A. Individual element concentration data as determined by pXRF and by fusion methods are plotted with respect to depth, and colour-coded with respect to stratigraphy, in Appendix B. It should be noted that for some of the transitional elements, at low concentrations, the multi-acid results may be more comparable with pXRF data given the higher detection limits for fusion chemistry.

Bivariate plots comparing pXRF analyses and fusion, multi-acid, and aqua regia digestions are also presented in Appendix B. For these plots, a one-to-one relationship is plotted as a dashed green line. Linear regression lines determined by the least squares approach are displayed on the figures in black. These regression lines are more dependent on the location of clustered data, rather than the overall shape of the data. For strongly ‘clustered’ data, the regression lines occasionally deviated from the expected trend. Where this occurred, a reduced major axis (RMA) regression method described in York (1966) and utilized by Kjarsgaard et al. (2014b) was better suited to delineate a calibration equation. RMA assumes there are errors to both y and x data. The RMA regression line is plotted as a blue line on the bivariate plots in Appendix B. The relationship between pXRF data and traditional laboratory methods for unconsolidated surficial sediments is discussed in Kjarsgaard et al. (2014) and Knight et al. (2015a).

In theory, for any element, the fusion (‘total analysis’) concentration should be equal to or greater than the multi-acid (‘near total’) concentration. For this reason only fusion data was plotted on the pXRF borehole graphs in Appendix B. It should be noted that a comparison between pXRF and aqua regia data is often poor since ‘apparent’ higher concentrations levels (i.e., relative concentration levels) can be observed, for elements that dominantly reside in minerals that are easily digested by aqua regia, but only form a small percentage of the overall composition of the material being analysed. Thus elemental concentration levels determined by aqua regia data can be higher, or lower, than that obtained by fusion or multi-acid methods.

Based on observations of the chemostratigraphic profiles in Appendix B for Fe, Sr, Ti, and V the pXRF results could be post calibrated to more closely match those of the fusion data plotted in the borehole logs. A comparison of pXRF spectrometry to fusion chemistry for Fe, Sr, and Ti and V is illustrated in figure 6. Fe, Sr and Ti underestimate concentrations by pXRF however they do display excellent r^2 values of .99, .90, and .87 respectively. For V, pXRF methods over estimates the concentration compared to fusion chemistry. Regardless, the precision of the collected data is excellent and post calibration would be able to correct for issues with accuracy (Fig. 6). Although the r^2 for K is 0.82 (Table 7) there is a considerable amount of clustering and scatter in the data plotted in Appendix B, however the downhole trends between pXRF data and fusion methods are similar.

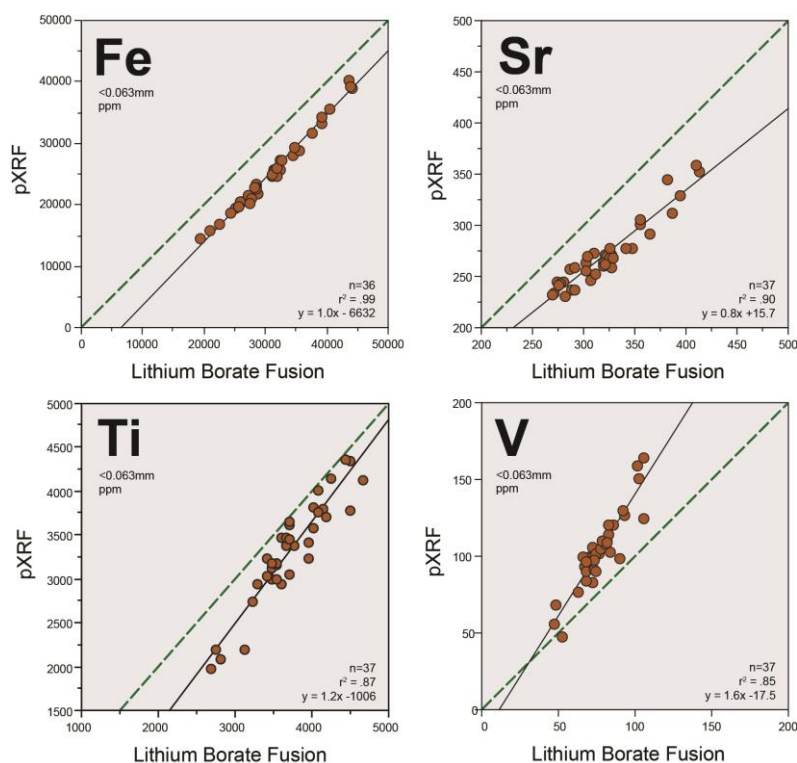


Figure 6: A comparison of pXRF results to fusion methods for Ca, Rb, and Cu. The green dashed line represents a 1:1 relationship.

Table 3. Summary statistics for Till-1 by pXRF spectrometry for the Warden Borehole.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	18	13	18	0.0	1.2	6.39	16	20
Ba	702	13	866	23.4	13.5	1.55	849	885
Ca	19440	13	17181	-11.6	174	1.01	16879	17388
Co	18	2	180	899	5.3	2.93	176	184
Cr	65	13	32	-51.1	5.8	18.23	21	43
Cs	1	13	47	4623	2.5	5.19	45	53
Cu	47	13	56	18.9	5.7	10.26	46	65
Fe	48100	13	40966	-14.8	265	0.65	40521	41301
K	18429	13	15256	-17.2	145	0.95	15027	15523
Mn	1420	13	1340	-5.6	33.0	2.46	1277	1388
Mo	2	4	4.4	122	1.6	36.5	3.2	6.7
Ni	24	13	81	237	9.4	11.56	64	94
Pb	22	13	12	-43.7	1.9	15.33	8	15
Rb	44	13	40	-8.5	1.0	2.37	39	42
S	< 500	2	348	-30.3	15.9	4.55	337	359
Sr	291	13	269	-7.4	2.5	0.92	266	274
Th	5.6	12	4.4	-21.9	0.7	16.4	3.5	5.7
Ti	5990	13	5331	-11.0	77.5	1.45	5111	5416
U	2.2	9	6.4	193	0.9	14.32	5.3	7.7
V	99	13	157	58.3	12.1	7.73	130	175
Zn	98	13	91	-6.7	3.1	3.42	88	97
Zr	502	13	562	11.9	15.0	2.67	528	576

Table 4. Summary statistics of Till-4 by pXRF spectrometry for the Warden borehole.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	111	13	104	-6.6	1.7	1.68	101	107
Ba	395	13	455	15.2	10.0	2.20	433	468
Ca	8934	13	8031	-10.1	85.1	1.06	7853	8145
Cr	53	13	23	-56.9	5.9	25.64	13	36
Cs	12	13	24	102	3.0	12.32	19	29
Cu	237	13	216	-8.9	5.7	2.64	208	224
Fe	39700	13	33274	-16.2	223	0.67	32874	33558
K	26980	13	23868	-11.5	168	0.7	23569	24124
Mn	490	13	449	-8.4	14.9	3.31	425	484
Mo	16	13	17	8.3	1.3	7.71	15	19
Ni	17	13	53	209	10.3	19.53	35	71
Pb	50	13	43	-14.7	1.8	4.26	39	45
Rb	161	13	152	-5.5	1.5	0.96	150	155
S	800	13	640	-20.0	104	16.23	407	761
Sr	109	13	106	-3.2	1.4	1.28	103	108
Th	17.4	13	42	141	0.7	1.58	41	43
Ti	4840	13	4659	-3.7	68.1	1.46	4532	4771
U	5	12	13	160	2.5	19.60	7	16
V	67	13	128	90.7	9.8	7.64	114	151
W	204	13	175	-14.0	16.7	9.54	151	214
Zn	70	13	65	-6.6	2.0	3.05	63	69
Zr	385	13	430	11.6	11.1	2.59	412	449

Table 5. Summary statistics of TCA 8010 by pXRF spectrometry for the Warden borehole.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	5.5	13	6.6	19.7	1.0	15.69	4.9	8.2
Ba	549	13	719	30.9	12.3	1.72	700	749
Ca	15509	13	14231	-8.2	220	1.54	13839	14612
Co	8	2	71	782	3.6	5.04	68	73
Cr	48	13	16	-67.2	5.4	34.15	8	26
Cs	1	13	56	5511	2.1	3.82	53	59
Cu	28	13	33	17.9	3.8	11.37	28	41
Fe	20290	13	14052	-30.7	163	1.16	13735	14329
K	19094	13	15864	-16.9	209	1.32	15590	16334
Mn	310	13	305	-1.6	17.0	5.56	266	322
Ni	17	13	68	301	8.7	12.79	55	86
Rb	54	13	49	-9.6	1.1	2.34	46	50
Sr	310	13	266	-14.1	2.2	0.84	262	269
Th	5	13	3.8	-23.6	0.7	19.40	2.7	5.0
Ti	2578	13	2512	-2.6	72.2	2.87	2384	2611
U	1	11	6.5	551	1.6	24.14	4.4	9.6
V	49	13	70	43.0	7.3	10.37	58	82
Zn	32	13	32	-1.0	1.6	5.14	29	35
Zr	272	13	319	17.2	9.6	3.02	306	336

Table 6. Detection limits using two matrix configurations and the filters used to detect these elements, provided by Thermo Scientific (pers. Comm.).

Element	Matrix		Filter
	SiO ₂	SiO ₂ + Fe +Ca	
As	4	7	High
Ba	35	45	Low
Ca	40	N/A	Low
Cu	10	13	Low
Cr	10	22	Main
Fe	25	N/A	Main
K	45	150	Low
Mn	35	50	Main
Mo	3	3	Main
Ni	25	30	Main
Rb	3	3	Main
S	75	275	Low
Sc	10	75	Main
Sr	3	3	Low
Ti	20	60	Low
V	10	25	Low
Zn	7	10	Main
Zr	3	4	Main

Table 7 provides a summary of the coefficient of determination (r^2), %RSD, and slope (m), to assess the quality of the pXRF results compared to the fusion, multi acid, and aqua regia results. From this table the following elements are classified as high quality for comparison to fusion analyses Ca, Cu, Fe, K, Mn, Rb, Ti, V, Zn, and Zr. Elements that do not compare well with fusion data include As, Ba, Ni, S, U, and Th.

4.1 Warden borehole chemostratigraphy

Chemostratigraphy of the Warden borehole can be divided into 8 units (Fig. 3b). The three lowermost units correspond to the Scarborough Formation, the overlying 3 units to the Thorncliffe Formation, while the uppermost two units represent the Newmarket Till.

Unit 1 76.2-67.8 m (Scarborough Formation)

The Scarborough Formation consists of a 36 m coarsening upwards succession of mud, silt and sand that has abundant detrital and in-situ organics. Unit 1 consists of the lowermost 8.4 m of the Scarborough Formation and represents a fining upwards sequence from coarse sand and gravel, to sand and clay rhythmites. This variation in grain size is reflected in the high degree of variability of elemental concentrations for Ba, Ca, Cu, Fe, K, Ni, Rb, Sr, V and Zn as well as the progressive decrease of elemental concentrations of Cu, Fe, K, Rb, Ti, V, and Zn over the lowermost 2 meters above the Blue Mountain Formation shale. These elements are likely concentrated in migratory fluids at the bedrock interface and decrease in abundance stratigraphically upwards. The contact between Unit 1 and Unit 2 at a depth of 67.8 meters corresponds to the change in grain size between the gravel/sand inter-beds and the overlying silt/clay rhythmites. Although the silt and clay size fraction is analyzed for elemental concentrations the erratic nature of the resulting data in Unit 1 may indicate high-energy sediment influx.

Table 7. Summary statistics for the comparison of pXRF data with fusion, multi acid, and aqua regia digestion methods, Warden borehole.

Element	pXRF vs fusion			pXRF vs multi acid			pXRF vs aqua regia		
	r ²	RSD%	slope (m)	r ²	RSD%	slope (m)	r ²	RSD%	slope (m)
As	N/A	N/A	N/A	0.11	16	0.35	0.22	37	0.57
Ba	0.00	15	0.00	0.00	15	-0.02	0.43	52	-1.03
Ca	0.99	50	1.28	0.99	50	1.29	0.99	61	1.31
Cu	0.78	34	0.89	0.76	32	0.85	0.81	37	0.85
Fe	0.99	20	1.04	0.99	21	0.96	0.93	31	1.01
K	0.82	14	0.78	0.76	16	0.65	0.83	54	2.46
Mn	0.96	27	0.94	0.97	25	0.91	0.88	42	0.82
Ni	0.15	24	-0.61	0.05	29	-0.26	0.05	35	-0.33
Rb	0.98	23	0.87	0.87	26	0.77	N/A	N/A	N/A
S	N/A	N/A	N/A	0.31	26	0.31	0.60	49	0.47
Sr	0.90	12	0.80	0.99	13	0.83	0.64	56	0.51
Th	0.72	23	0.68	0.65	23	0.66	0.64	27	0.75
Ti	0.87	13	1.17	0.83	13	1.15	1.39	43	0.47
U	0.02	27	0.33	0.05	17	0.96	N/A	N/A	N/A
V	0.85	18	1.58	0.85	20	1.60	0.81	29	2.07
Zn	0.96	27	1.05	0.94	26	0.96	0.94	38	0.94
Zr	0.92	42	1.02	0.82	24	4.36	N/A	N/A	N/A

Unit 2 67.8-43 m (Scarborough Formation)

Unit 2 displays less variability in elemental concentrations compared to the underlying Unit 1 sediments (e.g. Fe, Mn, S, Ti, Zn, Zr). This most likely is a reflection of the homogeneity of the sediments. At a depth of 53 m there is a spike in Cu, Fe, Mn, Ni, Ti, V, Zn and Zr, which is a departure from the normal elemental trends throughout the unit. Unit 2 sediments contain finer grained mud than those of the overlying Unit 3 sediments (Coffin et al., in press). The contact between unit 2 and unit 3 marks the transition from the Scarborough Formation to the overlying Thorncliffe Formation. Elemental variations within this unit can be accounted for by the occurrence of inter-beds of sand, mud and silt. A spike in element concentration for Cu, Fe, Mn, Ni, Ti, V, Zn, and Zr at 53.8m in depth can be attributed to a sand layer within the unit, with a likely more distal and potentially shield provenance.

Unit 3 43-39.5 m (Scarborough Formation)

Unit 3 sediments contain variable amounts of sand content and organic matter culminating with a six centimeter thick peat horizon defining the top of the Scarborough Formation. Chemically this contact is poorly defined. For some elements such as Mn the unit 3 sediments are more consistent in chemical signature to the overlying Thorncliffe Formation than with underlying Scarborough sediments. This is most likely a reflection of the variability in grain size as a result of poor sorting due to rapid sedimentation of the sands and the organic content of the sediments.

However for some elements, such as K, Rb, and Sr that are associated with a granitic provenance there is little to no change in chemical signature between the Scarborough Formation and the overlying Thorncliffe Formation.

Unit 4 39.5-27.5 m (Thorncliffe Formation)

The Thorncliffe Formation can be divided into 3 units consisting of approximately 14 meters of interbedded silt and clay to very coarse sand (unit 4) overlain by 10 meters of silt and clay (unit 5) and 4 meters of very coarse sand (unit 6). This sequence is similar to sediment successions logged in other local boreholes with sand, gravel and rhythmic mud, intercepted beneath the Newmarket Till (Sharpe et al., 2002; Logan et al., 2006). Unit 4 sediments, for many elements (Cu, Fe, Mn, Ti, Zn and Zr), are geochemically less variable than the underlying unit 3 sediments. A sample occurring at -39.07 meters in depth contains high values in some elements (e.g. Cu, Fe, Mn, Ti, V, Zr) that is similar to the variability to the underlying unit 3 sediment but occurs stratigraphically above the peat horizon used to define the formational contacts.

Variability in the geochemical signature of Unit 4 sediments is most prevalent in Ba, Mn, Ni, Ti, V, and Zr. From unit 4 to the top of the borehole Ca concentrations occur as distinct abundances either defining unit boundaries or interunit fluctuations most likely representing changes in carbonate rock content. This is especially notable within unit 4 at a depth of 32 meters where the underlying Ca content is ~34000-54000 ppm whereas the overlying concentration's range from ~101000-79000 ppm. Cu also displays a similar change in concentration. As a result a shortened dashed line has been added to the Appendix B chemostratigraphic representation in order to highlight these changes.

Unit 5 27.5-17.7 m (Thorncliffe Formation)

At the contact between Unit 4 and Unit 5, there is a decrease in Ca and Sr as well as an associated increase in Fe, K, Rb and Ti, that is attributed to a change in sediment provenance from carbonate-rich to granitic rich Precambrian Shield sediment. This was noted during core logging by a change in grain size from coarse-medium sand to silt (Coffin et al., in press). For the top 4 meters Ca concentrations increase markedly as the source of shield detritus is replaced by increased carbonate content. For the 28-22 meter interval a shield derived mud suspension event may have interrupted a high Ca and carbonate environment. For Mn there is little to no change in concentrations in Units 5 and 6. From Unit 5 to the top of the borehole Zr values remain very consistent.

Unit 6 17.7-11.2 m (Thorncliffe Formation)

The contact between Unit 5 and Unit 6 is difficult to delineate. For Ba, Cu, Fe, K, Rb, Sr, Ti, and Zn the contact occurs at a depth of 17.7 meters and corresponds to a change from silt to mud (Coffin et al., in press). However Ca displays no change in concentration until a depth of 16.5 meters where there is an influx of sand (Coffin et al., in press). The increase in Ca content from the underlying Unit 5 sediments likely represents a transition from a granitic provenance, to a carbonate provenance. Unit 6 also displays significantly lower amounts of Fe, K, Rb, Ti, V and Zn than both overlying and underlying Units. Carbonate sourced material appears to be the predominant basin fill as its overall concentration increases upwards within the Thorncliffe Formation. The top of Unit 6 also corresponds to the contact between the Thorncliffe Formation and the overlying Newmarket Till.

Unit 7 11.2-5.2 m (Newmarket Till)

The Newmarket Till consists of 7.5 meters of a sandy-silt diamicton with cobbles, pebbles and granules and is here divided into 2 units. Unit 7 displays an abrupt decrease in Ca concentrations as well as an associated increase in Ba, Fe, K, Rb, Ti, V and Zn and suggests that the <0.063 mm size fraction of the Newmarket Till has a different provenance than the underlying unit 6 (Thorncliffe Formation) sediments, or that the matrix of the Newmarket Till is not related to the matrix of the Thorncliffe Formation. The differences in geochemical signature between units 6 and 7 indicate that the Newmarket Till had a different sediment source (Shield dominant) from the underlying carbonate dominant Thorncliffe Formation. A similar decrease in Ca from the top of the Thorncliffe Formation to the base of the Newmarket Till also occurs at Purple Woods conservation area ~45 km to the northeast (Knight et al., in press).

Unit 8 5.2-2.5 m (Newmarket Till)

A thin clay horizon at a depth of 5.2 m within the Newmarket Till marks the contact between Units 7 and 8. Unit 8 is characterized by an increase in Ca concentration, which corresponds to a decrease in Ba, Fe, K, Rb, Ti, V, and Zn concentration. This change is most likely associated with a continued change in sediment provenance from shield terrain to a more carbonate-rich source.

5.0 Summary

This geochemical study expands the range of sediments that has been analyzed as part of a project to characterize surficial sediment aquifers and aquitards across Canada. Core geochemistry assessed within a regional stratigraphic framework and within borehole geochemical trends suggest a shift in provenance between granitic rocks and carbonate rocks and perhaps associated changes in sedimentary process. The variation in concentration of some elements (e.g. Ca, Fe, Rb, V) between the Thorncliffe Formation and the overlying Newmarket Till indicate that the silt and clay size fraction of the Thorncliffe Formation was not incorporated into the matrix of the Newmarket Till. To our knowledge, these results are among the first systematic geochemical characterization of glacial derived sediment associated with the regional Thorncliffe Formation aquifer. The borehole data collected at Warden Junior Public School using both traditional laboratory methods (fusion, multi-acid, and aqua regia digestions) and pXRF-derived geochemistry demonstrates that the pXRF methodology is a valuable and cost effective tool that provides comparable results to fusion and, to a degree, multi-acid methods for several elements. This data can provide information into the provenance of analyzed sediments and glacial processes responsible for sediment deposition and will be a useful tool for event reconstruction in the greater Toronto region.

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