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**GEOLOGICAL SURVEY OF CANADA
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and aqua regia results from the Queensville borehole,
Yonge Street Aquifer, 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 southern 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 (Sharpe et al., 2013). Although much work has involved sequence stratigraphy and basin analyses of sediments within this region, there is a lack of information on the regional geochemistry of sediments. Results from such studies are crucial to defining chemical and related mineralogical variations within sediments and supplements sediment description, grain size data, downhole geophysical and stratigraphic correlations. Geochemical data also provides an opportunity to establish a chemostratigraphic framework that complements other stratigraphic correlation techniques, for example, lithostratigraphy and biostratigraphy.

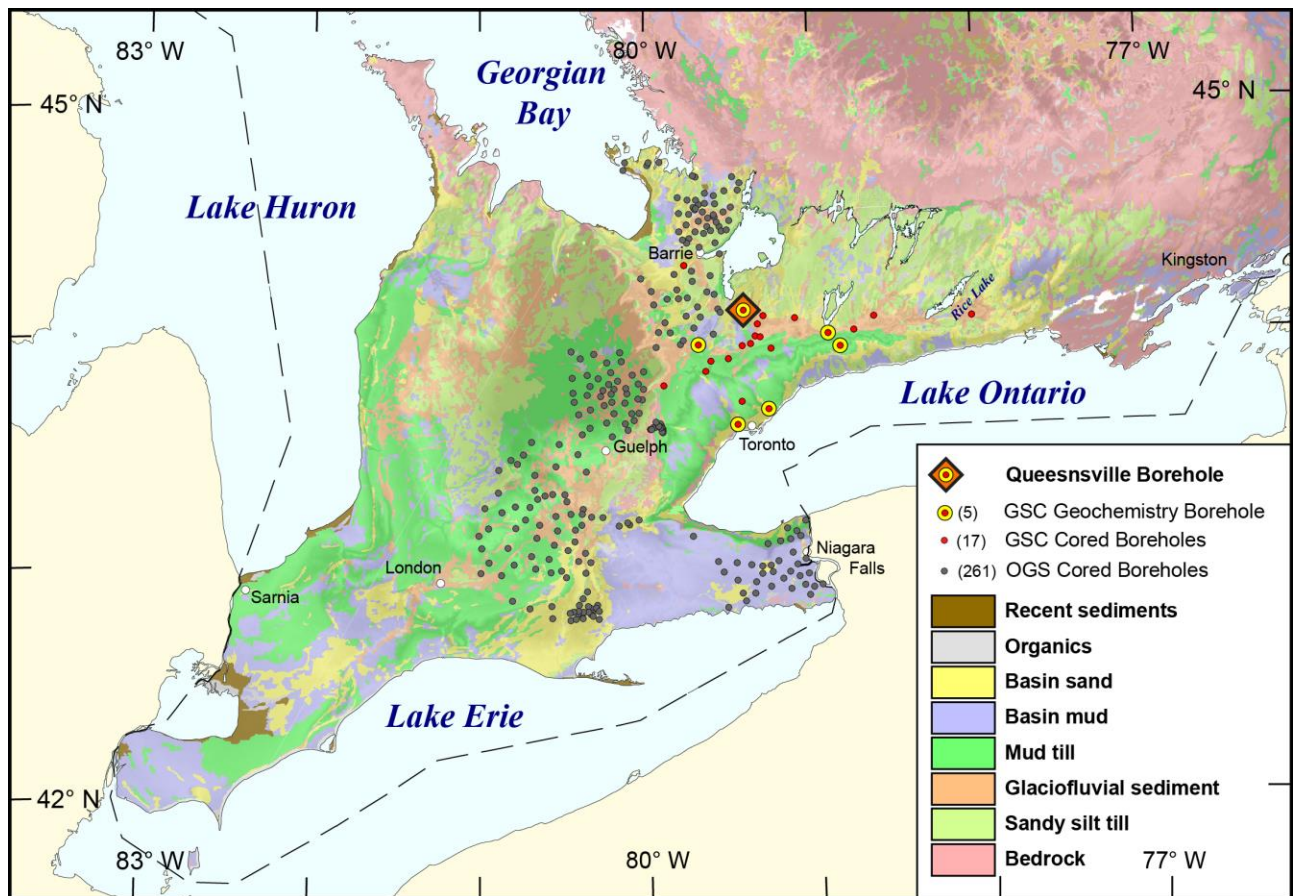


Figure 1: Location of the Queensville borehole with simplified regional geology of southwestern Ontario overlying a DEM. Note the distribution of OGS and GSC stratigraphic boreholes with continuous core descriptions. Geology simplified from Barnett et al. (1991).



Figure 2: Location of the Queensville borehole, east of the town of Queensville on the south side of Queensville Side Road East. Image from Goggle Earth, 2015.

For groundwater studies, the collection of geochemical 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 glacial derived sediments (e.g. Crow et al., 2012; Knight et al., 2015c, 2015b) and to augment 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 program at the GSC (Knight et al., 2015c, 2015b, 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 the geochemical analyses of 87 samples from a 96.2 m core retrieved near Queensville, Ontario (Fig. 2) and associated QA-QC data collected using a pXRF spectrometer and a sub-set of 32 samples that were analysed using ICP-ES and ICP-MS after digestions by aqua-regia, multi acid and lithium borate/tetraborate fusion methods. These data are interpreted within the stratigraphic context of the Queensville borehole; however more complete analysis and integration with sedimentological facies is provided by Popović et al. (in press).

2.0 Study Area Geological Setting

The borehole site is located at easting 626499 and northing 4889266 (UTM NAD 83 – Zone 17) near Queensville, Ontario, on an upland north of Newmarket and the Oak Ridges Moraine (Fig. 1 and 2). These uplands generally have a surface exposure of Newmarket Till (e.g. Sharpe et al., 2002; Boyce and Eyles, 2000), are drumlinized and are bounded by north-south valleys (Tunnel Valleys). Underlying the Newmarket Till is a succession of stratigraphic units commonly referred to as Lower Deposits (Sharpe et al. 2002) that are most completely described from the Scarborough Bluffs and Toronto area, and include Don Beds, Scarborough Formation, Pottery Road Formation, Sunnybrook Till, and Thorncliffe Formation (Fig. 3). A number of these formations, notably Scarborough and Thorncliffe formations have been mapped northward using downhole geophysical logs (Eyles et al., 1985; Fligg and Rodrigues, 1983) and continuously cored boreholes (Sharpe et al., 2013; Logan et al., 2008).

The 96.2 m Queensville core intercepted four stratigraphic units which from the base upwards include bedrock, Thorncliffe Formation, Newmarket Till, and surface soil (Fig. 3). The limestone bedrock is part of the Georgian Bay Formation. At the Queensville borehole, the overlying Thorncliffe Formation consists of an upward fining succession of sand and gravel capped by 59 metres of mud with minor sand horizons. The mud is interpreted as rhythmites based on similar sediment successions of rhythmic mud logged in local boreholes, their position beneath the Newmarket Till, and absence of organics (e.g. Sharpe et al., 2011). The till consists of massive, dense, calcareous silt to sandy silt with limestone clasts. It is interpreted to be Newmarket Till based on surficial geological mapping of the area around the borehole (Sharpe et al., 1997) and the density of the material sampled. Beds are often three to five meters in thickness and may be separated by stone lines (Sharpe et al., 1998; 2002; 2005). According to Barnett (1992) the matrix carbonate content of typical Newmarket Till varies from 30-40% with calcite dominant east of the Niagara Escarpment and dolomite dominant west or above the escarpment. The till has been mapped as a regional drumlinized unit from the Canadian Shield southward beneath the Oak Ridges Moraine to Lake Ontario, (e.g., Sharpe et al., 1994; Pugin et al., 1999). North of the Oak Ridges Moraine large valleys that truncate the Newmarket Till have been identified in the subsurface beneath the moraine (Barnett, 1992; Sharpe et al., 1994, 1996, 1997, 1998, 1999; Barnett et al., 1998; Pugin et al., 1999; Brennand et al., 2006). These incised, partly infilled, glaciofluvial valleys are in places buried by Oak Ridges Moraine sediment (Russell et al., 2003). Consistent lithology and a diagnostic high-velocity seismic reflector (~2000 m/s, Pullan et al., 2000) make Newmarket Till a regional marker across the area and beneath Oak Ridges Moraine (Sibul et al., 1977).

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-c).

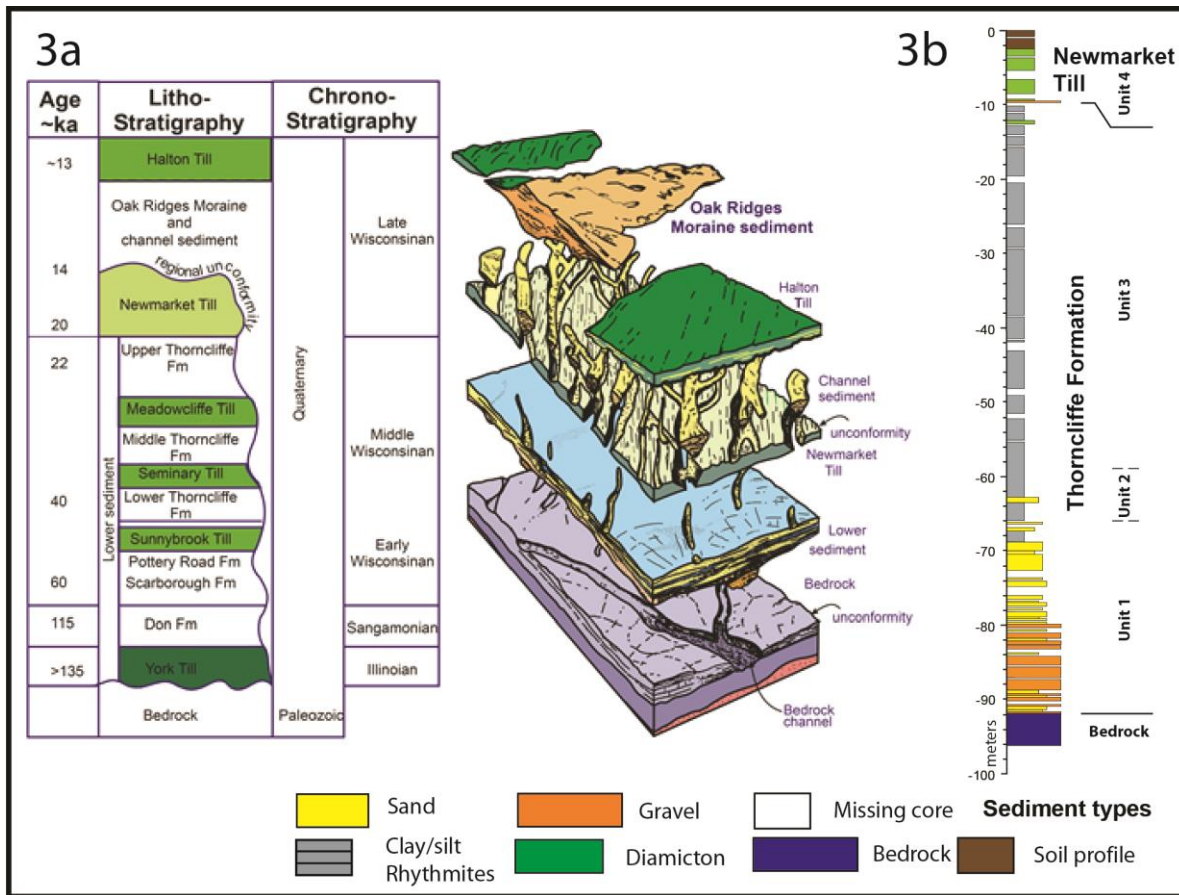


Figure 3a: Stratigraphy of the Greater Toronto Area. Modified from Sharpe et al. 2002. Key till units are highlighted in green. Figure 3b: Generalized lithostratigraphy of the Queensville borehole.

3.0 Sample collection, processing and analytical methods

The borehole was drilled in the fall of 2009 by Jagger Hims Ltd. using a full-sized, truck-mounted Sonic drilling. The hole was terminated four meters into bedrock. Borehole core was collected in ten foot runs. The sediment cores were placed in five foot PVC tubes, sealed with tape, and shipped to the Geological Survey of Canada, 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 <0.063 mm (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., 2015a), and sealed with 4 µm thick Chemplex® Prolene® Thin-Film. Portable XRF data were acquired using a handheld Thermo Scientific, Niton XL3t GOLDD spectrometer, equipped with Cygnet 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 32 samples were

sent to Bureau Veritas Commodities Ltd. (formerly Acme), Vancouver for traditional laboratory geochemical analyses. The three analytical procedures employed at Acme were: (1) aqua regia, a hot (95°C) $\text{HNO}_3\text{-HCl}$ digestion, followed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analysis; (2) multi-acid, a hot dissolution in $\text{HNO}_3\text{-HClO}_4\text{-HF}$, 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 Queensville 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 on the pXRF – which is recommended for elements expected to occur with <1% concentration. The X-ray emission lines used to determine elemental concentrations in Soil Mode are listed in Table 2. Elements listed in italics either did not occur in sufficient quantities to be detected or have peak interferences with other elements that rendered the returned value to be incorrect (e.g. Sc and Ca). In order to honor the protocol used for previous borehole studies (Knight et al., 2015c, 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.

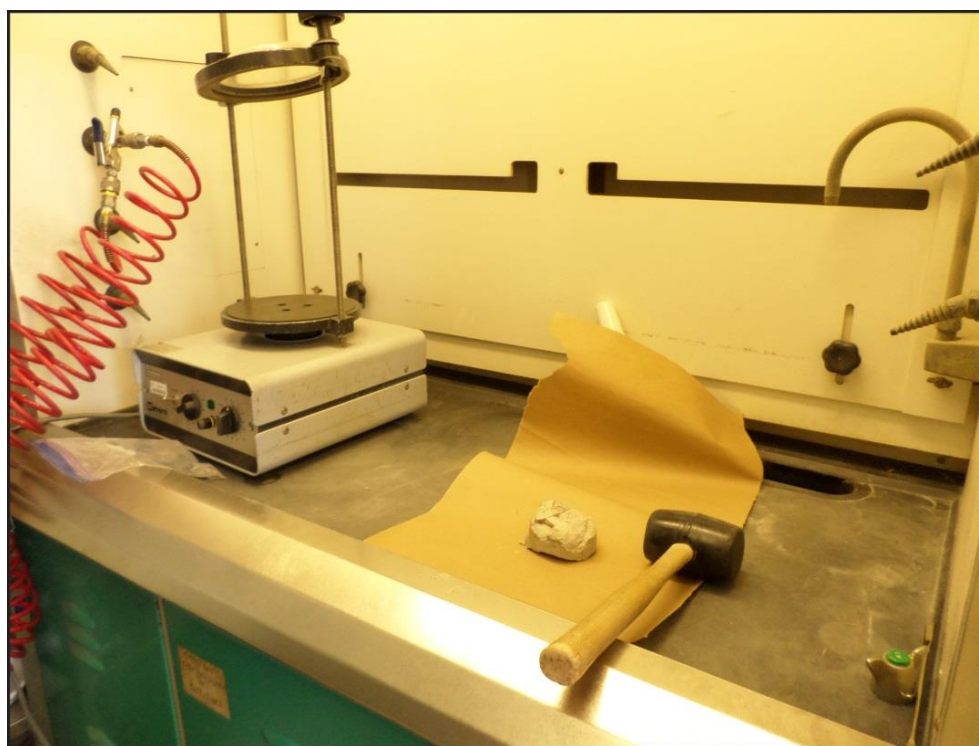


Figure 4: Prior to sieving sediment samples were disaggregated. The sample was placed between two pieces of brown construction paper and impacted with a rubber mallet.

Table 1: Summary of elements analyses by traditional geochemical methods. From Kjarsgaard et al. 2014a. 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. Elements in bold returned meaningful results. Elements in italics either did not occur in sufficient quantities to be detected or have interferences with other elements that rendered the returned value to be incorrect (e.g. Sc and Ca).

Element	Line	Energy (keV)	Window Low (keV)	Window High (keV)	Filter
As	<i>Kα_1</i>	10.54	10.33	10.73	Main
Ba	Kα_1	32.19	31.70	32.70	High
Ca	Kα_1	3.69	3.50	3.89	Low
<i>Cd</i>	<i>Kα_1</i>	23.17	22.60	23.60	High
Co	<i>Kα_1</i>	6.93	6.73	7.13	Main
Cr	<i>Kα_1</i>	5.41	5.24	5.59	Low
Cs	<i>Kα_1</i>	30.97	29.50	31.50	High
Cu	Kα_1	8.05	7.84	8.24	Main
Fe	Kα_1	6.40	6.20	6.60	Main
<i>Hg</i>	<i>Lα_1</i>	9.99	9.79	10.18	Main
K	Kα_1	3.31	3.10	3.49	Low
Mn	Kα_1	5.90	5.70	6.10	Main
Mo	Kα_1	17.48	17.23	17.68	Main
Ni	Kα_1	7.48	7.35	7.67	Main
<i>Pb</i>	<i>Lβ_1</i>	12.61	12.40	12.80	Main
Rb	Kα_1	13.39	13.18	13.60	Main
S	Kα_1	2.31	2.20	2.45	Low
<i>Sb</i>	<i>Kα_1</i>	26.36	25.90	26.90	High
<i>Sc</i>	<i>Kα_1</i>	4.09	3.90	4.19	Low
Se	<i>Kα_1</i>	11.22	11.01	11.41	Main
<i>Sn</i>	<i>Kα_1</i>	25.27	24.70	25.70	High
Sr	<i>Kα_1</i>	14.16	13.95	14.38	Main
<i>Te</i>	<i>Kα_1</i>	27.47	27.00	28.00	High
<i>Th</i>	<i>Lα_1</i>	12.97	12.80	13.15	Main
Ti	Kα_1	4.51	4.21	4.70	Low
<i>U</i>	<i>Lα_1</i>	13.61	13.48	13.90	Main
V	Kα_1	4.95	4.80	5.10	Low
<i>W</i>	<i>Lα_1</i>	8.40	8.26	8.49	Main
Zn	Kα_1	8.64	8.49	8.83	Main
Zr	Kα_1	15.77	15.53	15.98	Main



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

3.1 Reproducibility and Precision of Standards

Three standards (Till-1, Till-4, and TCA 8010) and 2 blanks (SiO_2 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 SiO_2 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, such as the 616 ppm Ca for one Teflon analysis, the operating environment (test stand) was purged with compressed air and wiped clean with Methanol until values returned were normal. The Chemplex[®] Prolene[®] thin-film that separates the sample from the spectrometer may contain trace amounts of Ca, P, Fe, Zn, Cu, Zr, Ti and Al. For the SiO_2 blank, Ba, Cd, K and V returned values below the recommended limits of detection ($< \text{LOD}$), 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 samples used as standards on a regular bases to minimize potential for 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 curve is required to correct the data or that the data is not reliable. As an example Ni values obtained from Till-1 have a %error of 251.

Similarly, U values obtained from Till-4 have a %error of 161. Although care must be taken when interpreting data with a high %error it is useful to plot these elements since chemostratigraphy utilizes the relative changes in concentration, making high precision 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 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. V) results 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.

3.3 Erroneous Analysis

During analyses of the Teflon blank, an erroneous value of 616 ppm for Ca was recorded. The spectrometer window and test stand were cleaned until the analytical value returned to normal. This emphasizes the importance of monitoring results in real time to ensure that such a returned result is not caused by inappropriate operating of the pXRF. No other unexplained or potential erroneous data were collected from the borehole samples.

Table 3. Summary statistics for SRM Till-1 by pXRF spectrometry for Queensville Borehole.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	18	12	19	7.10	1.3	6.45	17	21
Ba	702	12	871	24.13	20	2.25	835	904
Ca	19440	12	17268	-11.17	372	2.15	16677	17780
Co	18	3	145	707	24	16.44	126	172
Cr	65	12	31	-51.64	5.8	18.31	19	39
Cs	1	12	47	4645	3.41	7.19	41	52
Cu	47	12	54	15.40	3.94	7.27	47	62
Fe	48100	12	40920	-14.93	247	0.60	40271	41261
K	18429	12	15283	-17.07	168	1.09	14950	15584
Mn	1420	12	1371	-3.47	33	2.39	1314	1414
Mo	2	5	5	159	1.23	23.76	4.1	7.3
Ni	24	12	84	251	11	13.04	67	101
Pb	22	12	12	-47.21	1.8	15.18	9	15
Rb	44	12	41	-7.40	0.7	1.74	40	42
S	< 500	2	343	-31.47	27	7.84	324	362
Sr	291	12	270	-7.37	1.9	0.71	266	272
Th	5.6	9	4	-19.90	0.85	18.95	2.87	5.5
Ti	5990	12	5319	-11.20	77	1.44	5172	5441
U	2.2	9	6.4	191	0.8	11.74	5.6	7.8
V	99	12	157	59.08	13	7.97	134	178
Zn	98	12	93	-4.70	2.5	2.63	89	97
Zr	502	12	565	12.54	11.6	2.06	545	582

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

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	111	12	104	-6.4	1.9	1.88	100	107
Ba	395	12	462	16.9	16.0	3.46	431	492
Ca	8934	12	8118	-9.1	319	3.93	7656	8606
Cr	53	12	26	-51.2	4.8	18.53	21	34
Cs	12	12	26	120	3.0	11.28	21	30
Cu	237	12	213	-10.0	7.5	3.49	201	225
Fe	39700	12	33208	-16.4	134	0.40	32953	33491
K	26980	12	23928	-11.3	269	1.12	23504	24252
Mn	490	12	456	-7.0	17	3.72	423	476
Mo	16	12	18	13.1	1.8	9.81	15	21
Ni	17	12	54	220	10.6	19.48	37	75
Pb	50	12	42	-16.5	1.8	4.32	38	45
Rb	161	12	151	-6.3	1.9	1.26	147	154
S	800	12	598	-25.3	121	20.29	362	767
Sr	109	12	105	-3.4	1.4	1.29	103	107
Th	17.4	12	43	145	1.7	3.96	39	45
Ti	4840	12	4664	-3.6	84	1.79	4475	4749
U	5	11	13	161	3.4	26.30	6	18
V	67	12	127	89.6	8.1	6.40	114	140
W	204	12	183	-10.4	15	8.18	162	216
Zn	70	12	66	-5.4	2.9	4.40	61	71
Zr	385	12	435	13.0	11.9	2.73	421	459

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

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	5.5	12	7	20.3	1.3	19.06	5	9
Ba	549	12	724	31.8	17.9	2.47	694	753
Ca	15509	12	14293	-7.8	355	2.48	13844	14819
Co	8	2	72	801	5.9	8.19	68	76
Cr	48	12	19	-60.5	4.2	22.29	10	24.8
Cs	1	12	56	5532	3.0	5.25	50	60
Cu	28	12	33	19.3	3.0	8.96	29	41
Fe	20290	12	14039	-30.8	122	0.87	13756	14233
K	19094	12	15974	-16.3	196	1.23	15618	16262
Mn	310	12	309	-0.31	23	7.42	250	331
Ni	17	12	67	293	6.2	9.19	59	77
Rb	54	12	49	-8.7	1.3	2.61	47	52
Sr	310	12	265	-14.6	2.3	0.88	261	268
Th	5	12	4	-28.3	0.8	21.03	2	5
Ti	2578	12	2467	-4.3	72	2.91	2335	2580
U	1	9	6	474	0.8	14.42	5	7
V	49	12	72	46.2	7.7	10.78	57	88
Zn	32	12	33	2.7	3.7	11.23	27	38
Zr	272	12	314	15.3	15.9	5.07	292	344

Table 6. Elements detected in the Queensville borehole with corresponding detection limits for the pXRF using two matrix configurations and the filters used to detect these elements, provided by Thermo Scientific.

Element	Matrix		Filter
	SiO ₂	SiO ₂ + Fe +Ca	
Ba	35	45	High
Ca	40	N/A	Low
Cu	10	13	Low
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
Sr	3	3	Low
Ti	20	60	Low
V	10	25	Low
Zn	7	10	Main
Zr	3	4	Main

4.0 Results and Surficial chemostratigraphy

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 (Table 2). Elemental concentrations as determined by pXRF spectrometry and by ICP-ES/MS for the Queensville borehole samples as well as blank samples and standard reference materials are listed by method and digestion type in Appendix A and displayed graphically 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. The pXRF data is interpreted using single element trends from the base to the top of the boreholes.

The subset of samples submitted for traditional chemistry was 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 verify the validity of the pXRF value (e.g. Fe, V, and Zr from unit 1 of the borehole chemostratigraphy graphs). Bivariate plots comparing analytical data determined from a subset of pXRF analyses with fusion, multi-acid, and aqua regia digestions are also presented in Appendix B. For the bivariate plots, a one-to-one relationship is plotted as a dashed green line. Linear regression lines determined by the least squares approach to the data are displayed on the figures in black. Due to ‘clusters’ of points within the dataset, the regression lines are more dependent on the location of the clusters, 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 regression (RMA) that assumes there are errors to both y and x data was also carried out. 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. (2014b) and Knight et al. (2015c).

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.

For this study, based on r^2 values Mn, Rb, V, Zn, and Zr produce pXRF results that are similar to that of fusion and multi-acid chemistry (see Table 7 and regression plots Appendix B). Although the r^2 value for V as determined by aqua regia digestion is 0.838, the concentrations are under reported compared to multi-acid and fusion methods.

Table 7. Summary statistics for the comparison of pXRF data with fusion, multi acid, and aqua regia digestion methods, Queensville 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	/	/	/	/	/	/	0.62	22	1.0
Ba	0.26	14	1.3	0.17	12	8.5	0.53	47	2.5
Ca	0.96	13	1.4	0.88	14	1.2	0.91	16	1.2
Cu	0.41	51	0.7	0.45	51	0.7	0.42	58	0.7
Fe	0.98	46	0.8	0.96	47	0.8	0.82	30	2.0
K	0.61	9	1.0	0.61	10	0.9	0.81	47	3.2
Mn	0.96	28	0.9	0.97	26	0.9	0.05	16	0.5
Ni	/	/	/	0.00	23	0.0	0.21	34	2.3
Rb	0.92	18	1.0	0.96	19	0.9	/	/	/
S	/	/	/	0.24	27	0.5	0.12	25	0.2
Sr	0.63	7	0.5	0.67	5	0.7	0.32	17	0.2
Th	0.47	34	0.5	0.46	36	0.4	0.42	26	0.8
Ti	0.97	54	0.6	0.98	57	0.6	0.04	33	1.3
U	0.01	45	0.1	0.13	41	0.01	/	/	/
V	0.88	40	0.9	0.89	53	1.0	0.84	49	1.9
Zn	0.82	23	0.9	0.80	23	0.8	0.23	44	0.5
Zr	0.98	119	1.2	0.98	82	1.0	/	/	/

Based on observations of the chemostratigraphic profiles in Appendix B for Ba, Ca, Cu, Sr, Ti, and to a lesser degree Fe, and K, 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 Ca, Rb, and Cu is illustrated in figure 5. Both Ca and Rb display excellent r^2 values of .96 and .92 respectively. For Ca, pXRF methods overestimates the concentration compared to fusion chemistry. This may be due to using soil mode and Compton normalization for the analyses compared to mining mode and fundamental parameters when concentrations are greater than 1%. Regardless, the precision of the collected data is excellent and post calibration would be able to correct for issues with accuracy. For Rb, pXRF methods slightly under estimate concentrations compared to fusion methods (Fig. 6). The bivariate plot for Cu (Fig. 6) illustrates the difficulty of determining elemental concentrations by pXRF methods when returned values are near the detection limit (D.L. = 13 ppm). Although the r^2 for Cu is 0.41 (Table 7) and there is a considerable amount of scatter in the data plotted in figure 5, the downhole trends between pXRF data and fusion methods are similar (Fig. 6).

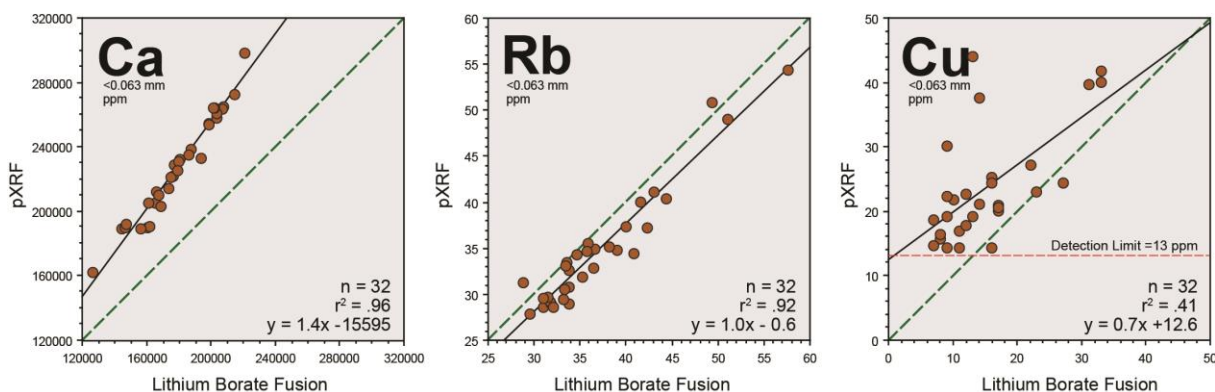


Figure 6: A comparison of pXRF results to fusion methods for Ca, Rb, and Cu. The green dashed line represents a 1:1 relationship. The red dashed line in the Cu scatterplot indicates the detection limit of 13 ppm.

For Ba, the regression line r^2 value (Appendix B) is poor; however, the data distribution does not match the linear regression lines suggesting that a reduced major axis (RMA) regression method described in York (1966) and utilized by Kjarsgaard et al. (2014b) would be better suited to delineate a calibration equation. As such, a second RMA line in blue has been added to the bivariate plots for Ba in Appendix B. Calibration equations using linear regression methods are outlined in Knight et al. (2013). Surprisingly, for a borehole located in Kinburn, Ontario (Knight et al., 2012) the results for Ba by pXRF were considerably lower than results obtained by fusion chemistry. However for the Queensville borehole, Ba results by pXRF are considerably higher than those results obtained by fusion chemistry. It should be noted that the Ti results for the Queensville borehole are almost half the value of Ti results from the Kinburn borehole. This suggests that the peak interference to differentiate between Ba and Ti may be more difficult to differentiate with higher values of Ti.

Further description and interpretation of the borehole sediment lithofacies and the relationship of pXRF spectrometry to depositional environments are presented in Popović et al. (in press). For sediments analysed in the Queensville borehole, Na, K, Ti, Zn, and Zr likely represent granitic provenance and Cu, Fe and Ni most likely represent a mafic to ultramafic provenance with Ca representing carbonate terrains. It is important to note that pXRF spectrometry can only infer generalizations with regards to source rock types.

Chemostratigraphy of the Queensville borehole can be divided into 4 units (Fig. 7). Three of these units correspond to the Thorncliffe Formation, while a fourth unit represents the overlying Newmarket Till. For Ca, chemostratigraphic trends mimic those of the carbon content while Cu concentrations may be somewhat controlled by sediment type even though all analyses are carried out on the <0.063 mm size fraction (Fig. 7). Rubidium displays very little variation with the exception of unit 2 and 4 (Fig. 7).

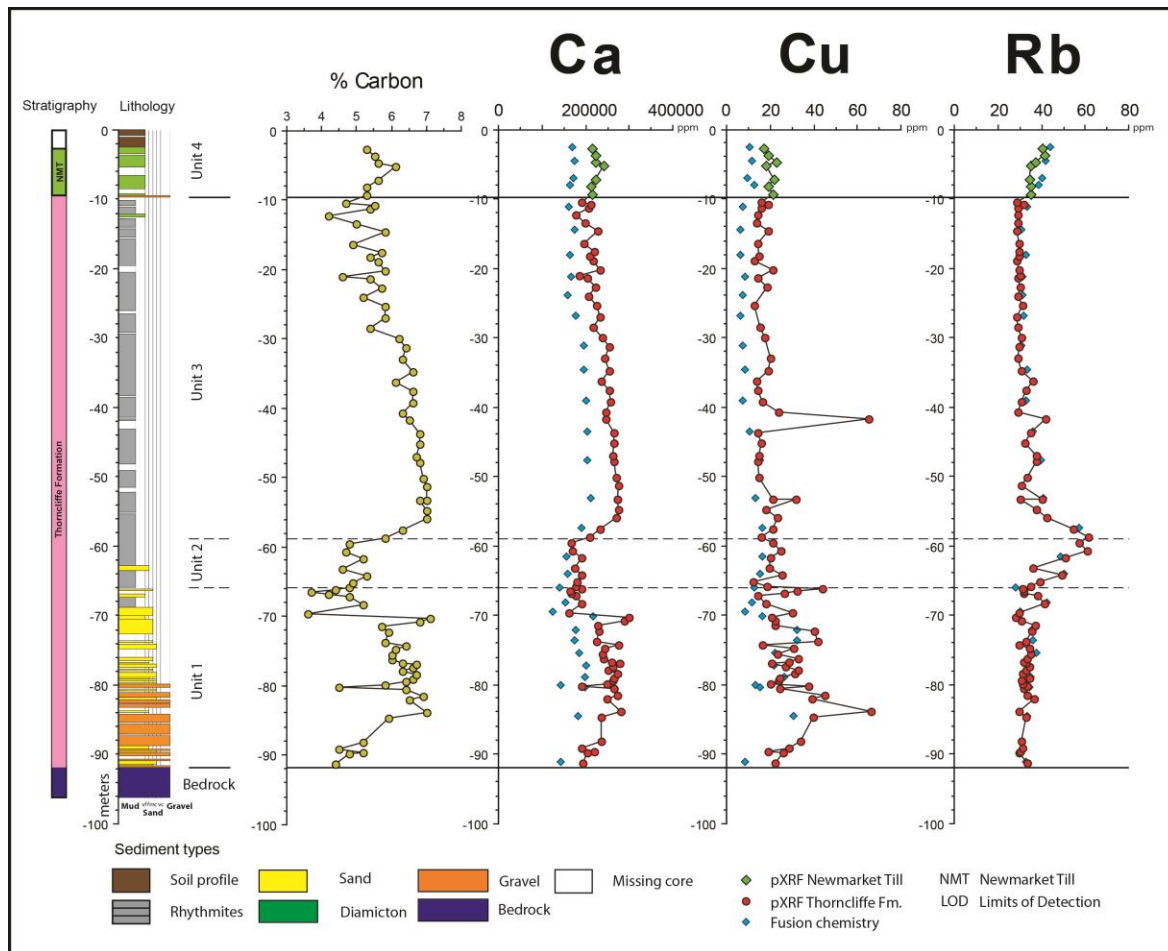


Figure 7: Lithostratigraphy, carbon content, and chemostratigraphy for Ca, Cu and Rb by pXRF and fusion chemistry methods.

Unit 1 92-66 m (Thornccliffe Formation)

The most distinctive characteristic of the lowermost unit is the high degree of variability of concentrations for most elements (e.g. Ba, Cu, V, Zr). This variability most likely reflects the small scale fining upwards sequences observed during core logging and is attributed to dynamic changes in depositional processes. However, some elements, such as Ca, Fe, K Mn, and Rb, however, display minimal variability throughout the unit. The contact between unit 1 and unit 2 corresponds to the change in grain size between the gravel/sand interbeds and the overlying silt/clay rhythmites. This contact is also reflected by a spike in the geochemical signature for Cu, Fe, Mn, Ti, V, Zn and Zr.

For most elements other than K, Rb and to a lesser degree Fe, variable concentrations in the lower sediments of the Thornccliffe Formation (unit 1) confirm a high degree of variability in sediment provenance, as noted during the core logging (Popović in press). Potassium and Rb concentrations most likely represent a stable and continuous input of sediment from shield terrain whereas variations in Ba and Ca most likely represent fluctuations in sediment input from carbonate terrains.

Unit 2 66-59 m (Thorncliffe Formation)

Unit 2 displays much less variability in elemental concentrations compared to the underlying unit 1 sediments (e.g. Fe, S, Ti, V, Zr). According to Popović (in press) the rhythmites of unit 2 are transitional from unit 1 and are thinner and more frequent than the overlying unit 3 rhythmites

Unit 3 59-8 m (Thorncliffe Formation)

The change in elemental concentrations between unit 2 and unit 3 is most notable for Ca and Sr where there is an overall increase in concentration over the interval from 59-56 m in depth (Fig. 6), whereas K, Rb, Ti, V, Zn display a decrease in concentrations over the same interval. This may reflect the mobility of elements above the unit 2 contact. For some elements (Ca, Fe, K, Mn, Sr, Ti, Zr) concentrations remain similar throughout the rest of unit 3. Barium is the only element that displays a constant increase in concentration from the base of unit 3 (~200 ppm) to the contact between unit 3 and unit 4 (~600 ppm). At a depth of 42 meters there is a spike in Cu and Zn, and to a lesser degree, in Rb, K, and S which is a departure from the normal trends throughout unit 3. It should be noted, however, that the sediments just below the base of unit 4 were not recovered.

Unit 4 8-3 m (Newmarket Till)

Geochemically, there is minimal elemental signal change between unit 3 and unit 4 for elements such as Ca, Cu, Fe, K, Mn, Rb, Sr, Ti, V, and Zr. Barium and Ni both display a decrease in concentration at the contact; however the remaining elements display little if any change in concentration from the underlying unit 3 sediments. This suggests that the <0.063 mm size fraction of unit 4 has the same provenance as the underlying unit 3 sediments, or that the matrix of the Newmarket Till is derived from the Thorncliffe Formation.

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. The geochemical signal in the Queensville core is less pronounced than work from further east at the Purple Woods conservation area (Knight et al., in press a).

Core geochemistry trends suggest that provenance of Queensville core sediment was relatively consistent and depositional processes did not partition sediment to impart a highly variable geochemical signal between stratigraphic units. For Ca the concentrations obtained by pXRF spectrometry mimic the % carbon content for all units (Fig. 7). For many elements (e.g. Ca, Cu, Fe, K, Mn, etc.) the transition from Thorncliffe rhythmites to overlying Newmarket Till displays very little to no change in concentration. This indicates that for the <0.063 mm size fraction the rhythmites and the till have the same provenance or that sediment derived from the rhythmites may have been incorporated into the overlying till matrix. This observation differs from the contact between the Thorncliffe Formation and Newmarket Till in both the Aurora (Knight et al., 2015b) and Purple Woods Conservation area (Knight et al., in press a) boreholes.

The borehole data collected at Queensville 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 for many elements multi-acid methods. These data can provide insight into the provenance of analyzed sediments. This geochemical study complements other chemostratigraphic studies being carried out in Southern Ontario (Coffin, et al., in press; 2015; Knight et al. (2015b); Knight in press, a, b, c, d; Popovic, et al., in press).

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