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**GEOLOGICAL SURVEY OF CANADA
OPEN FILE 7919**

**Portable XRF spectrometry, fusion, multi acid,
and aqua regia results from the Aurora borehole,
Yonge Street Aquifer, southern Ontario**

R.D. Knight, D.R. Sharpe, L.J. Valiquette

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Publications in this series have not been edited; they are released as submitted by the author.

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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 (ORM) (Sharpe et al., 2013). Although much work has involved sequence stratigraphy and basin analyses of sediments within this region, there is a paucity of information on the regional geochemistry of sediments. Results from such studies are helpful for defining chemical and related mineralogical variations within sediments and contributes to information collected by 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.

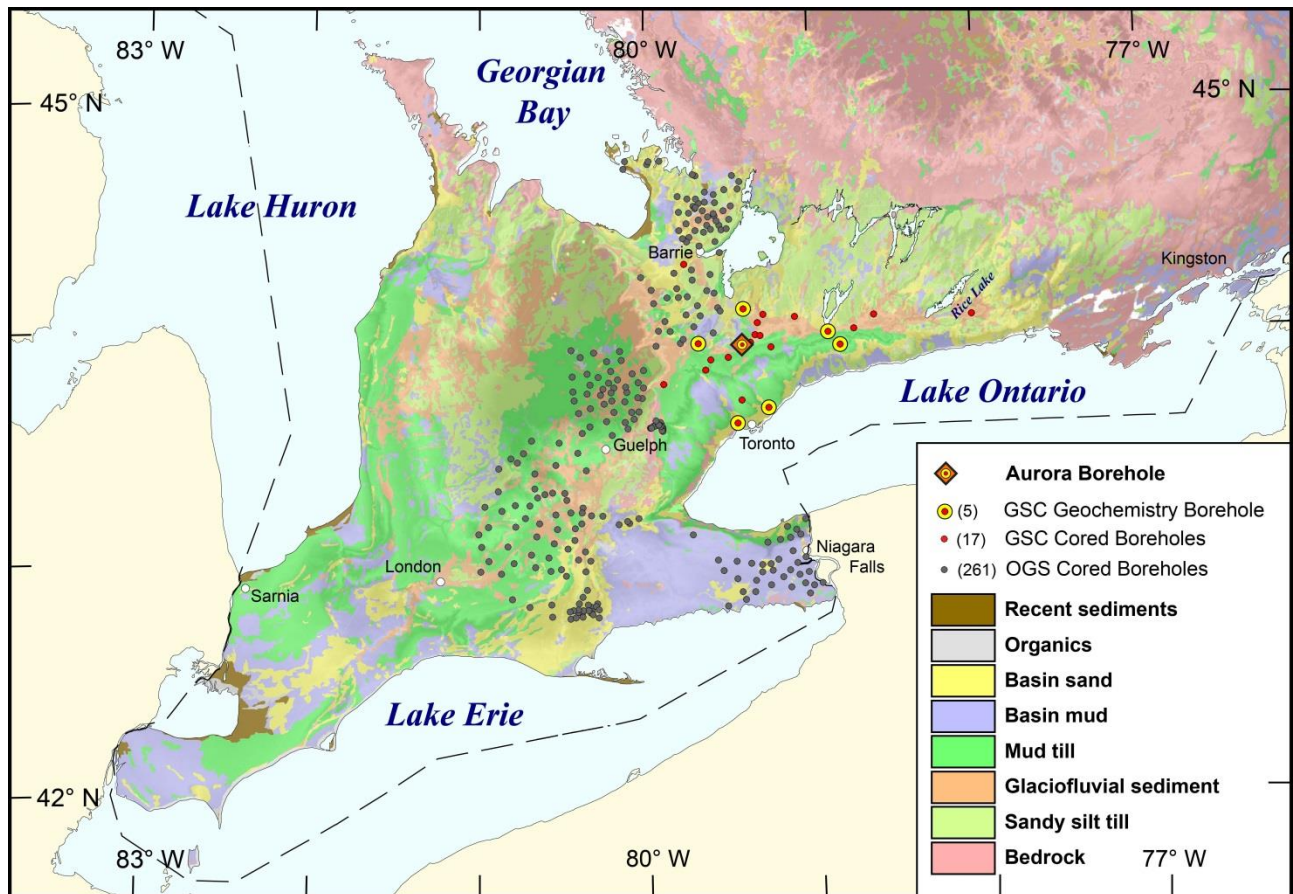


Figure 1: Location of the Aurora borehole with simplified regional geology of southwestern Ontario. Note the distribution of OGS and GS stratigraphic boreholes with continuous core descriptions. Geology simplified from Barnett et al. (1991).

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., in press; Knight et al., 2015) and to improve 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. The method is best suited to unconsolidated or crushed bedrock detritus and reworked surficial sediments that are <0.063 mm (silt and clay) in size (Plourde et al., 2012, Knight et al., 2012). The resulting data sets provide 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 120 samples from a 141 m borehole drilled near Aurora, Ontario, and associated QA-QC data collected using a pXRF spectrometer. This data release also contains 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 Aurora borehole as documented by Sharpe, et al. (2011) in GSC Current Research 2011-1. Additional pXRF data and sedimentological information have been collected in 2015 for a number of borehole cores in the Greater Toronto Area (GTA) (Coffin, et al., in press, a, b; Knight et al., in press, a, b, c, d, e; Popovic, et al., in press).

2.0 Study Area Geological Setting

The Aurora borehole is located on Bloomington fan sediments at an elevation of ~267 m a.s.l. in the Holland River watershed (Sharpe et al., 2011) and intersects the Yonge Street Aquifer. Approximately 130 m of sediment unconformably overlies shale of the Whitby Formation. These sediments are assigned to the Thorncliffe Formation, the Newmarket Till and the Oak Ridges Moraine. Generally, sediments underlying the Newmarket Till form a succession of stratigraphic units commonly referred to as Lower Deposits (Sharpe et al., 2002) which are most completely described from the Scarborough Bluffs and Toronto area, and include Don Beds, Pottery Road Formation, Scarborough Formation, Sunnybrook Till, and Thorncliffe Formation (Fig. 2). In the Aurora borehole for the Lower Deposits only the Thorncliffe Formation is present. 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).

3.0 Sample collection, processing and analytical methods

The borehole was drilled in the spring of 1997 by All Terrain Drilling using a mud rotary/wireline system. The 141 meter hole was terminated 2 meters into bedrock. Borehole core was collected in 10 ft runs. The sediment cores were placed in five foot PVC tubes, sealed with tape, and shipped to GSC Tunney's Pasture facility in Ottawa for further logging, sampling, and storage. A suite of downhole geophysical logs, including magnetic susceptibility, apparent conductivity, P- and S- wave velocities, gamma, and fluid temperatures were obtained for the borehole (Pugin et al., 1999). A tabulated list of drilling parameters is available in Sharpe et al. (2003).

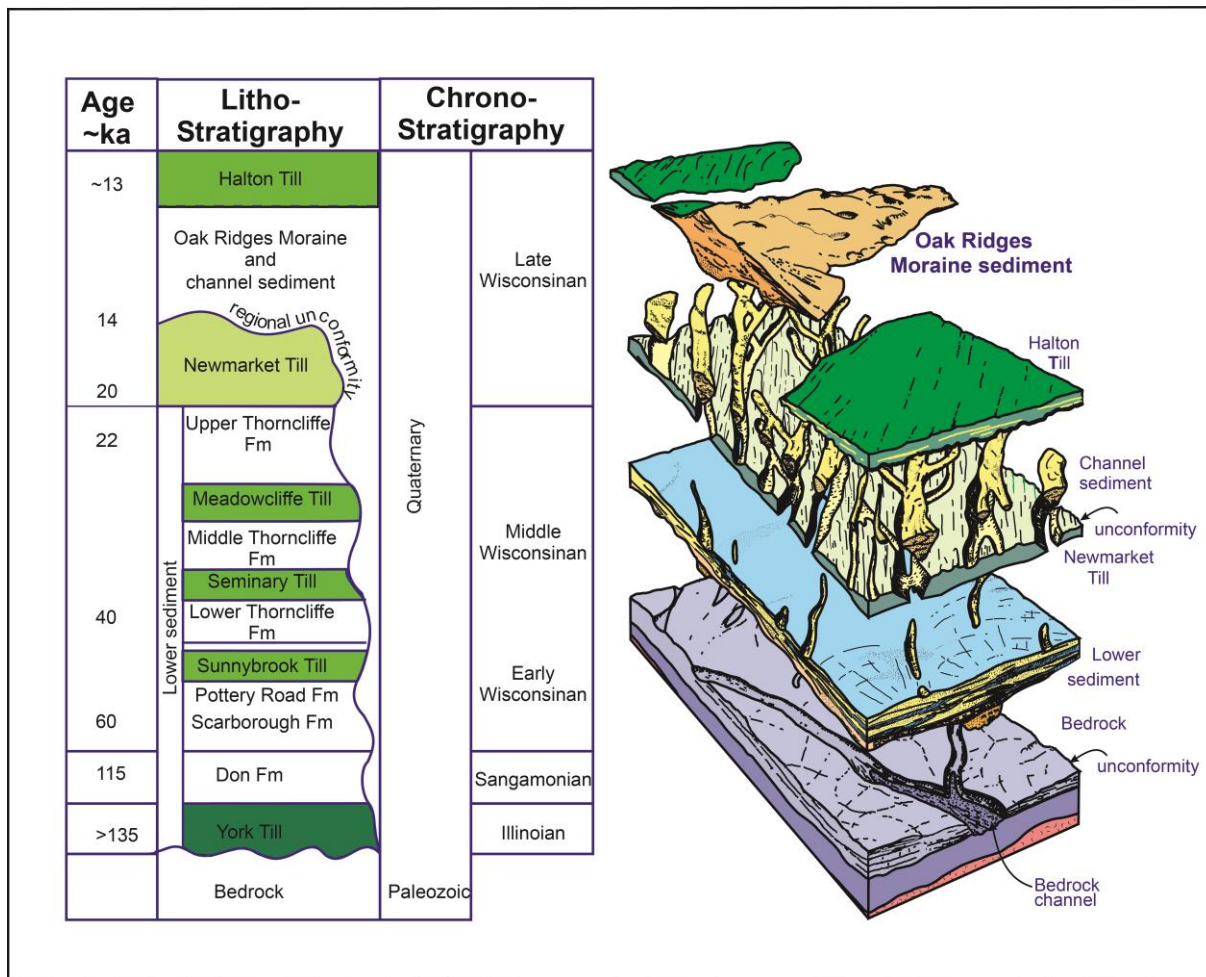


Figure 2: Stratigraphy of the Greater Toronto Area. Modified from Sharpe et al. 2002. Key till units highlighted in green.

Grain size was determined for each sample being analysed for geochemistry using a Camsizer particle scanner and a Lecotrac LT100 laser diffractometer. All grains > 2 mm in diameter were removed prior to grain size analysis. Numerical results are tabulated in Appendix A and graphically displayed in Appendix B.

Prior to pXRF analyses the sediment was disaggregated by impacting the sample placed between brown construction paper with a rubber mallet (Fig. 3). Seventeen samples from the Newmarket Till and the rhythmites above the till were too compact to disaggregate by this method and were placed between brown paper in a stainless steel receptacle (that had been cleaned by sand blasting followed by air blasting) and shattered using a hydraulic press (Fig 4a-d). These samples were further disaggregated with a rubber mallet prior to sieving. Post disaggregation all samples were sieved to <63 μm (silt + clay) at the GSC Sedimentology Laboratories in Ottawa. The processed samples were placed in 23 mm diameter plastic vials, to an approximate height of 30 mm, to obtain infinite thickness, 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 was sent to Bureau Veritas Commodities Ltd. (formerly AcmeLabs), 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 verify the validity of the pXRF value (e.g., Fe, V, and Zr from unit 1 of the borehole chemostratigraphy graphs).

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 analyzed by each method is presented in Appendix A along with a second .xls file containing data on QA-QC for duplicate sample analyses and standard reference materials that were analyzed with the samples from the Aurora borehole. A summary list of elements detected by these 3 traditional geochemical methods and the limits of detection is presented in Table 1.

For pXRF spectrometry 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., in press, a, b; 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. However, Knight et al. (2013) has documented that dwell times as low as 30 seconds for some elements can return precise and accurate results.

The pXRF data are interpreted using single element trends from the base to the top of the borehole. Seventeen elements (As, Ba, Ca, Cu, Fe, K, Mn, Ni, Rb, S, Sr, Th, Ti, U, V, Zn, and Zr) were detected in sufficient quantities to produce meaningful results using the pXRF spectrometer. The X-ray emission lines used to determine elemental concentrations in Soil Mode are listed in Table 2. Results for all methods are presented in Appendix A, and displayed graphically in Appendix B for pXRF and fusion methods. 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 fusion, multi acid, and aqua regia data are compared to pXRF data using single element regression plots to determine accuracy (Appendix B).

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
SiO2	%	0.01	Ti	%	0.001	Ti	%	0.001
TiO2	%	0.01	Al	%	0.02	Al	%	0.01
Al2O3	%	0.01	Fe	%	0.02	Fe	%	0.01
Cr2O3	%	0.002	Ca	%	0.02	Mg	%	0.01
Fe2O3	%	0.04	Mg	%	0.02	Ca	%	0.01
MnO	%	0.01	Na	%	0.002	Na	%	0.001
MgO	%	0.01	K	%	0.02	K	%	0.01
CaO	%	0.01	P	%	0.001	P	%	0.001
Na2O	%	0.01	S	%	0.04	S	%	0.02
K2O	%	0.01	Li	ppm	0.1	Li	ppm	0.1
P2O5	%	0.01	Rb	ppm	0.1	Rb	ppm	0.1
LOI	%	0.10	Cs	ppm	0.1	Cs	ppm	0.02
TOT/C	%	0.02	Be	ppm	1	Be	ppm	0.1
TOT/S	%	0.02	Ba	ppm	1	Sr	ppm	0.5
Rb	ppm	0.1	Sr	ppm	1	Ba	ppm	0.5
Cs	ppm	0.1	Zr	ppm	0.2	Zr	ppm	0.1
Be	ppm	1	Nb	ppm	0.04	Nb	ppm	0.02
Sr	ppm	0.5	Hf	ppm	0.02	Hf	ppm	0.02
Ba	ppm	1	Ta	ppm	0.1	Ta	ppm	0.05
Zr	ppm	0.1	Y	ppm	0.1	Y	ppm	0.01
Nb	ppm	0.1	Sc	ppm	0.1	Sc	ppm	0.1
Hf	ppm	0.1	V	ppm	1	V	ppm	2
Ta	ppm	0.1	Cr	ppm	1	Cr	ppm	0.5
Y	ppm	0.1	Mn	ppm	2	Mn	ppm	1
Sc	ppm	1	Co	ppm	0.2	Co	ppm	0.1
V	ppm	8	Ni	ppm	0.1	Ni	ppm	0.1
Cr	ppm	14	Cu	ppm	0.02	Cu	ppm	0.01
Co	ppm	0.2	Zn	ppm	0.2	Zn	ppm	0.1
Ni	ppm	20	Pb	ppm	0.02	Pb	ppm	0.01
Cu	ppm	5	Mo	ppm	0.05	Tl	ppm	0.02
Zn	ppm	5	W	ppm	0.1	Mo	ppm	0.01
Pb	ppm	1	As	ppm	0.2	W	ppm	0.1
Mo	ppm	1	Sb	ppm	0.02	As	ppm	0.1
W	ppm	0.5	Bi	ppm	0.04	Sb	ppm	0.02
Ga	ppm	0.5	Ga	ppm	0.02	Bi	ppm	0.02
Sn	ppm	1	Cd	ppm	0.02	B	ppm	20
La	ppm	0.1	Sn	ppm	0.1	Se	ppm	0.1
Ce	ppm	0.1	La	ppm	0.1	Te	ppm	0.02
Pr	ppm	0.02	Ce	ppm	0.02	Ga	ppm	0.1
Nd	ppm	0.30	Pr	ppm	0.1	Ge	ppm	0.1
Sm	ppm	0.05	Nd	ppm	0.1	Cd	ppm	0.01
Eu	ppm	0.02	Sm	ppm	0.1	Sn	ppm	0.1
Gd	ppm	0.05	Eu	ppm	0.1	In	ppm	0.02
Tb	ppm	0.01	Gd	ppm	0.1	La	ppm	0.5
Dy	ppm	0.05	Tb	ppm	0.1	Ce	ppm	0.1
Ho	ppm	0.02	Dy	ppm	0.1	Pr	ppm	0.02
Er	ppm	0.03	Ho	ppm	0.1	Nd	ppm	0.02
Tm	ppm	0.01	Er	ppm	0.1	Sm	ppm	0.02
Yb	ppm	0.05	Tm	ppm	0.1	Eu	ppm	0.02
Lu	ppm	0.01	Yb	ppm	0.1	Gd	ppm	0.02
Th	ppm	0.2	Lu	ppm	0.1	Tb	ppm	0.02
U	ppm	0.1	Th	ppm	0.1	Dy	ppm	0.02
			U	ppm	0.1	Ho	ppm	0.02
			Au	ppm	0.1	Er	ppm	0.02
			Ag	ppb	20	Tm	ppm	0.02
						Yb	ppm	0.02
						Lu	ppm	0.02
						Th	ppm	0.1
						U	ppm	0.1
						Pd	ppb	10
						Ag	ppb	2
						Re	ppb	1
						Pt	ppb	2
						Au	ppb	0.2
						Hg	ppb	5

Table 2: X-ray energy intensities used to determine elemental concentrations in Soil Mode, as provided by Thermo Scientific (2015).

Element	Line	Energy (keV)	Window Low (keV)	Window High (keV)	Filter
As	K α_1	10.54	10.33	10.73	Main
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
Th	L α_1	12.97	12.80	13.15	Main
Ti	K α_1	4.51	4.21	4.70	Low
U	L α_1	13.61	13.48	13.90	Main
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

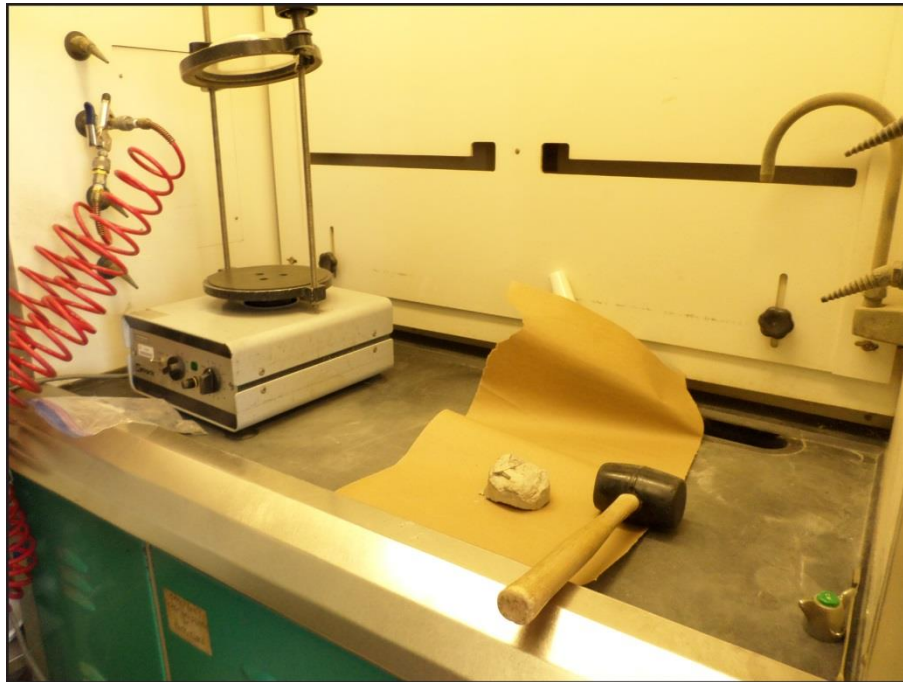


Figure 3: Prior to sieving sediment samples were disaggregated. The sample was placed between two pieces of brown construction paper and impacted with a rubber mallet.

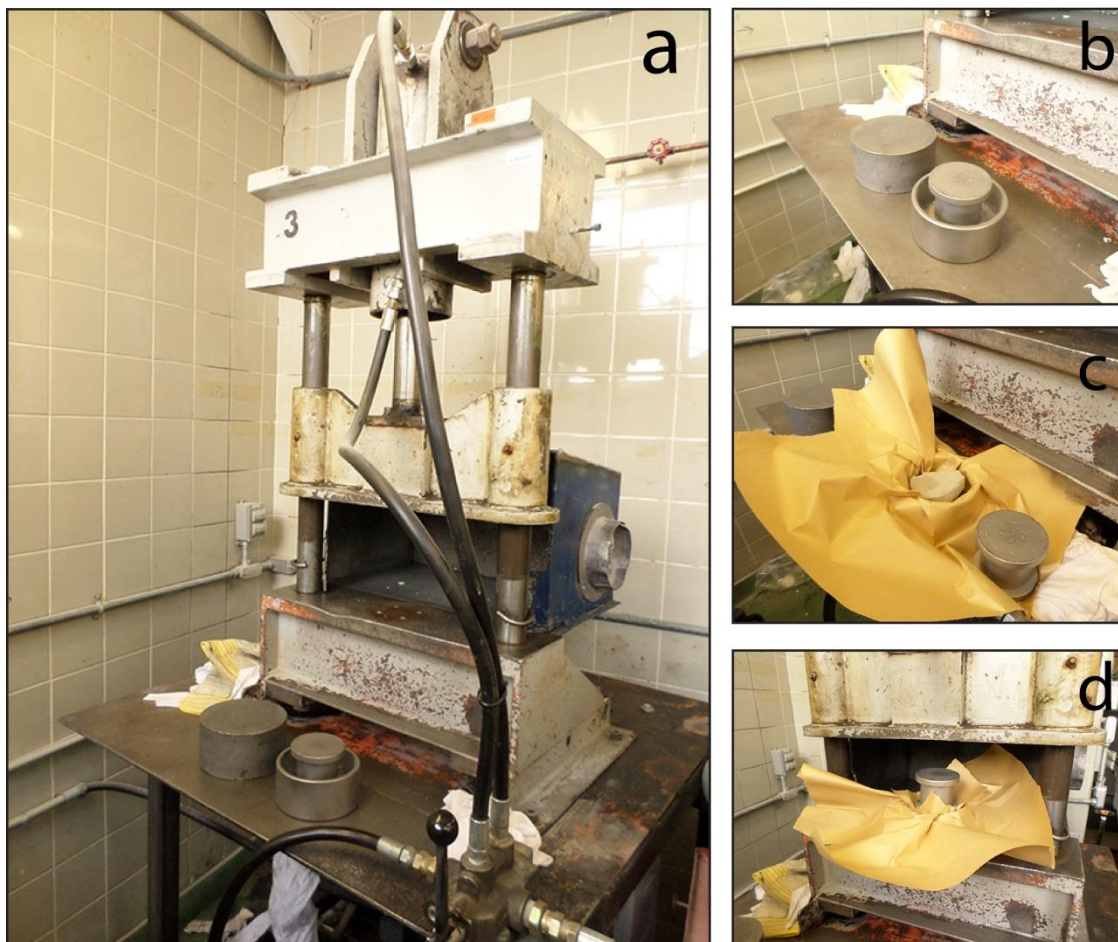


Figure 4: Sediment from the Newmarket till and the clay rhythmities above the till was disaggregated by placing the sediment between a sheet of construction paper in a stainless steel holder (photo a, b and c) and compressing the sample in a hydraulic press (photo a, and d) until it shatters.

3.1 Reproducibility and Precision of Standards

A Teflon blank and a SiO_2 blank were analysed to determine the cleanliness of the pXRF window and sample stand environment. After approximately 10 analyses the operating environment (test stand) was purged with compressed air and wiped clean. Commonly the Teflon blank returns values in the 10's of ppm Ti and may return trace amounts of Mo. 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 SiO_2 blank, Ba, Cs, K and V returned values below the recommended limits of detection (< LOD). These elements are not listed as known impurities on the Chemplex Prolene thin-film and most likely represent internal detector noise. Ca and Fe returned values above the limits of detection and which may be associated with the impurities in Chemplex Prolene thin-film, or represent contamination of the thin film. We recommend that the Chemplex Prolene thin-film be replaced 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 as determined by traditional wet chemistry methods are listed for Till-1 (Table 2), Till-4 (Table 3), and TCA 8010 (Table 4). 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 are not reliable. As an example Cs values obtained from Till-1 have an error of 4592% with a recommended value of 1 ppm and a pXRF mean value from 15 analyses of 47 ppm. Similarly, U values obtained from Till-4 have an error of 193%. These values are consistent with those reported in Knight et al. (in press, a) for a borehole located near Queensville, Ontario. Although care must be taken when interpreting data with a high error it may be useful to plot these elements to see if their relative changes in chemostratigraphy correlate with those of other more reliable elements. Since chemostratigraphy utilizes the relative changes in concentration, high precision in returned values is more important than accuracy. It is also important to note that the precision and accuracy are affected by concentration. Lower concentrations, especially those near the limit of detection (LOD) tend to result in lower precision, and thus higher %RSD.

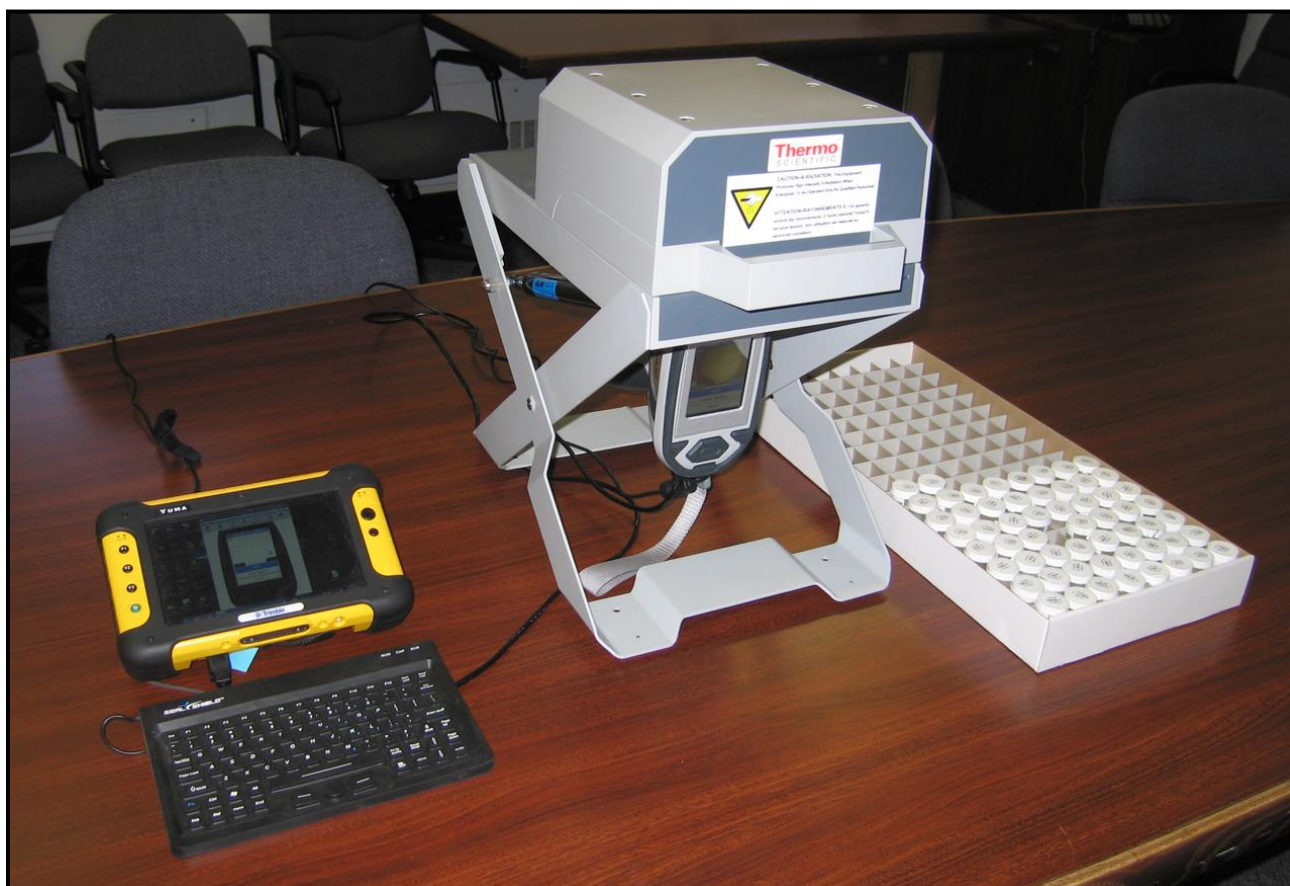


Figure 5. Example of pXRF spectrometer mounted in a test stand with microcomputer for analysis of processed sediment samples.

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. As and Th) the pXRF returned analyses lower than the recommended 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 recommended LOD value. It should be noted that for V three returned values (34, 34, and 39 ppm) are very close to the LOD of 25 ppm. 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 Whitby Formation at the base of the borehole, one result (15-AUR-pXRF-002) returned very high concentrations for Cu, Ni, W, and Zn. This data was initially thought to be erroneous however subsequent analyses by traditional geochemical methods substantiated the pXRF result. This emphasizes both the importance of monitoring results in real time to ensure that such a result is not caused by inappropriate operating and to have any potential anomalies results reanalyzed using traditional geochemical methods. No anomalous or potential erroneous data were observed from the borehole samples.

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

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	18	15	18	0	1.3	7.18	16	20
Ba	702	15	866	23.4	21	2.37	831	899
Ca	19440	15	17315	-10.93	119	0.81	16994	17459
Co	18	3	168	652.6	14	10.31	127	152
Cr	65	15	34	-48.2	7.7	14.05	26	41
Cs	1	15	47	4592	3.57	7.61	41	52
Cu	47	15	55	17.6	3.42	6.2	49	62
Fe	48100	15	41105	-14.5	175	0.43	40851	41390
K	18429	15	15406	-16.4	188	1.22	15174	15774
Mn	1420	15	1378	-2.9	29	2.14	1318	1417
Mo	2	5	5	145	1.6	32.4	3.2	7.0
Ni	24	15	83	245	7.8	9.54	66	97
Pb	22	15	13	-41.5	1.4	10.92	11	15
Rb	44	15	40	-8.4	1.0	2.53	39	42
S	< 500	4	425	-15.0	115	27	337	592
Sr	291	15	270	-7.4	2.2	0.8	266	273
Th	5.6	11	4.54	-18.9	0.94	20.65	2.83	5.91
Ti	5990	15	5348	-10.71	65	1.22	5227	5451
U	2.2	13	7	224	1.7	23.8	4.88	10.15
V	99	15	160	61.1	17.3	10.8	135	191
W	< 1	5	33	3149	5.42	16.7	27	41
Zn	98	15	90	-8.7	3.0	3.34	83	94
Zr	502	15	564	12.4	13.4	2.37	550	593

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

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	111	15	104	-6.2	1.7	1.65	100	106
Ba	395	15	453	14.7	3.8	3.75	424	486
Ca	8934	15	8108	-9.3	138	1.70	7819	8280
Co	8	2	146	1727	9.9	6.74	139	153
Cr	53	15	24	-55.6	4.2	17.92	18	33
Cs	12	15	24	103	3.4	13.73	16	30
Cu	237	15	215	-9.2	4.3	2.02	209	225
Fe	39700	15	33277	-16.2	234	0.70	32815	33671
K	26980	15	23942	-11.3	283	1.18	23441	24352
Mn	490	15	449	-8.3	13.1	2.91	424	472
Mo	16	15	17	8.2	2.3	13.41	14	22
Ni	17	15	57	236	6.2	10.86	43	68
Pb	50	15	42	-15.2	2.0	4.62	39	47
Rb	161	15	152	-5.7	2.2	1.46	149	158
S	800	15	621	-22.3	95.3	15.35	451	759
Sr	109	15	105	-3.4	1.3	1.19	103	107
Th	17.4	15	42	141	1.4	3.35	39	44
Ti	4840	15	4673	-3.4	98.4	2.11	4435	4849
U	5	15	15	193	4.8	32.51	8	22
V	67	15	123	83.1	11.0	8.94	102	140
W	204	15	178	-12.6	10.9	6.14	165	198
Zn	70	15	67	-4.6	3.0	4.53	62	73
Zr	385	15	433	12.5	11.5	2.66	416	463

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

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	5.5	15	6	17.4	0.8	11.93	5	8
Ba	549	15	722	31.4	17.9	2.48	688	752
Ca	15509	15	14184	-8.5	205	1.45	13809	14585
Co	8	3	89	1021	9.7	10.92	83	100
Cr	48	15	18	-63.5	6.1	34.59	10	31
Cs	1	15	57	5552	3.2	5.60	52	63
Cu	28	15	34	21.9	4.4	12.77	26	40
Fe	20290	15	14071	-30.7	184	1.31	13767	14374
K	19094	15	16029	-16.0	341	2.13	15592	16636
Mn	310	15	309	-0.2	16.1	5.22	287	339
Ni	17	15	66	281	8.6	13.04	50	78
Pb	12	2	4.5	-61.1	0.3	5.67	4	5
Rb	54	15	50	-7.6	0.7	1.35	48	51
Sr	310	15	265	-14.6	1.3	0.49	263	268
Th	5	15	4	-27.9	0.62	16.86	2	5
Ti	2578	15	2449	-5.0	112	4.57	2317	2601
U	1	13	8	598	1.5	19.52	5	10
V	49	15	76	55.2	7.7	10.18	59	94
W	1	3	25	4990	0.7	2.55	25	26
Zn	32	15	33	3.4	2.4	7.19	29	37
Zr	272	15	312	14.7	11.0	3.53	289	322

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

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

4.0 Results and Surficial chemostratigraphy

Elemental concentrations as determined by pXRF spectrometry and by ICP-ES/MS for the Aurora borehole samples as well as blank samples and standard reference materials are listed in Appendix A, by method and digestion type. Individual element concentration data as determined by pXRF and by fusion methods are plotted with respect to depth in Appendix B. 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 line. Where clustering of data occurs a reduced major axis regression (RMA) that assumes there are errors to both y and x data was also carried. 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. (in press, a). 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 analyzed. 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 r^2 values of >0.90 Ca, Fe, Mn, and Zr have pXRF results that are similar to that of fusion and multi acid chemistry (see Table 7 and regression plots Appendix B). Using multiple criteria Knight et al. (2012) proposed 5 categories for assessing pXRF data by comparing the data quality with published results for standard reference materials Till-1, -2, -3, and -4. The categories were based on the relationships between the coefficient of determination (r^2), %RSD, and slope (m), to represent linearity, precision, and the factory calibration, respectively. Elements were categorised using an r^2 value of 0.97 and 0.75 as a break point, and slopes with a range of $0.95 \leq m \leq 1.05$ represent the fit of a near-perfect factory calibration. It should be noted that %RSD is the least reproducible of the three variables as it is strongly dependent on the elemental concentrations in the analysed materials. Table 7 provides a summary of these parameters 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 Ca, Fe, K, Mn, Rb, Ti, V, Zn, and Zr. Elements that do not compare well with fusion data include As, Ba, Cu, Ni, S, U, and Th. It should be noted that for chemostratigraphic purposes changes in the vertical trend of elemental concentrations are of greater importance than the accuracy of the data.

Chemostratigraphy of the Aurora borehole can be divided into 7 units that span 5 formations. The base of the borehole is represented by bedrock of the Whitby Formation. Overlying this bedrock are unconsolidated sediments representing the Thorncliffe Formation, Newmarket Till, silt-clay rhythmites, and Oak Ridges Moraine sediments.

Table 7. Summary statistics for the comparison of pXRF data with fusion, multi acid, and aqua regia digestion methods, Aurora 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	/	/	/	/	/	/	0.10	37	0.5
Ba	0.02	19	0.2	0.04	18	0.3	0.42	79	-1.5
Ca	0.96	26	1.4	0.96	27	1.3	0.91	28	1.4
Cu	0.00	32	0.0	0.07	31	0.3	0.03	36	0.2
Fe	0.97	32	0.8	0.95	33	0.7	0.48	24	1.2
K	0.90	20	1.0	0.59	17	1.1	0.85	68	3.7
Mn	0.96	29	0.9	0.96	26	0.9	0.04	35	0.2
Ni	/	/	/	0.19	30	-1.6	0.36	47	-2.2
Rb	0.99	34	0.9	0.84	29	1.0	/	/	/
S	/	/	/	0.65	105	0.6	0.97	92	0.7
Sr	0.85	11	0.7	0.92	10	0.8	0.45	30	0.3
Th	0.10	21	0.0	0.08	21	0.3	0.29	29	0.6
Ti	0.88	44	0.6	0.87	43	0.6	0.00	47	0.1
U	0.20	33	1.1	0.18	28	1.5	/	/	/
V	0.69	33	0.9	0.66	37	0.9	0.74	33	2.3
Zn	0.86	22	0.8	0.82	23	0.7	0.40	38	0.5

4.1 Whitby Formation (bedrock)

The lowermost 4 m of the borehole intersect black shale of the Ordovician Whitby Formation. The uppermost meter of the formation consists of soft silt to clay-silt shale with shale fragments (Sharpe et al., 2011). The Whitby Formation is noted for hydrocarbon concentrations (Barker et al., 1983) and excellent preservation of fossils (Tuffnell and Ludvigsen, 1984).

Five samples were collected for pXRF spectrometry. From the lowermost sample upwards to the unconsolidated post glacial sediments Ca and Sr display an marked increase in concentration whereas Cu, Fe, K, Rb, Th, Ti, U, V, and Zn, displays a marked decrease in concentration. Zircon displays no change in concentration over this interval. The second sample from the base of the borehole displays high values for Cu (926 ppm), Ni (608 ppm), and W (2732 ppm) which could be attributed to mineralization in the shale. This sample has been highlighted in red in the Appendix A dataset.

4.2 Unconsolidated Sediments

Unit 1 138-57 m (Thorncliffe Formation)

Thorncliffe Formation sediments are 81 m thick and overlie the Whitby Formation shale. The lower 40 m comprises 5 – 10 m thick interbedded sand and gravel units where the sand display cross bedding and cross lamination (Sharpe et al., 2011). The upper 40 m of sediment comprises 1-2 m thick graded sand units. Sharpe et al (2011) interprets these sediments to represent a fining-upwards subaqueous fan sequence.

Fifty eight samples from the Thorncliffe Formation were analyzed by pXRF spectrometry. Many of the results for As, Th, and V are near or below the detection limit. There is very little variation throughout this unit for K, Rb, and Sr. For many elements, including K and Rb there is a spike (or decrease for some elements) in concentrations at a depth of 113 m (sample 028) that occurs at the base of a gravel unit. For most elements (e.g. Ba, Ca) there is often a large variation in concentration from one sample to the next. Several elements (Ca, Cu, Fe, Mn, Ni, Ti, V, Zn, and Zr) display a marked increase in concentration at a depth of 90 meters – there is also an increase in silt content, and a corresponding decrease in sand content at this depth. There is a considerable amount of fluctuation in amount of sand and silt between 65 to 75 meters depth. This fluctuation is reflected in the fluctuation in Ba, Fe, Ni, V, and Zr.

Unit 2 57-46 m (Newmarket Till)

The Newmarket Till sediments comprise 11 m of dense pebbly, sandy silt diamicton with interbeds of sandy diamicton (Sharpe et al., 2011). A discussion of the origin of these sediments is presented in Sharpe et al., (2011) where they are interpreted to represent sediment gravity flows deposited into pre-existing depressions.

Newmarket Till sediments display a steady increase in the silt and clay content and a decrease in sand content from the base to the top of the till. Compared to the highly variable geochemical signature of the underlying Thorncliffe Formation, the Newmarket Till displays little variation for most elements detected. There is an increase in the concentration of Ba and Zr and a decrease in Ca and K that correspond to an increase in sand, and a decrease in silt and clay at a depth of 55 meters (sample 066).

Unit 3 46-41 m (Silt-clay rhythmites)

This unit is 5 m thick and consists of about 340 silt-clay rhythmites. Sharpe et al. (2011) discuss that these sediments, and the overlying unit 4 sediments, are unique to the Aurora basin and represent low energy suspension deposits associated with an existing depression in the top surface of the Newmarket Till. Although the depositional processes of the underlying Newmarket Till and the silt-clay rhythmites are different, several elements such as K and Mn display little change between these sediments.

Unit 3 sediments display a steady increase in clay content from the underlying Newmarket Till. This change in clay content is likely reflected in the slight decrease in Ba, Cu, Fe, Ti, Zn, Zr from the underlying Newmarket Till, and an increase in Ca.

Unit 4 41-30 m (Silt-clay rhythmites)

The upper unit of the silt-clay rhythmites consists of 12 m of banded silt and clay with brecciated diamicton interbeds. The clay content is slightly higher than the Newmarket Till. The geochemical characterization of unit 4 compared to both the underlying unit 3 sediments and the overlying Oak Ridges Moraine sediments are more pronounced. From unit 3 to unit 4 there is an increased concentration shift in Cu, Fe, K, Rb, Ti, V, and Zn. There is also a corresponding decrease in Ca and Sr.

Unit 5 30-11.5 m (Oak Ridges Moraine sediment)

Unit 5 contains little clay content and a highly variable silt and sand content. The basal 2 m thick gravel horizon forms the base of the Oak Ridges Moraine sediment sequence. This horizon is overlain by 2-8 cm graded coarse to fine sand horizons that in turn are overlain by ripple cross laminated fine sands and silt. Unit 5 is clearly defined in the returned geochemical signature as a departure in concentration from the underlying silt-clay rhythmites by an increase in Ca and Sr and a corresponding decrease in K and Rb. For several elements (e.g. Fe, Mn, Zn) the lower most two samples of Oak Ridges Moraine sediment displays results similar to the underlying silt-clay rhythmites. For other elements (e.g. Ni and Zr) the lowermost two samples represent a transition in concentration between the two facies. The high degree of variation in the silt content may be reflected in high degree of variability of Fe, Ti, U, V, Zn and Zr. For example, the spike in Fe, Ti, V, and Zr concentrations at a depth of 27 meters corresponds to a dramatic increase in silt content. It should be noted that other elements such as K, Rb, S, and Sr are relatively unaffected by this change in the silt content.

Unit 6 11.5-6 m (Oak Ridges Moraine sediment)

Unit 6 represents Oak Ridges Moraine sediments that are differentiated from both the underlying and overlying sediments by their silt and clay content as well as pXRF spectrometry. This unit combines approximately 10 silt-clay rhythmites and the overlying interbedded silt diamicton. For some elements (K, Mn, and Rb) these sediments are not distinguishable from the underlying or overlying sediments. There are however subtle changes in Ba, Cu, Ni, Sr, Ti, and V.

Unit 7 6-0 m (Oak Ridges Moraine sediment)

The uppermost unit of the Oak Ridges Moraine sediments displays an increase in silt and clay content similar to that of the Newmarket Till and the silt-clay rhythmites. Geochemically this is reflected in an increase in Fe, K, Mn, Rb, Ti, V, and Zn. The uppermost few samples have probably been affected by post-glacial weathering processes or human activities as reflected in the dramatic decrease in Ca concentration and increase in Mn.

5.0 Summary

This geochemical study complements other chemostratigraphic studies being carried out in Southern Ontario (Coffin, et al., in press; 2015; Knight et al., in press, a, b, c, d, e; Popovic, et al., in press).

The collected data expands the range of geological sediments that have been analyzed as part of a study to characterize surficial sediment aquifers and aquitards across Canada. The geochemical signal in the Aurora core is less pronounced than work from the Ottawa valley, or from borehole sediments collected from the Nanaimo region on Vancouver Island (Knight et al., 2015; Medioli et al., 2011). Core geochemistry assessed within a regional stratigraphic framework, and within borehole geochemical trends suggests that the provenance of Aurora core sediment was relatively consistent as depositional processes did not partition sediment to impart a strong change in geochemical signal. To our knowledge, these results are among the first systematic geochemical characterization of glacial-derived sediment associated with the Yonge Street Aquifer. The borehole data collected at Aurora using both traditional laboratory methods (fusion, multi-acid, and aqua regia digestions) as well as pXRF-derived geochemistry which 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. These data can provide insight into the provenance of analyzed sediments.

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