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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 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 the opportunity to establish a chemostratigraphic framework that complements other stratigraphic correlation techniques, such as lithostratigraphy and biostratigraphy.

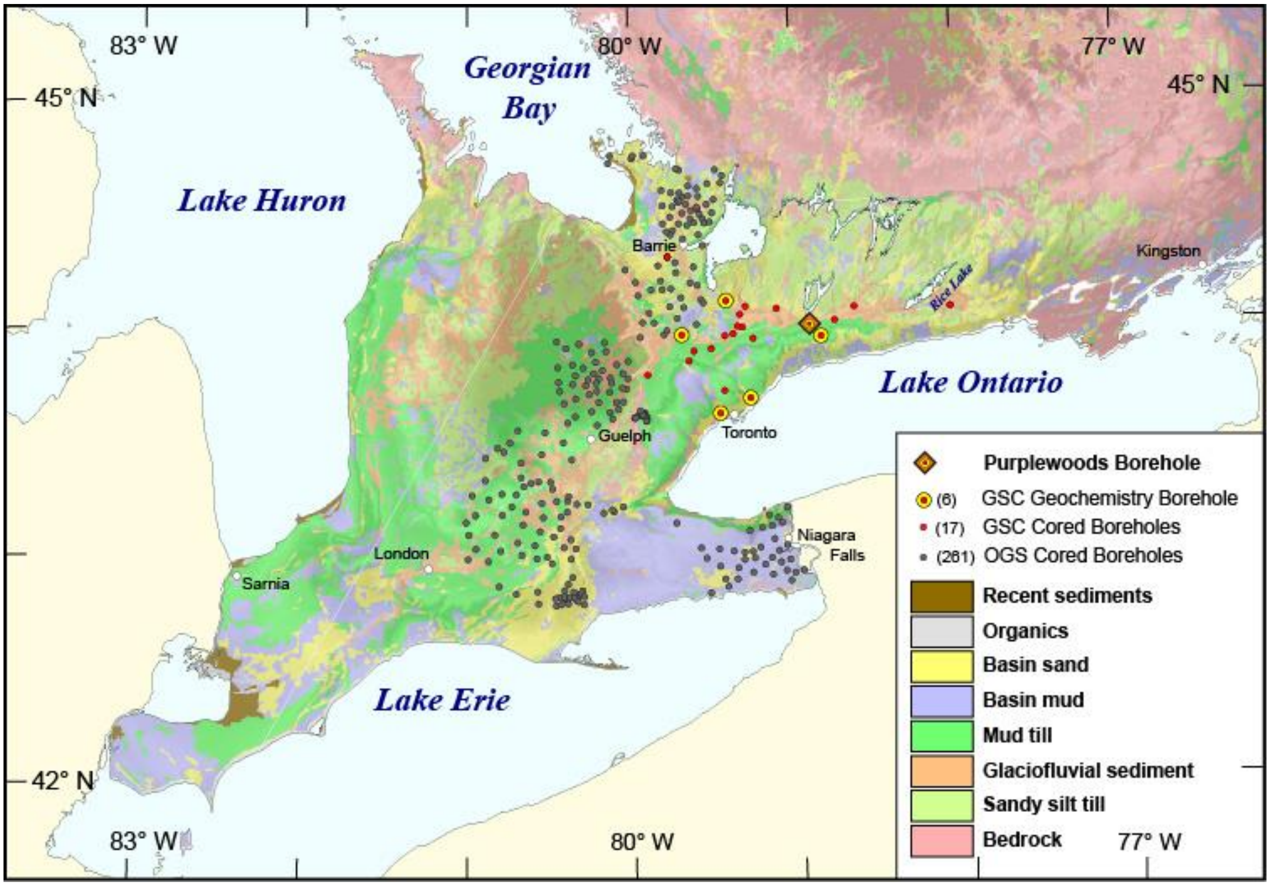

Figure 1: Location of the Purple Woods borehole with simplified regional geology of southwestern Ontario overlying a DEM. Note the distribution of OGS and GSC stratigraphic boreholes with continuous core descriptions. Geology simplified from Barnett et al. (1991).

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, 2015b) 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, 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 this 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 135 samples retrieved from a 151.8 m borehole located in the Purple Woods Conservation Area, Ontario (Fig. 2) and associated QA-QC data collected using a pXRF spectrometer. These data are interpreted in a stratigraphic context in GSC Open File 7899 (Coffin, et al. in press).

Figure 2: Location of Purple Woods, Clarington, and Grasshopper Road boreholes. Image from Goggle Earth, 2015

2.0 Study Area Geological Setting

The borehole is located south of Port Perry and north of Oshawa in the Purple Woods Conservation Area, 38 Coates Road East (Concession 10), Ontario at easting 666073 and northing 4878158 (UTM NAD 83 - Zone 17) and ~301 m.a.s.l. (Fig. 1-3). The site is located on the Oak Ridges Moraine. The Conservation Area comprises 17-hectares of open meadow and sugar maple forest on the western extent of the Oak Ridges Moraine. Borehole investigations collected continuous core to the southeast at the Clarington HydroOne substation (Knight et al., in press) and east at the Grasshopper road site (Sharpe et al., 2003). The Grasshopper site also has a p-wave seismic reflection profile oriented approximately north-south and approximately 3.25 km in length (Sharpe et al., 2003). To the east a cluster of streamlined landforms are mapped trending from northeast to southwest. Approximately 152m of unconsolidated sediment lies unconformably on top of bedrock. Based on shoreline geology and quarry operations, bedrock intercepted in the Purple Woods borehole (Coffin et al., in press) is assigned to the Blue Mountain Formation. This is overlain by a progressively thicker succession of sediment with distance northward from the Lake Ontario shoreline. At Purple Woods, 45 m of Thorncliffe sands are overlain by 69 m of Newmarket Till, which in turn is overlain by 34 m of Oak Ridges Moraine sediment.

Thorncliffe Formation:

Based on lateral continuity in outcrop along the Lake Ontario shoreline, Thorncliffe Formation sediment or equivalents consists of well laminated muds and sands (Brookfield et al., 1982; Martini and Brookfield, 1995) that can be divided into 3 members (Lower, Middle and Upper) separated by the Seminary Till and the Meadowcliffe Till (Fig. 5). The Lower Thorncliffe Formation is composed 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 under flows, or turbidity currents with the clay cap representing later pelagic sedimentation. According to Barnett, (1992) these sediments were deposited approximately 30,000 to 50,000 years ago during the middle Wisconsinan by glacial meltwaters into an ice dammed lake. At the Purple Woods borehole Thorncliffe Formation sediment consists of rhythmically bedded muds with only minor, rare sand beds (Coffin et al., in press). A similar mud-dominated succession is documented in the Pontypool continuous core by Russell et al. (2003). Further to the northwest in the Aurora – Newmarket area continuous core intercepting Thorncliffe Formation of the Yonge Street Aquifer forms a fining upward succession interpreted to be a subaqueous fan (Sharpe et al., 2011).The Seminary Till and the Meadowcliffe Till (Fig. 5a) are not present in the borehole where sediments assigned to the Newmarket Till directly overlie sand, silt and clay of the Thorncliffe Formation.

Newmarket Till:

The Newmarket Till consists of massive, dense, 10–70 m thick, calcareous silt to sandy silt till with striated limestone clasts. Beds are often 3-5 meters in thickness and may be separated by stone lines (Sharpe et al., 1997; Boyce et al., 1995). According to Barnett (1992) the matrix carbonate content 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

Figure 3: Location of Purple Woods borehole within the Purple Woods Conservation Area. Image from Goggle Earth, 2015.

Figure 4: Location of Purple Woods borehole (person in center of photograph) within the Conservation Area. Photograph courtesy of Gayle Soo Chan.

al., 1999). North of the Oak Ridges Moraine large valleys that truncate the Newmarket Till are 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 the 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). To date the Purple Woods borehole records the greatest thickness of Newmarket Till in the GTA at ~68 m.

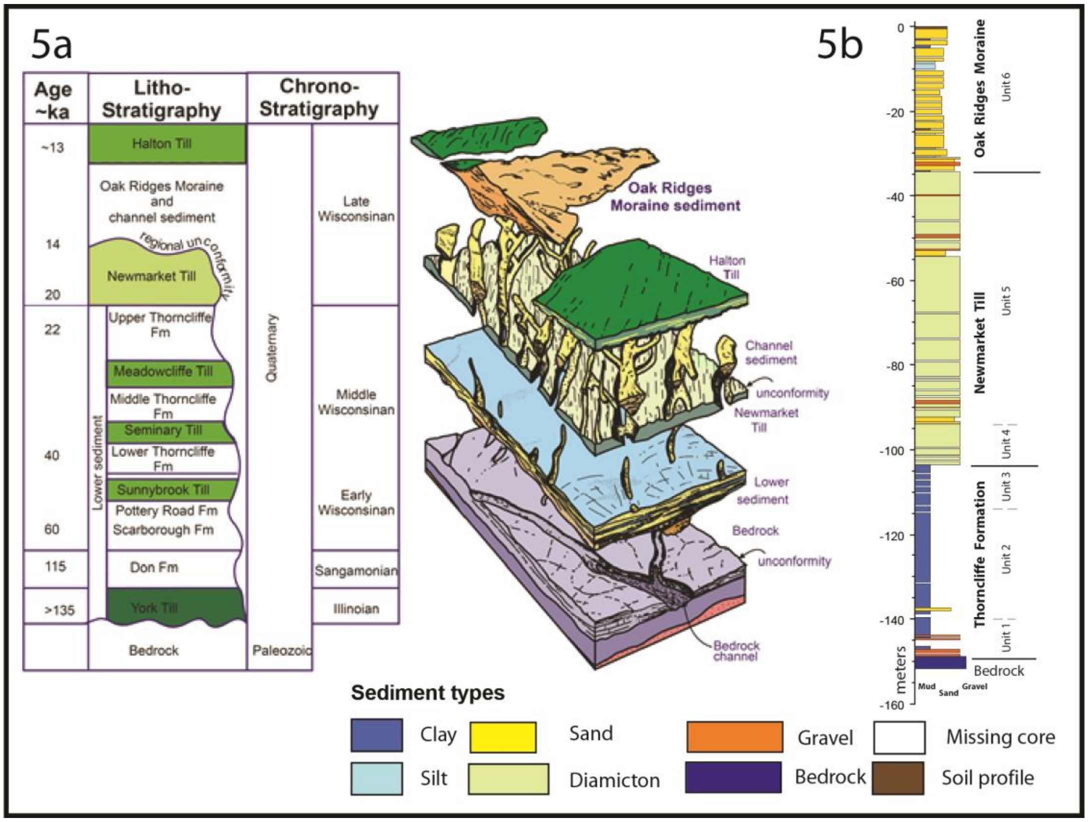

Figure 5a: Stratigraphy of the Greater Toronto Area. Modified from Sharpe et al. 2002. Key till units are highlighted in green. Figure 5b: Generalized lithostratigraphy of the Purple Woods borehole.

Oak Ridges Moraine:

Oak Ridges Moraine sediment overlies the Newmarket Till and extends eastward from the Niagara Escarpment to Trenton. The moraine comprises four wedge-shaped landform elements (Rice Lake, Pontypool, Uxbridge, and Albion Hills) that generally broaden from east to west. The Purple Woods site is located south of and between the Pontypool wedge to the northeast and Uxbridge wedge to the northwest. Sedimentological studies of core and surface exposures have found the moraine to consist of silt, sand and gravel with only minor clay and diamicton (e.g., Gilbert, 1997; Paterson and Cheel, 1997;

Barnett et al., 1998; Russell et al., 2003, 2004). Recent interpretations of moraine genesis recognize it to represent several stages of sedimentation in a variety of subglacial and ice-contact glaciolacustrine depositional environments (Barnett et al., 1998; Russell et al., 2003; Sharpe et al., 2002). Early moraine sedimentation was predominantly within tunnel channels and consists of coarse-grained gravel and diffusely graded sand (Shaw and Gorrell, 1991; Barnett et al., 1998; Russell et al., 2003). Channel-fill strata are characterized by a number of seismic facies interpreted to be high-energy scour and fill, bedform foresets, and slump or mass-flow deposits (Pugin et al., 1999). A succession of low-energy glaciolacustrine silt and clay rhythmites overlies the channel fill sediment (Russell et al., 2003). The rhythmite succession is, in turn, overlain by sand and gravel deposited from east to west during the main esker-subaqueous fan, ridge-building stage of the ORM (Paterson and Cheel, 1997; Barnett et al., 1998; Russell and Arnott 2003). Along the southern flank of the moraine muddy lacustrine- rich Halton Till forms the final episode of moraine sedimentation (Sharpe and Russell, 2013).

3.0 Sample collection, processing and analytical methods

The borehole reached a depth of 151.8m and was collected in collected in ten foot runs, placed in 5 ft PVC tubes, and sealed with tape (Fig. 7). Core was transported and stored at the GSC storage facility at Tunney's Pasture in Ottawa. Following delivery of the core to the GSC it was logged, photographed in 44 cm segments, (generally 5 images per 1.5 m run). In the winter of 2015, 135 samples were collected for pXRF analysis and grain size (Appendix A). Subsequent to the initial sampling an additional 31 samples were collected across a 1.5 meter interval in the upper Thorncliffe Formation to further delineate a contact that was identified during pXRF examination.

Prior to pXRF analyses many of the sediment samples were disaggregated with a rubber mallet by pulverizing the samples between sheets of packing/butcher paper (Fig. 8). The majority of samples collected from the Newmarket Till were too compact to be disaggregated using this method. These samples were first placed in a steel receptacle (that had been cleaned by sand blasting followed by air blasting) and shattered using a hydraulic press (Fig 9a-d). After disaggregation, all samples were sieved to <0.063mm (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 (Knight et al., 2015c), 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. 10). A 60 second dwell time per filter (Main, Low, High) was used in soil mode, in order to follow suite with previous borehole studies (Knight et al., 2015a, Knight et al., 2012, Plourde et al., 2012), for a total of 180 seconds. In mining mode 45 second dwell time was used per filter, to allow for a total of 180 seconds of analysis. Soil Mode uses Compton normalization which is recommended for elements expected to occur with < 1% concentration. Mining Mode uses Fundamental Parameters which is recommended for elements expected to exceed >1% concentration. A summary list of elements detected and their X-ray intensities is presented in Table 1.

Fourteen elements (Ba, Ca, Cu, Fe, K, Mn, Ni, Rb, S, Sr, Ti, V, Zn, and Zr) had sufficient quantities to produce results in soil mode and mining mode, however in mining mode Cu, Ni and V did not produce meaningful results. Results are listed in Appendix A, and graphical displayed in Appendix B.

Figure 6: Extracting core from the Purple Woods borehole.
Photograph courtesy of Gayle Soo Chan.

Figure 7: Photograph of extracted rhythmitic sediments (see red box for split core) in a PVC tube from the Purple Woods borehole. Photograph courtesy of Gayle Soo Chan.

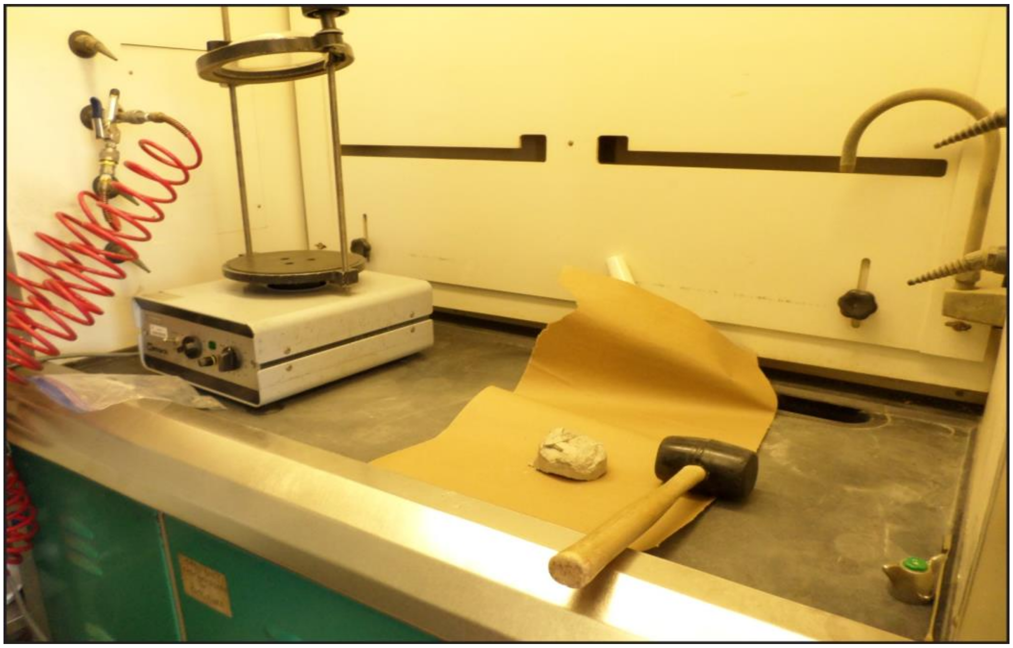

Figure 8: To disaggregate, samples were placed between two pieces of brown packing/butcher paper and impacted with a rubber mallet.

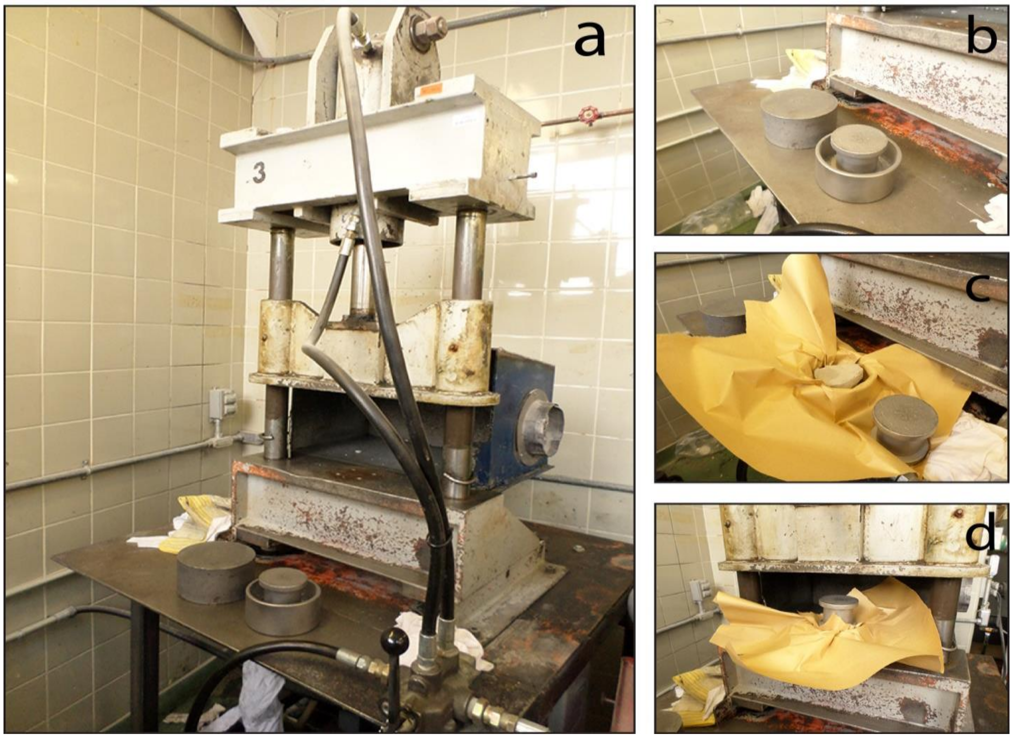

Figure 9: Many Newmarket till samples were initially disaggregated by placing the sediment between a sheet of packing/butcher paper in a stainless steel holder (photo a, b and c) and impacting the sample in a hydraulic press (photo a, and d).

Figure 10: 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. 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 in soil mode, Cd, Hg, K, Pd, Sr, and V returned values below the recommended limits of detection (< LOD). For the SiO_2 blank in mining mode, Al 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. Calcium and Fe returned values above the limits of detection and 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 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 as determined by traditional wet chemistry methods are listed for both soil and mining mode for Till-1 in Table 2a, and b, for Till-4 in Table 3a, and b, and for TCA 8010 in Table 4a, and b. 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. In soil mode for TCA-8010, Cd lists a mean of 9.41ppm compared to a recommended value of 0.11with a resulting percent error of 8452%. Elements that return a high degree of error are not plotted in the chemostratigraphic graphs. Plotted elements consist of Ba, Ca, Cu, Fe, K, Mn, Ni, Rb, S, Sr, Ti, V, Zn, and Zr. The down borehole plots of these elements are displayed in Appendix B for analyses carried out in both soil and mining mode (excluding Cu. Ni and V in mining mode). Although care must be taken when interpreting data with a high error it may 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.

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. Some elements however return results that are 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 recommended LOD value. Elements detected by each filter and the corresponding lower limits of detection are listed in Table 5a for soil mode and in Table 5b for mining mode.

Table 1: Elements and corresponding X-ray energy intensities used to determine concentrations in Mining Mode (m) and Soil Mode (s), as provided by Thermo Scientific (2015).

Element	Line	Energy (keV)	Window Low (keV)	Window High (keV)	Filter
Ba	Kα_1	32.19	31.70	32.70	High
Ca	Kα_1	3.69	3.50	3.89	Low
Cu	Kα_1	8.05	7.84	8.24	Main
Fe	Kα_1	6.40	6.20	6.60	Main
K	Kα_1	3.31	3.10	3.49	Low
Mn	Kα_1	5.90	5.70	6.10	Main
Ni	Kα_1	7.48	7.35	7.67	Main
Rb	Kα_1	13.39	13.18	13.60	Main
S	Kα_1	2.31	2.20	2.45	Low
Sr	Kα_1	14.16	13.95	14.38	Main
Ti	Kα_1	4.51	4.21	4.70	Low
V	Kα_1	4.95	4.75 (m) 4.80 (s)	5.15 (m) 5.10 (s)	Low
Zn	Kα_1	8.64	8.49	8.83	Main
Zr	Kα_1	15.77	15.53	15.98	Main

Table 2a. Summary statistics for SRM Till-1 by pXRF spectrometry for (soil mode) Purple Woods borehole. RSD=relative standard deviation.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm	%RSD	Minimum (ppm)	Maximum (ppm)
As	18	15	19	3.5	13.34	7.21	16	21
Ba	702	15	840	19.7	19.81	2.36	818	877
Ca	19440	14	18833	-3.1	3933	20.88	17302	32401
Cr	65	15	30	-54.5	4.05	13.67	23	38
Cs	1	15	41	3988.5	2.98	7.29	37	46
Cu	47	15	52	10.8	3.36	6.46	45	59
Fe	48100	15	41414	-13.9	358	0.86	40423	41781
K	18429	15	16814	-8.8	161	0.96	16543	17099
Mn	1420	15	1369	-3.6	30.11	2.20	1332	1416
Ni	24	15	82	240.2	10.47	12.82	64	101
Pb	22	15	12	-44.9	1.58	12.99	10	16
Rb	44	15	41	-7.6	2.50	1.02	39	42
S	< 500	4	381	-23.9	23.71	6.23	365	416
Sb	7.8	6	12	53.3	2.57	21.46	9.7	16.6
Sc	13	14	42	226.1	8.06	19.01	32	63
Sr	291	15	272	-6.6	2.55	0.94	267	277
Te	-	15	41		8.03	19.57	31	60
Th	5.6	14	4.0	-27.8	0.69	17.11	2.74	5.05
Ti	5990	15	5559	-7.2	164	2.95	5211	5844
U	2.2	8	5.78	162.6	0.86	14.97	4.58	7.33
V	99	15	180	65.8	10.88	6.63	147	180
Zn	98	15	90	-8.2	2.84	3.15	85	95
Zr	502	15	569	13.3	13.87	2.44	542	592

Table 2b. Summary statistics of Till-1 by pXRF spectrometry (mining mode) for the Purple Woods borehole. RSD=relative standard deviation.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
Al	-	14	44596		2428	5.44	40227	47888
As	18	14	24	34.8	1.99	8.20	21	28
Ba	702	14	700	-0.4	11.6	1.66	680	722
Ca	19440	14	18580	-4.4	454	2.44	17534	19196
Ce	-	14	234		16	6.98	207	262
Cl	-	14	125		14	9.05	125	174
Cu	47	10	26	-45.2	4.4	17.16	19	33
Fe	48100	14	48709	1.3	412	0.85	48083	49456
K	18429	14	18168	-1.4	189	1.04	17811	18469
La	-	14	214		13	5.94	192	230
Mg	-	14	5447		1357	24.91	3177	7760
Mn	1420	14	1322	-6.9	33	2.46	1261	1371
Nb	-	14	9		0.75	8.57	8	10
Nd	-	14	559		44	7.90	456	620
P	-	14	1499		214	14.28	1077	1808
Pb	22	14	20	-7.5	1.7	8.34	17	24
Rb	44	14	21	-52.0	0.73	3.48	20	23
S	<500	14	661	32.1	57	8.59	567	767
Si	-	14	259029		8039	3.10	244841	268535
Sr	291	14	217	-25.3	2.7	1.24	213	222
Th	5.6	13	15	165.9	3.2	21.71	11	20
Ti	5990	14	5089	-15.1	352	6.91	4510	5771
Zn	98	14	96	-2.3	4.9	5.16	88	104
Zr	502	14	440	-12.3	11.4	2.58	409	453

4.0 Results and Surficial chemostratigraphy

The pXRF data are interpreted using single element trends from the base to the top of the borehole.
In Soil Mode 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. In Mining Mode fourteen elements (Al, Ba, Ca, Fe, K, Mn, Pb, Rb, S, Si, Sr, Ti, Zn, and Zr) were detected in sufficient quantities to produce meaningful results using the pXRF spectrometer. Results are presented in Appendix A and displayed graphically in Appendix B. Bivariate plots comparing soil mode to mining mode for twelve elements (Ba, Ca, Fe, K, Mn, Rb, S, Sr, Th, Ti, Zn, and Zr) are also displayed graphically in Appendix B. For some elements (e.g. Ca and K) there is very little difference between data collected in either mode. For Fe mining mode returned values consistently higher that soil mode. For Sr mining mode returned values consistently lower than soil mode. For the bivariate plots in Appendix B, 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 (Mn S, Th, Ti, and Zr) a reduced major axis regression (RMA), as described in York (1966) that assumes there are errors to both y and x data was also carried out. For Th the standard linear regression produced a line that clearly does not define the data. The RMA method produced a regression line that more closely defines the distribution

Table 3a. Summary statistics of SRM Till-4 by pXRF spectrometry (soil mode) for the Purple Woods borehole. RSD=relative standard deviation.

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	111	15	103	-7.0	2.37	2.30	100	108
Ba	395	15	463	17.1	20.4	4.42	430	497
Ca	8934	15	7994	-10.5	576	7.21	7494	9686
Cr	53	15	22	-58.1	3.4	15.42	13	26
Cs	12	15	26	117.1	3.2	12.14	21	32
Cu	237	15	213	-9.9	6.2	2.91	206	224
Fe	39700	15	33018	-16.8	310	0.94	32525	33619
K	26980	15	23338	-13.5	418	1.79	22449	24032
Mn	490	15	446	-8.9	19	4.27	410	476
Mo	16	15	17	9.3	1.3	7.34	15	20
Ni	17	15	61	258.5	6.4	10.55	46	73
Pb	50	15	42	-16.3	1.6	3.83	39	44
Rb	161	15	150	-6.6	1.8	1.21	147	154
S	800	15	633	-20.9	88.3	13.96	481	757
Sr	109	15	105	853.5	1.6	1.50	102	108
Th	17.4	15	43	144.4	1.6	3.84	40	46
Ti	4840	15	4566	-5.7	126	2.77	4332	4772
U	5	14	13	159.3	3.1	23.70	7	19
V	67	15	124	85.2	9.7	7.79	109	141
W	204	15	178	-12.6	7.8	4.39	160	191
Zn	70	15	66	-5.6	2.4	3.65	62	71
Zr	385	15	434	12.7	8.4	1.93	424	456

of data. Where the RMA method was used the regression line is plotted as a blue line on the bivariate plots in Appendix B. Due to the similarity of results obtain from both modes and to simplify discussion the chemostratigraphic results will be referring specifically to soil mode.

The Purple Woods borehole can be divided in 4 stratigraphic units that are further subdivided using changes in trends of elemental concentrations. The major stratigraphic horizons comprise bedrock of the Blue Mountain Formation, Thorncliffe Formation (unit 1, 2, and 3), Newmarket Till (unit 4.5, and 6) and Oak Ridges Moraine Sediment (unit 7 and 8). Detailed lithofacies descriptions and depositional interpretations are presented in Coffin et al. (in press).

Basal sediment of the Thorncliffe Formation consists of a gravel horizon siting onto of the Blue Mountain Formation shale. The gravel is overlain by a 1.5 meter coarsening upwards sequence from fine- to course -grained sand. The reaming sediments consist of clay and clay silt rhythmites with numerous small thicknesses of no recovery.

Table 3b. Summary statistics of Till-4 by pXRF spectrometry (mining mode) for the Purple Woods borehole. RSD=relative standard deviation

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	111	14	138	24.5	4.4	3.23	129	145
Ba	395	14	391	-0.9	16	4.13	365	413
Ca	8934	14	9468	6.0	449	4.74	8669	10321
Cu	237	14	212	-10.7	7.6	3.58	196	223
Fe	39700	14	40679	2.5	221	0.54	40256	40983
K	26980	14	25953	-3.8	326	1.26	25426	26684
Mn	490	9	302	-38.3	36	11.80	260	370
Mo	16	14	11	-31.6	1.4	13.08	9	14
Pb	50	14	51	2.9	3.1	6.02	46	56
Rb	161	14	80	-50.6	0.97	1.22	78	82
S	800	14	1447	80.9	70	4.85	1304	1551
Sr	109	14	85	-22.1	1.4	1.65	83	88
Th	17.4	14	22	27.7	2.97	13.38	17	27
Ti	4840	14	4318	-10.8	281	6.51	3857	4730
U	5	12	5	3.3	0.7	13.67	4	6
Zn	70	14	70	-0.1	4.8	6.92	63	78
Zr	385	14	344	-10.7	2.5	8.90	330	367

Table 4a. Summary statistics of SRM TCA 8010 by pXRF spectrometry (soil mode) for the Purple Woods borehole. RSD=relative standard deviation

	Recommended Value (ppm)	Count	Mean (ppm)	%error	Std Dev (ppm)	%RSD	Minimum (ppm)	Maximum (ppm)
As	5.5	15	6	12.0	0.9	14.73	5	8
Ba	549	15	724	31.9	16.4	2.26	698	750
Ca	15509	15	13881	10.5	423	3.05	13331	15010
Cr	48	12	10	79.1	1.6	16.05	7	13
Cu	28	15	31	7.4	3.7	12.25	25	36
Fe	20290	15	13806	32.0	185	1.34	13514	14154
K	19094	15	15655	-18.0	287	1.83	15178	16058
Mn	310	15	291	6.1	25	8.67	226	322
Ni	17	15	62	262.4	9.5	15.19	47	82
Rb	54	15	49	8.8	0.7	1.45	48	50
Sr	310	15	266	14.2	2.6	0.99	261	271
Th	5	14	4	24.1	0.9	23.0	3	6
Ti	2578	15	2396	7.0	154	6.43	2204	2639
U	1	12	6	435.1	1.2	20.50	4	8
V	49	15	70	43.4	7.2	1024	60	85
Zn	32	15	31	2.7	1.7	5.53	27	34
Zr	272	15	312	14.5	15.2	4.87	288	338

Table 4b. Summary statistics of SRM TCA 8010 by pXRF spectrometry (mining mode) for the Purple Woods borehole. RSD=relative standard deviation

	Recommended Value (ppm)	**Count**	**Mean (ppm)**	**%error**	**Std Dev (ppm)**	**%RSD**	**Minimum (ppm)**	**Maximum (ppm)**
As	5.45	13	7.30	34.0	1.31	17.94	5	9
Ba	549	14	502	-8.6	17.7	3.52	469	528
Ca	15509	14	14904	-3.9	511	3.43	14067	15825
Fe	20290	14	19464	-4.1	263	1.35	18954	19902
K	19094	14	17695	-7.3	632	3.57	16868	18735
Pb	12.2	14	9.75	-20.1	1.92	19.71	6.32	14.32
Rb	53.6	14	26	-51.0	0.48	1.84	25	27
Sr	310	14	217	-29.9	2	0.92	214	222
Th	5.1	12	12	138.6	2	16.56	8.97	15.88
Ti	2578	14	2443	-5.2	254	10.39	1969	2880
Zn	31.9	14	33	3.7	3.5	10.50	28	40
Zr	272	14	239	-12.2	12	5.23	222	267

Table 5a. Elements detected in the Purple Woods borehole with corresponding detection limits for the pXRF using two matrix configurations and the filters used to detect these elements in Soil mode, Thermo Scientific (2015).

Element	Matrix		Filter
	SiO_2	SiO_2 + Fe +Ca	
Ba	35	45	Low
Ca	40	N/A	Low
Cu	10	13	Low
Fe	25	N/A	Main
K	45	150	Low
Mn	35	50	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

Table 5b. Elements detected in the Purple Woods borehole with corresponding detection limits for the pXRF using two matrix configurations and the filters used to detect these elements in Mining mode, Thermo Scientific (2015). *indicated LOD when used with He

Element	Matrix		Filter
	SiO_2	SiO_2 + Fe +Ca	
Ba	35	40	High
Ca	50	N/A	Low
Cu	12	15	Main
Fe	35	N/A	Main
K	40	N/A	Low
Mn	60	65	Main
Ni	25	30	Main
Rb	3	3	Main
S	70/55*	90/75*	Light
Sr	3	3	Main
Ti	10	20	Main/Low
V	10	20	Main/ Low
Zn	8	15	Main
Zr	3	3	Main

Bedrock 151.8m-148m (Blue Mountain Formation)

Bedrock constitutes the lower 3m of the borehole, and is characteristic of the Blue Mountain Formation, of Paleozoic Age. It is a black, fissile, petroliferous shale (Armstrong and Dodge, 2007; Sharpe et al., 2011) distinguished by hydrocarbon concentrations (Barker et al., 1983) and the preservation of fossils (Tuffnell and Ludbigse, 1984). One sample was collected and processed with a mortar and pestle to obtain a <0.063 mm size fraction for pXRF spectrometry.

4.1 Unconsolidated Sediments

Sediments of the Thorncliffe Formation comprise the lowermost succession in the borehole. These sediments consist of a 45m thick mud dominated (see grain size, Appendix B) succession of 1-4 cm thick horizons that are interbedded with up to 5 cm thick planar laminated silt horizons. The sediments can be subdivided into three units, based on a combination of pXRF spectrometry of 42 samples and lithologic changes observed during core logging (Coffin et al., in press).

Unit 1 Thorncliffe Formation (149-140m)

The lowest most unit is 9 meters thick and extends upwards from the bedrock to a depth of 140m. These sediments are dominated by angular shale clasts and sub-rounded Precambrian shield pebbles in a coarse sand matrix. For many elements the underlying elemental concentration of the Blue Mountain Formation is either considerably higher or lower than the concentration in the unit 1 sediments. This suggests that although there is considerable amounts of Blue Mountain Formation clast visible in the unit 1 sediments that clast have not been comminuted down to the <0.063 mm size fraction. Calcium displays a constant increase from the base to the top of the unit where it then decreases from a value of 188301ppm to a value of 121915 ppm marking the transition from Unit 1 to Unit 2. This increase in Ca corresponds with an increase in clay content. The upper portion of this unit consists of grey clay, closely spaced rhythmites that are disturbed in places. The unit is further defined by a decrease in Ti, V and Zr over the same interval.

Unit 2 Thorncliffe Formation (140-113m)

Unit 2 sediments consist of grey to occasionally reddish closely spaced clay rhythmites. The uppermost 4 meters of the unit incorporates grey silt (see grain size, Appendix B) with the rhythmites with minor sulphorous odor to the sediment. This is also reflected in decrease in Fe, K, Mn, Rb, Ti, V, and Zn. Overall the Ca content of unit 2 displays a marked decrease in concentration compared to the underlying sediment but is still greater than the content of the overlying unit 3 sediments. A thin sand horizon occurs at a depth of 138 meters (see grain size, Appendix B). Chemically this horizon is noted by a marked increase in Ba, Ti, and Zr and a decrease in K, Rb, and Zn. A similar spike in Ba occurs at a depth of 115 meters near the top of the unit. At this depth there is no increase in the concentration of Ti or Zr however there is a small increase in the concentration of sand as depicted in the grain size plot of Appendix B. Barium may be concentrated in the sand as a placer type heavy mineral however this is not reflected in a change in concentration for any other elements at this depth. In the top 5 meters of the unit Fe, K, Mn, R, Ti, V, and Zn all display a consistent decrease in concentration with Sr and Zr displaying a slight increase in concentration.

Unit 3 Thorncliffe Formation (113m-103m)

Lower contact sediments consist of silt in sharp contact with the underlying unit 2 medium sized sand and silts. These sands and silts are overlain by dark grey coloured clay as displayed in the increase in clay content (see grain size in Appendix B graphic display). The sediments that comprise unit 3 display a sharp decrease in the concentration of Ca, Sr, and Zr and an increase in the concentration of Fe, K, Mn, Rb, Ti, V, a Zn. A detailed examination of the contact between unit 2 and unit 3 was carried on 31 samples to determine where this dramatic change in elemental concentrations occurred and how sharp the contact is with the underlying sediments (Fig.11 and Appendix B). During disaggregation of the samples it was noted that unit 3 was far more difficult to obtain sufficient amounts of <0.063mm (silt + clay) sized fraction to achieve infinite thickness. From this observation, and the pXRF results, the contact between unit 2 and unit 3 occurs over a 20 cm interval between 113.08 and 113.10 meters in depth. Results for this interval indicate a change in provenance from carbonate sourced rocks of unit 2 to a shield dominant source of unit 3. The contact for 10 elements is graphically displayed in Appendix B in a .pdf file labelled Thorncliffe Fm. unit 2_unit 3 contact. In both soil and mining modes there are some elements that display concentrations for an individual sample that more closely resembles the value obtained for either the unit above or below (e.g. Fe, Ti, Ti, V, Zn, Zr), however these data could also be erroneous. It should be noted that overall in unit 3 there is no change in S content and Ni displays the same degree of variability with both the underlying and overlying sediments. The variability in Ni concentrations is most likely due to the proximity of concentrations to the limits of detection.

Unit 4 Newmarket Till (103- 94m)

In general element concentrations for unit 4 return to values similar to those of the uppermost 4 samples of unit 2, however this observation does not hold true for the grain size graphs displayed in Appendix B. However Ca concentrations are considerably higher than the underlying units but are comparable to the highest concentrations obtained from the top of unit 1. The lowermost 3 samples in unit 4 display values slightly higher or lower (depending on the element) than the overlying 4 samples.

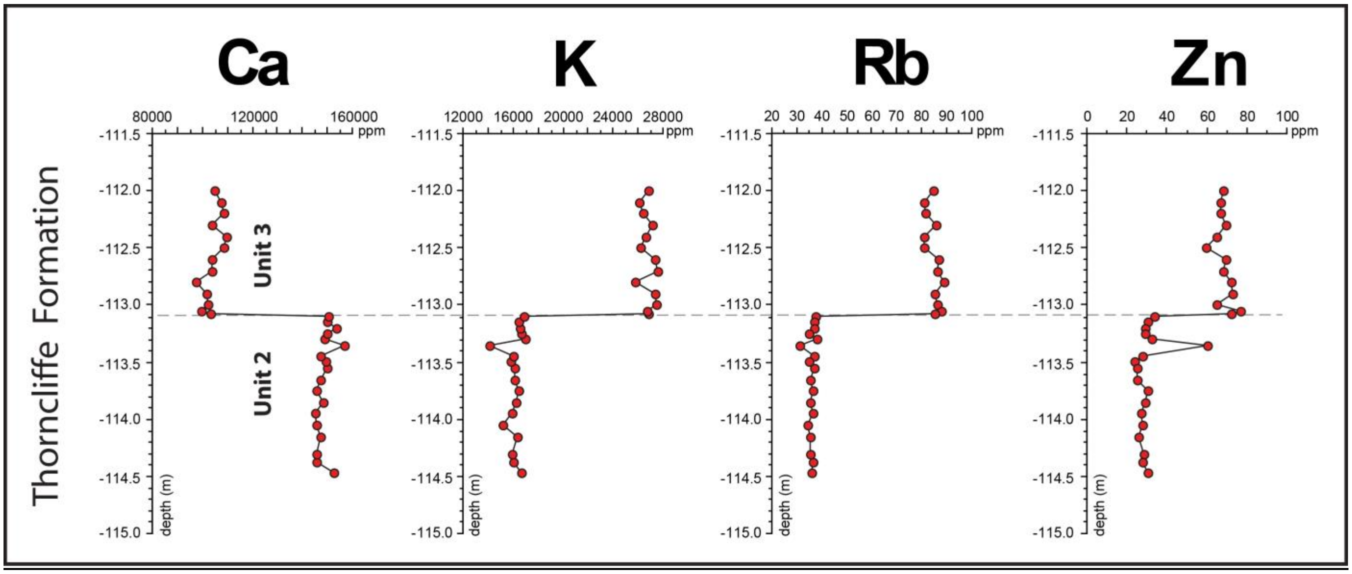

Figure 11. Chemostratigraphy of the upper Thorncliffe unit 2 – unit 3 contact at a depth of 115-111.5 m. Note the sharp decrease in Ca concentrations and increase in K, Rb, and Zn concentration over a 20 cm interval.

Unit 5 Newmarket Till (94m-34m)

Lowermost sediments of unit 5 and sediments at 54 meters in depth comprise sand horizons that display an increase in Ba, Fe, Mn, Ni, Ti, and Zr. Some elements, (e.g. Cu and S) display no change in concentration between unit 4 and unit 5. For Ca the seven samples above the lowermost spike in concentration for the sand unit display a consistent increase. Similar trends, but to a lesser degree, occur for K and Rb. Titanium displays a decrease in concentration over this same interval. This trend could be the result of a steady adjustment to a change in provenance or to element mobility due to fluid migration within the diamicton above the sand horizon contact. For the uppermost sand horizon at ~54 m Ca concentrations decrease for 2 samples before returning back to consistent values for the diamicton. Generally elemental concentrations for unit 5 are very consistent (eg. K, Rb, and Sr) even though there is a coarsening upwards overall trend as displayed in the plotted grain size data.

Unit 6 Oak Ridges Moraine sediment (34-0m)

The uppermost unit in the Purple Woods borehole consists of sand with varying degrees of interbedded silt, minor gravel horizons and very low concentrations of clay. The high degree in the variability of sand and silt is only reflected in Cu, Ti, V, and Zr whereas some elements such as Ca, K, Rb and Sr display little variation in concentration. The inter-bedding of fine to course sand and gravel in the basal 5 m of the unit is reflected the high degree of variability in the chemistry of many elements. A gravel horizon at a depth of 32 m returns Cu values of 142 ppm. This may be an erroneous value as samples with high amounts of sand stratigraphically below and above this sample do not display similar hih values. This sample should be checked by traditional wet chemistry methods; however several studies by Knight et al 2015a, 2015b have shown that these spikes are often not erroneous. Some elements such as K, Rb, and Sr display little to no variability throughout the unit and with the underlying unit 5 chemistry, until the uppermost 3 samples where surficial soil forming processes are reflected in a shift in elemental concentrations for many elements (e.g. Ca, K, Rb, Sr, Ti, and V). Some elements such as Fe, Mn, Ti, V, and Zr display a high degree of variability throughout unit 6 compared to the underlying unit

5 sediments. This is most likely a reflection of the variability in the provenance of the silt and clay size fraction being analyzed by the spectrometer.

5.0 Summary

This geochemical study expands the range of sediments that has been analyzed as part of an effort to characterize surficial sediment aquifers and aquitards across Canada. This study expands the use of pXRF spectrometer to collect meaningful geochemical data that can be used to address both provenance and depositional process. A comparison of analyses between soil and mining modes displays, for many elements, very little difference in elemental concentrations. Each mode does provide for detection of several elements that were not detected in the alternate mode.

For the Purple Woods borehole trends in core geochemistry suggest that provenance and depositional processes partitioned some elemental concentrations within the Thorncliffe Formation and the lower part of the Newmarket Till. Although shale clasts are visible in the lower part of Thorncliffe Formation unit 1 sediments, the chemistry of the <0.063 mm size fraction does not reflect the chemistry of the underlying bedrock. This suggests that the local bedrock is not a primary contributor to the <0.063 mm size fraction of the unconsolidated sediments.

Based on variabilities in elemental concentrations the Thorncliffe Formation can be subdivided into 3 units. The lowermost unit displays a constant increase in Ca concentration from the base to the upper contact with the overlying sediments. Unit 2 is relatively consistent in concentration for most elements; however Fe, K, Mn, Rb and Ti display a decrease in concentration near the top of the unit. Unit 3 sediments display a sharp increase or decrease in elemental concentrations for many elements (e.g. Ca and Fe) compared to both the underlying and overlying sediments.

Newmarket Till can be divided into 2 units with the lowest stratigraphic unit being approximately 10 m thick overlain by an additional 60 m of sediment. The Newmarket till contains two thin sand horizons. Other than these sand horizons and the sediments just above these horizons the Newmarket till displays a very uniform chemical signature for all elements suggesting a very homogenous mixing of sediment in the till. The sharp change in chemical signature from the underlying Thorncliffe sediments indicates that there was no incorporation of the silt and clay into the matrix of the Newmarket Till. To date this is possibly the thickest succession of Newmarket till measured.

Sediments of the Oak Ridges Moraine comprise the uppermost 34 m of the borehole. For some elements there is a greater degree of variability than the underlying Newmarket Till (e.g. Fe, Mn, Ti, Zn, and Zr). For Ca, K, Rb, S, and Sr there is little to no change in elemental concentrations between the Newmarket till and the overlying Oak Ridges Moraine sediments. The uppermost meter of the borehole displays elevated concentrations in many elements possibly associated with a combination of soil forming processes and anthropogenic activities.

The borehole data collected at Purple Woods Conservation area demonstrates that pXRF derived data is a valuable and cost effective tool to characterize the chemistry of Quaternary sediments. These data can provide insight into the provenance of the analyzed sediments and the glacial process responsible for their deposition. Interpretation of the data is augmented by relating chemical concentrations to the variability in grain size.

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