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Characterizing the geogenic background of the Midwest: a detailed mineralogical and geochemical investigation of a glacial till in southwestern Ohio

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Abstract

The state of Ohio has a long history of industrial pollution over numerous decades. Scientific investigations of the sources and impacts of this pollution are becoming increasingly common, particularly in the southwest region of the state, with a strong focus of recent studies being carried out within the context of air, urban soil and sediment quality, and aquatic environments. A key supporting issue in these, and future pollution investigations, is understanding the contribution from, and background concentrations of, natural geogenic materials. A glacial till sampled from Peffer Park, a publicly accessible site in Butler County southwest Ohio, was studied in detail to characterize its mineralogical and geochemical properties. The till sampled, a result of Wisconsin-aged glaciation, represents the regionally extensive glacial drift across the region and is the ideal candidate for targeting in efforts to quantify the background, geogenic environment. Samples were characterized for their elemental abundances using ICP-OES and ICP-MS, while mineralogy was investigated using powder X-ray diffraction, transmission electron microscopy, X-ray computed tomography, and reflective spectroscopy. Chemically, the till sampled is akin to the Earth's bulk continental crust with characteristic light REE (LREE) enrichment and depleted middle/heavy REE signatures. Of the 39 minor and trace elements analyzed, 74% (n=29) vary by less than 10 ppm between the 20 sites sampled, and of the ten major element oxides, there is a < 3 wt. % variation with a < 1 wt. % variation observed for seven of the major element oxides. All standard deviations (reported at 2σ) are < 1. Major minerals detected by powder XRD include illite, chlorite (ripidolite), quartz, calcite, dolomite and feldspar minerals with lesser amounts of amphibole, consistent with inferences from bulk chemistry. X-ray computed tomography on a selected sample highlights five orders of magnitude variation with respect to particle size, which is demonstrably skewed toward fine particle size. Accompanying reflective spectral features are dominated by signatures from the high clay mineral (e.g., illite) and carbonate contents, consistent with inferred source materials from the regionally extensive Ordovician stratigraphy associated with the Cincinnati Arch and the ancient crystalline continental basement of Canada. Through a wide variety of analytical techniques, it is demonstrated that the Peffer Park till of southwest Ohio has a remarkably low variation in composition and is highly representative of the geogenic background of this region of the USA. Its characteristics reported here therefore justify its use and application as a broad environmental reference material for the Midwest.

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Introduction

Metal pollution in the environment is a worldwide problem that has the potential to cause significant impacts on human health (e.g., Laden et al. 2000; Jarup 2003; Kampa and Castanas 2008; Lim et al. 2012). Globally, interest in metal pollution research is growing with an increasing number of studies investigating and documenting the sources of potentially toxic metals in the environment (e.g., China: Wei and Yang 2010; Li et al. 2014; Chen et al. 2015, Europe: Manta et al 2002; Nicholson et al. 2003; Mico et al. 2006; Ciarkowska et al. 2019, and Africa: Keskinen et al. 2019; Oyetibo et al. 2019, among other regions).

Compared to many other regions of the USA, the Midwest generally does not receive as much environmental attention as other regions such as the deserts in the American west, coastlines, wetlands and other settings (e.g., Clements et al. 2014; Metcalfe et al. 2017; Jabbar and Grote 2019). However, the Midwest has a long legacy of manufacturing and coal mining and, as a result, significant levels of various types of pollution have been documented throughout the region (e.g., in the air and (ground)water: Pettyjohn 1971; McClenahen and Dochinger 1985; Youger and Mitsch 1989; Baker 1990; Schwartz and Dockery 1992; Napier and Brown 1993; Dietrich et al. 2018; Lazar et al. 2019) with recent attention being given to issues associated with petroleum operations (e.g., wastewater injection: Skoumal et al. 2018; Currie et al. 2018a; Kozłowska et al. 2018).

With respect to modern-day metal pollution, several areas of the Midwest have received more attention than others such as Gary, Indiana and northwestern Indiana (e.g., Parker et al. 1978; Miller and McFee 1983; Cole et al. 1990; Esser et al. 1991; Perkins et al. 2000; Souch et al. 2002; Ingersoll et al. 2002; Dietrich et al. 2019). Additionally, there have been several investigations specifically looking at historic heavy metal pollution in soils in parts of the Midwest (e.g., Latimer et al. 2016; Carter et al. 2015; Rabinowitz 2005). Nonetheless, a gap in the number of environmental studies on metal pollution in the Midwest exists compared to other parts of the continent.

Specifically within the context of air pollution, investigations of metal contributions in the state of Ohio are becoming increasingly common (Tong 1998; Martuzevicius et al. 2004; Adhikari et al. 2006; Wojas and Almquist 2007; Haynes et al. 2011; Vedantham et al. 2014) with relatively fewer studies focusing on aquatic environments (Matisoff and Eaker 1992; Bradley et al. 1998; Evans and Gottgens 2007; Tully 2013; Gbolo and Lopez 2015). For example, metal pollution studies of urban soil and sediment in Ohio have focused on vacant lots in the Hough and Weinland Park communities of the city of Cleveland in northern Ohio (Sharma et al. 2015a, b) with comparatively less work in the southern region of the state (e.g., Cincinnati) where studies have primarily focused on traffic pollution and its impact on local soil geochemistry (Turer et al. 2001; Mishra et al. 2004). For areas in this southern region, such as the cities of Hamilton and Dayton, pollution associated with manufacturing extends well over 150 years (e.g., Barff 1987; Sundstrom 1990; Winland et al. 1991; Crowell 1995; Curtis 2002; Wright et al. 2015; Jones and Ruppert 2017; Michaud 2018). In particular, the City of Hamilton in Butler County has been the focus of several recent metal pollution studies,

as it represents many American Midwest cities struggling to recover from the effects of a long industrial legacy. Specifically, Hamilton has a history of metal, coke and coal processing and, until recently, a large paper mill industry (Constantinides and Sank 1994; Blount 2014). Presently, Hamilton is predominantly a post-industrial city with a minor metal working industry and a municipal coal plant that has recently converted to natural gas. Previous metal pollution studies in the city have been undertaken on street sediment with an emphasis on characterizing the distribution and abundances of Pb, Zn, and Cu (LeGalley et al. 2013; LeGalley and Krekeler 2013; White et al. 2014; Flett et al. 2016). Previous investigations of metal pollution in the area's aquatic sediments include that by Tully (2013) who investigated the form of metal pollutants in the Great Miami River (which flows through Hamilton), aquatic sediment in local lakes of the region (Castro et al. 2013; Baldwin et al. 2014), and subaerial flood sediments of the Great Miami River (Waldecker and Krekeler 2012). Components of this work also centered around quantifying potential U pollution from releases over several decades by the Fernald Feed Materials Production Center (FFMPC), a \$4.4 billion superfund site managed by the DOE which is located 13 miles to the SW of Hamilton (Tortorello et al. 2013; Conte et al. 2015; McHugh et al. 2015).

Thus, there is a documented increase in the number of studies investigating urban pollution across the southwest Ohio region, especially with respect to the potential impact on the City of Hamilton from the FFMPC. In addition, investigations centered on Middletown, a heavily industrialized city ~ 14 miles to the northeast of Hamilton, and several other outlying areas are currently underway (e.g., Osborne et al. 2016; Dietrich et al. 2018). One important aspect of these investigations that could be improved on and strengthened is better characterization of the environmental geogenic background, i.e., the concentrations of metals in the local, but extensive, drift and its accompanying mineralogy. A dominant contributor to the naturally occurring geogenic background material throughout Butler County is the pervasive glacial till, a result of the Wisconsin glaciation (~75–11 ka), and which underlies approximately 90% of the county (Ohio Department of Natural Resources). The glacial till of Butler County therefore makes an excellent environmental comparative material for urban pollution studies, as it is functionally isolated from contaminants introduced into the environment over at least 150 years.

Detailed geochemical and mineralogical investigations of glacial tills, especially within the context of establishing an environmental background, are relatively uncommon throughout the scientific literature. This is likely because glacial tills have the potential to cause a significant variation in a wide variety of geologic and environmental properties of near-earth surface settings including hydrology (e.g., Eyles and Meriano 2009; McArthur et al. 2011), soil composition, and soil nutrient levels (Fausey et al. 2000; Middleton et al. 2011). As a material, tills have several important geotechnical applications, being applied as a landfill capping material, or as a permeability barrier, due to their mineralogical and permeability characteristics (e.g., Phillips et al. 2010) and have been used in mineral exploration efforts (e.g., McClenaghan 2005; Loukola-Ruskeeniemi et al. 2010; van Geffen et al. 2012; Sarapaa and Sarala 2013). However, the geochemistry of a glacial till is not often comprehensively characterized in detail (e.g., mineralogy, chemistry, texture, spatial variability) for the purpose of environmental studies. Conventional wisdom suggests that glacial tills are likely lithologically, mineralogically, and chemically heterogeneous, especially tills which result from continental glaciation due to the wide variety of potential material sourced from numerous geographic regions, and the potential for signatures to be concentrated or diluted (e.g., Klassen 1998). Nonetheless, there are documented examples of tills being utilized as environmental background reference materials (e.g., Salonen and Korkka-Niemi 2007). Tills are appropriate materials to be considered as geogenic background reference materials, because they contain mixtures of local and reworked bedrock and hence represent a broad sampling of a region. Tills also have a low permeability and are sufficiently thick such that translocated atmospheric pollutants, such as micrometer-scale coal spherules or soluble metal or salt particulates, likely do not contribute to its chemical composition. Within this context, the use of near surface soils as environmental reference materials always has the potential to introduce risk associated with the contribution from anthropogenic metals. Thus, for certain geographic areas such as the US Midwest, glacial till samples may provide the best targets for quantifying the pristine environmental background concentrations of metals. Of course, ideally, background or reference materials are homogenous in nature. However, whether the heterogeneity of a given till is excessive and/or significantly problematic for background determination is currently unknown.

The hypothesis to be tested in this work is as follows: the bulk chemical composition and associated mineralogy of a glacial till are significantly heterogeneous and demonstrably not suitable for use as a background reference material. It is expected that there should be a significant variation in elemental concentrations and mineralogical components, because the till is a mixture of a Canadian-sourced continental basement (e.g., granite, gneisses, diorites, quartzites) mixed locally with the underlying Ordovician bedrock that comprises thin limestone and shale beds. If this hypothesis is supported, then this glacial till would indeed be demonstrably unsuitable for use as a geogenic background reference material. If rejected, then the till studied would be an appropriate, and important, environmental reference material, particularly within the context of the growing number of studies which aim to evaluate and quantify the environmental impact of anthropogenic practices in the southwest Ohio region (Flett et al. 2016; Dietrich et al. 2018; Lazar et al. 2019).

Materials and methods

Twenty samples were collected from a well-recognized Wisconsin age outcrop located outside of Oxford, in north central Butler County, Ohio, which lies 14 miles to the northwest of the City of Hamilton, and 21 miles to the west of the City of Middletown (Fig. 1). The stratigraphy consists of $a \sim 19,000$ (radiocarbon)-year-old glacial till from the Wisconsin glaciation above upper Ordovician limestones and shales. Fluvial deposits overlie the till unit sampled. Specifically, the outcrop is exposed along Collins Creek in Peffer Park. Samples correspond to unit 8 of Ekberg et al. (1993) which is described as a till with 20–40% clast concentrations that are interpreted to be locally derived. The till is interpreted as a subglacial lodgement till by Ekberg et al. (1993).

From the recently eroded bank, approximately 30 cm of till exposed at the surface were removed to collect fresh material with no anthropogenic component, approximately 30-60 cm deep relative to the exposed wall and approximately 1.5-2.0 m above the upper water level limit in Collins Creek. In preparation for bulk chemical analysis, samples were measured out to approximately 20 g. Their initial weights were recorded before being dried at 110 °C and then reweighed. This was done to determine the percent of water present in each sample. After being dried and reweighed, samples were then placed in an oven at 550 °C to remove organic material. Each sample was then reweighed upon being removed from the oven and subsequently milled using an aluminum oxide SPEX mini mill for 15 min to generate a fine powder. The bulk major element chemistry of each till sample was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). Bulk minor and trace elements were determined via inductively coupled plasmamass spectrometry (ICP-MS). Preparation for ICP-OES and ICP-MS analysis consisted of placing the powdered samples in a dehydrator at 105 °C for 24 h. Samples were then mixed with a lithium flux and placed in a furnace at 950 °C for 30 min. This heating process produced a molten bead which was then cooled to a solid. Approximately, 100 mg of the cooled bead was placed in a nitric acid solution in 30 ml Savillex Teflon vials to which 2 ml of double distilled 70% HNO₃ was added. These were then allowed to shake on a table for 24 h to achieve 100% dissolution. The entire contents of each container were then transferred into 125 ml polypropylene bottles and diluted to 125 ml using distilled water.

Fig. 1 a An aerial image of Peffer Park and Collins Creek showing the sampling trend.b A geographic map showing Ohio and the study site location in Butler County. c Field image of the Peffer Park till outcrop with scale



Solutions were analyzed for their major element concentrations using an Agilent 720ES axial-viewing ICP-OES instrument in the Department of Geology and Environmental Earth Science at Miami University. An Rh 233.4 nm wavelength was used as the internal standard. The operating plasma conditions were 1.2 kW Rf power, 16.5 L/min argon plasma, 1.5 L/min auxiliary, and 0.7 L/min nebulizer flow rates. Sample solutions were introduced to the axial torch using a SeaSpray pneumatic nebulizer and cyclonic spray chamber and signals were integrated over six 10 s intervals. Solutions were analyzed for their minor and trace element concentrations using a Varian 810 ICP-MS in the Department of Chemistry at Miami University. A 100 ppb solution of Ge, In, Re, and Bi was used for internal standardization. Five replicates of 20 readings each were averaged for each analytical solution. For both ICP-OES and ICP-MS, external calibration standards were made from 10 µg/ml solution standards purchased from Inorganic Ventures and ten geological standards were used: BE-N, DNC-1, RGM-1, SY-2, GSP-2, AGV-2, DR-N, BHVO-2, STM-1 and BCR-2. The relative standard deviation was calculated from repeat analysis of AGV-2.

A Scintag powder X-ray diffractometer (XRD) was used to analyze powdered samples to determine their mineralogical composition. Varying angles of incidence from 2° to 65° for bulk powders were used, with $2^{\circ}-35^{\circ}$ for clay separate samples, using 0.01° step increments. Minerals observed in bulk powder diffraction data were identified using the following PDF cards for quartz PDF No. 00-046-1045, calcite PDF No. 00-047-1743, dolomite No. 00-036-0426, feldspars, including calcian ordered albite PDF No. 00-041-1480, ordered microcline PDF No. 00-019-0926, intermediate microcline PDF No. 00-019-0932 and orthoclase PDF No. 00-031-0966. Amphibole was identified by a (020) of 8.44 Å, based on a comparison to several PDF cards. To determine the clay mineral components of samples, unmodified till subsamples were disaggregated by hand and put into suspension in deionized water. Suspensions were allowed to settle for 3 h and 50 min to obtain the spherical equivalent of the $< 2 \mu m$ -size fraction (Moore and Reynolds 1997). The <2 μ m-size fraction suspensions were then exchanged with a 0.1 M solution of MgCl₂·H₂O five times and washed with deionized water. Samples were then pipetted out, centrifuged, and applied to glass slides using the smear technique outlined in Moore and Reynolds (1997). For clay mineral identification, slides were X-rayed under ambient air, ethylene glycol, and heated conditions using scan parameters of 2°–35° by 0.01° increments. Minerals were identified using the criteria of Moore and Reynolds (1997).

For further mineralogical characterization via transmission electron microscopy (TEM) analysis, two selected samples (MK-1 and MK-4) were suspended in methanol and allowed to stand for 10 min. A drop of this suspension was then placed on a 300 mesh lacey carbon-coated copper TEM grid and allowed to dry under ambient air conditions covered in a plastic Petri dish. Samples were then analyzed using a JEOL JEM 2100 TEM operated at 200 kV at the Center for Advanced Microscopy and Imaging (CAMI) at Miami University.

Computed tomography (CT) datasets for samples MK-2, MK-3, and MK-4 were collected using a North Star Imaging ImagiX series µCT scanner at Vanderbilt University (Tennessee, USA). The MK-2 tomography dataset was collected at 83 kV and had a scan resolution of 62.8 µm/voxel. MK-3 was collected at 110 kV with a scan resolution of 38.8 µm/voxel. MK-4 was collected at 99 kV and had a scan resolution of 51.4 µm/voxel. All datasets were acquired with a focal spot of 8 µm. Reconstructed datasets were segmented using Dragonfly 4.0 (theobjects.com). Segmentation was accomplished by iteratively adjusting voxel intensity thresholds, and then manually adding voxels corresponding to discrete sediment grains to a region of interest (ROI). The ROI was then de-noised by removing features of less than a radius of three voxels using an opening kernel, as beneath this scale distinguishing between signal and noise could not be confidently done. A series of closing kernels was applied to ensure that all voxels within a grain were included in the ROI. This single ROI was then analyzed within Dragonfly to generate a distribution of discrete grains.

An ASD FieldSpec 4 High Resolution spectroradiometer, housed at Miami University, with a five-degree foreoptic attachment was used for the collection of spectra from 350 to 2500 nm on five of these samples. This instrument has a spectral range from 350 to 2500 nm with a 3 nm resolution in the VNIR (350–1000 nm) and an 8 nm resolution in the SWIR (1000–2500 nm). White reference calibration with SpectralonTM was performed prior to the commencement of data collection and every 15 min after. For each sample, ten spectra were collected while the sample was dry and wet, and these ten spectra were averaged to give a representative spectrum. These averaged spectra were then splice corrected with a splice correct gap of 1 to correct for gaps in spectra where different detectors do not have a crossover. 'Dry' sample collections were not altered before a data collection, while 'wet' sample collections were sprayed with a water bottle three times (mass of ~ 3 g) at a distance of 10 cm before data collection. All samples were placed in a matte black Petri dish on a matte black block to ensure that the total signal received was derived purely from the samples. Samples were illuminated with an ASD Illuminator reflectance lamp with a 70 W quartz-tungsten-halogen light source in an otherwise dark room.

Results

Bulk chemistry

Bulk major element concentrations are presented in Table 1. Bulk minor and trace element concentrations are presented in Table 2. Bulk chemical results indicate that the tills sampled are relatively homogenous with respect to major element oxides. Signatures are summarized in Fig. 2. Concentrations for seven of the ten major oxides shown exhibit a less than 1 wt% variation along the transect sampled: TiO₂, Al₂O₃, MnO, MgO, Na₂O, K₂O, and P₂O₅. For SiO₂, Fe₂O₃, and CaO variations range as 2.95 wt%, 3.98 wt% and 1.79 wt% respectively. For eight of the ten major oxides, 2σ values are less than ± 1 with the exception of wt% SiO₂ at ± 1.76 and wt% Fe₂O₃ at \pm 1.27. Considering the wt% Fe₂O₃ data, there is one notable outlier (see Fig. 1) at location 1. Considering the remaining 19 sites, the wt% Fe_2O_3 average is 3.15 ± 0.34 (2 σ) compared to 3.29 ± 1.27 (2 σ , n = 20). Clear correlations also exist between certain major element oxides (Fig. 2), specifically wt% TiO₂ vs. wt% Al₂O₃, and wt% K₂O vs. wt% TiO₂ and wt% Al₂O₃. Covariation between these three major oxides is interpreted as being consistent with variable proportions of amphibole where site A in the amphibole crystal structure can be occupied by K, and sites C and T by both Al and Ti. With respect to the co-variation in wt. % K₂O and wt% Al₂O₃, this could also be explained by the variable presence of illite and chlorite (ripidolite) and potassium feldspar minerals if present. Both of these scenarios would be consistent with mineralogical observations by XRD (see later).

Figure 3 summarizes the geochemical nature of the till sampled with respect to trace element abundances, shown normalized to Earth's primitive mantle and plotted alongside several of Earth's bulk crustal geochemical reservoirs. As shown, the till sampled is clearly distinct from a lower continental crust reservoir (as would be expected) and is chemically the most similar to the Earth's bulk continental crust. In Fig. 4, the rare earth elements (REEs) are shown normalized ($_N$) to a chondritic reservoir, again also shown alongside the Earth's bulk crustal reservoirs. Consistent with Fig. 3,

	1	2	3	4	5	6	7	8	9	10
SiO ₂	46.13	44.17	43.52	44.53	45.90	45.48	45.23	45.43	44.88	43.18
TiO ₂	0.44	0.43	0.47	0.47	0.43	0.43	0.45	0.46	0.42	0.40
Al_2O_3	8.03	7.79	7.95	8.05	7.89	8.00	7.91	8.20	7.91	7.75
Fe ₂ O ₃	5.88	3.21	3.05	3.60	2.94	3.46	3.20	3.37	3.13	3.08
MnO	0.06	0.06	0.06	0.07	0.05	0.06	0.06	0.06	0.06	0.06
MgO	5.51	5.39	5.12	5.13	5.17	5.21	5.37	4.77	5.18	5.35
CaO	14.64	14.23	14.14	14.61	13.90	14.51	14.34	13.75	14.01	14.41
Na ₂ O	0.93	1.00	0.89	0.85	0.87	0.91	0.90	0.75	0.91	0.89
K ₂ O	2.03	1.87	1.96	1.97	1.94	1.92	1.98	2.00	1.95	1.86
P_2O_5	0.13	0.13	0.13	0.14	0.12	0.13	0.12	0.16	0.13	0.12
	11	12	13	14	15	16	17	18	19	20
SiO ₂	45.22	43.27	44.27	44.56	44.38	43.59	45.72	45.40	44.74	45.33
TiO ₂	0.43	0.42	0.40	0.42	0.40	0.39	0.42	0.38	0.42	0.43
Al_2O_3	7.83	7.59	7.55	7.57	7.56	7.63	7.63	7.33	7.43	8.04
Fe ₂ O ₃	3.19	3.10	3.01	3.04	3.03	3.02	3.15	3.21	2.90	3.15
MnO	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.05	0.06	0.06
MgO	5.38	5.26	5.59	5.43	5.41	5.55	5.31	4.96	5.01	5.28
CaO	14.40	14.58	14.62	14.63	14.42	14.92	14.22	13.13	14.74	14.22
Na ₂ O	0.94	0.87	0.89	0.90	0.93	0.94	0.93	0.98	0.82	0.95
K ₂ O	1.91	1.86	1.88	1.89	1.84	1.83	1.87	1.79	1.85	2.00
P_2O_5	0.12	0.13	0.13	0.12	0.11	0.12	0.12	0.11	0.15	0.13

Table 1 Bulk major element concentrations of sampled till (values in wt %)

the till sampled is chemically akin to the Earth's bulk continental crust with a characteristic light REE (LREE) enrichment (La_N/Sm_N: 1.93–2.76) and slightly enriched middle/heavy REE signatures (Gd_N/Lu_N: 1.45–1.82). All absolute REE concentrations from Sm to Lu across all till samples show little variation between sites with 2σ at $\pm < 1$ (n=20). With respect to other trace and minor elements determined (Table 2), 2σ is at $\pm < 1$ for the following elements: Be, Ga, Sn, Sb, and Cs (n=20).

For geochemically relevant minor and trace metals, populations and trends are summarized in Fig. 5a-j. The strongest correlation exists between Zr and Hf (Fig. 5a) which defines an average Zr/Hf value of 40.4 ± 2.6 (2σ , n = 20). This is attributed to a variable contribution from the heavy mineral zircon into which Zr and Hf readily partition and which is a common accessory phase in the source material (e.g., granites, diorites) to the sampled till. In Fig. 5b-d, the correlations shown are acknowledged to be defined, generally by one outlier. In the case of Cr, Cu, and Mo, this is consistently the sample at site no. 1, and in the case of Co and Ni, this is consistently the sample at site no. 18. In Fig. 5e, the correlation of Ga and V, which defines a V/Ga value of 6.07 ± 0.29 (2σ , n = 20), is attributed to the variable occurrence of the heavy mineral magnetite into which V and Ga readily partition. Figure 5f-h shows the clustering $(\pm a)$ few ppm) for several elements of environmental concern. In Fig. 5f, As concentrations cluster at 4.64 ± 2.11 ppm (2σ , n = 19) with one outlier at 20.95 ppm at site no. 18 and Pb at 11.26 ± 1.35 ppm (2σ , n = 20). In Fig. 5g–i, Co vs. Cr, Ni vs. Cu, and W vs. Co and Ni are shown. For Co, concentrations cluster at 8.17 ± 1.21 ppm (2σ , n = 19) if site no. 18 is not considered. With site no. 18, the average Co concentrations are 8.40 ± 2.36 ppm (2σ , n = 20). Without the consideration of site no. 18, the average Cr concentrations are 41.22 ± 3.78 ppm (2σ , n = 19). In Fig. 5i, the limited range of W is illustrated $(0.61 \pm 0.12 \text{ ppm at } 2\sigma, n = 20)$ plotted against Co (~8 ppm, see Fig. 5d, g) and Ni at an average concentration of 26.74 ± 2.54 ppm at 2σ , n = 19 $(27.11 \pm 4.16 \text{ ppm}, 2\sigma, n = 20)$. With respect to the absolute concentrations of LREE (La) and HREE (Lu), La is variable, up to 12 ppm across the sampled sites compared to Lu which varies only by ~0.06 ppm. Across all samples, moisture losses range between 8.57 and 12.37%, and total organic content ranges between 1.27 and 3.45%. Of particular note here is the grouping of metals relevant to urban pollution (e.g., Pb, Cu, Zn, Cr) which shows a limited variation between sites (Table 2). Other metals relevant to machining operations or U production in the region (e.g., W, Ni, Co, U, Th) show variable degrees of clustering with U vs. Th (Fig. 5k) highlighting the limited range in U $(1.22 \pm 0.39 \text{ ppm}, 2\sigma, n = 20)$ and relatively restricted variability in Th (5.11 \pm 1.72 ppm, 2σ , n = 20).

Table 2	Bulk minor and trace element co	ncentrations of sampled till (values in ppm)
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	1	2	3	4	5	6	7	8	9	10
Be	1.7	1.4	1.5	1.6	1.6	1.6	1.6	1.6	1.6	1.6
V	58.5	53.9	56.9	60.4	57.9	57.6	58.2	60.3	56.6	55.3
Cr	58.4	43.7	41.7	44.0	42.7	41.5	40.3	42.1	40.1	40.6
Co	8.6	7.9	7.9	10.3	8.6	7.9	8.3	8.7	8.2	7.8
Ni	30.1	26.3	26.9	28.6	27.2	26.1	27.7	26.6	26.1	26.1
Cu	20.4	14.8	16.2	16.3	16.5	15.4	15.9	16.3	15.2	15.6
Zn	25.8	17.4	34.5	25.0	32.4	18.3	31.8	16.9	27.0	19.8
Ga	9.6	9.2	9.4	9.6	9.5	9.7	9.5	10.0	9.4	9.4
As	6.0	5.0	3.7	5.0	5.9	5.2	7.0	5.3	4.6	5.0
Rb	69.4	64.0	69.0	69.9	70.2	69.9	70.2	74.5	68.6	67.4
Sr	225.0	223.3	220.1	226.6	209.9	220.3	221.0	209.2	221.5	217.0
Y	19.4	17.8	18.1	18.0	18.0	18.6	19.3	20.9	18.1	17.2
Zr	158.9	198.9	203.7	202.1	162.5	279.9	195.9	164.4	174.3	134.5
Nb	5.4	5.4	6.6	5.8	5.1	4.7	5.2	5.9	4.6	4.2
Мо	11.9	5.7	4.0	4.6	3.9	4.1	3.9	3.2	3.6	3.8
Sn	0.4	0.3	0.3	0.3	0.3	0.3	N0.1	0.5	0.1	0.1
Sb	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Cs	2.1	1.8	2.1	2.1	2.2	2.1	2.1	2.4	2.1	2.0
Ba	374.6	402.9	319.1	329.1	308.0	317.5	340.2	325.4	368.5	306.8
La	18.5	16.0	16.2	16.6	17.6	17.0	17.2	18.2	16.2	16.0
Ce	43.9	39.2	40.1	40.8	41.9	41.9	41.5	43.8	39.9	39.1
Pr	3.7	3.2	3.3	3.3	3.4	3.6	3.4	3.7	3.3	3.1
Nd	22.5	20.9	21.3	21.3	21.5	22.5	21.6	22.8	21.3	20.7
Sm	4.6	4.3	4.4	4.4	4.4	4.6	4.4	4.6	4.4	4.2
Eu	0.9	0.9	0.8	0.9	0.8	0.9	0.9	0.9	0.9	0.8
Gd	3.6	3.4	3.5	3.5	3.4	3.6	3.5	3.7	3.5	3.4
Tb	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Dy	3.7	3.5	3.5	3.5	3.5	3.6	3.7	3.8	3.5	3.4
Но	0.7	0.6	0.6	0.6	0.6	0.6	0.7	0.7	0.6	0.6
Er	1.9	1.7	1.8	1.7	1.7	1.8	1.8	2.0	1.7	1.7
Tm	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Yb	2.0	1.8	1.9	1.9	1.9	1.9	2.0	2.1	1.8	1.8
Lu	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Hf	4.1	5.0	4.8	4.8	4.0	6.4	5.1	4.2	4.3	3.5
Та	0.5	0.6	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5
W	0.5	0.6	0.7	0.6	0.7	0.7	0.7	0.7	0.6	0.6
Pb	12.9	10.3	10.7	12.2	11.5	11.0	11.3	11.3	10.6	11.2
Th	5.7	4.6	4.8	5.2	5.0	6.7	5.3	5.5	5.3	5.3
U	1.3	1.1	1.2	1.1	1.7	1.2	1.4	1.1	1.2	1.5
	11	12	13	14	15	16	17	18	19	20
Be	1.6	1.6	1.6	1.6	1.5	1.5	1.5	1.5	1.5	1.6
v	57.6	56.3	55.7	56.6	54.6	54.1	58.4	51.0	53.0	56.5
Cr	43.3	40.9	40.7	42.2	41.5	40.3	42.4	38.4	35.9	41.1
Co	7.8	7.8	8.2	8.1	7.6	8.0	8.1	12.7	7.6	8.0
Ni	26.2	25.8	26.8	27.0	26.0	27.2	27.0	34.2	23.6	26.6
Cu	15.3	15.4	15.6	17.1	18.2	15.3	16.4	14.4	14.0	15.8
Zn	13.5	11.4	16.2	16.4	16.1	16.8	19.1	19.3	26.4	18.2
Ga	9.3	9.0	9.0	9.1	9.0	9.0	9.1	8.6	8.9	9.6
Δs	37	3.2	52	4 1	43	34	32	21.0	33	49

Table 2 (continued)

	11	12	13	14	15	16	17	18	19	20
Rb	67.0	66.3	66.5	66.5	65.5	65.0	66.8	60.7	66.1	70.1
Sr	234.2	221.8	227.1	225.0	224.4	224.8	227.9	219.4	219.5	227.4
Y	18.1	17.3	17.2	18.5	17.0	17.0	18.9	17.3	17.5	20.5
Zr	210.4	145.5	149.6	214.3	170.2	127.8	208.3	169.0	180.5	173.9
Nb	5.1	4.7	4.3	4.5	4.4	4.0	4.6	4.4	4.1	5.4
Мо	3.2	3.1	3.7	3.9	3.3	3.3	3.3	3.6	2.7	3.4
Sn	0.0	0.0	0.1	0.2	0.2	0.1	0.2	0.1	0.1	0.1
Sb	0.3	0.3	0.4	0.4	0.4	0.3	0.4	0.4	0.4	0.4
Cs	2.0	2.0	2.0	1.9	1.9	1.9	1.9	1.6	1.9	2.1
Ва	343.6	312.5	376.3	321.3	334.2	304.2	327.4	359.9	316.7	352.9
La	14.5	15.5	15.7	15.3	13.6	13.9	15.6	12.1	14.0	24.4
Ce	36.9	38.4	38.9	37.6	34.9	34.9	38.1	31.9	35.5	55.8
Pr	3.0	3.1	3.2	3.0	2.7	2.6	3.2	2.4	2.7	5.1
Nd	20.5	20.5	20.8	20.5	19.3	19.2	20.5	18.3	19.4	26.6
Sm	4.4	4.2	4.2	4.3	4.1	4.0	4.3	3.9	4.1	5.3
Eu	0.9	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.9
Gd	3.4	3.3	3.4	3.4	3.2	3.2	3.4	3.1	3.2	4.1
Tb	0.6	0.6	0.6	0.6	0.5	0.5	0.6	0.5	0.6	0.7
Dy	3.5	3.4	3.4	3.5	3.3	3.3	3.5	3.3	3.4	4.0
Но	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.7
Er	1.7	1.7	1.7	1.7	1.7	1.7	1.8	1.7	1.7	1.9
Tm	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Yb	1.9	1.8	1.7	1.9	1.8	1.8	1.9	1.8	1.8	2.0
Lu	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Hf	5.1	3.7	3.7	5.3	4.2	3.2	5.2	4.3	4.5	4.3
Та	0.5	0.5	0.5	0.5	0.5	0.4	0.5	0.6	0.5	0.6
W	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.6	0.6
Pb	12.1	11.4	10.3	11.0	10.5	11.0	11.3	11.3	10.9	12.1
Th	4.4	4.6	4.8	5.0	4.3	5.4	4.8	3.6	4.3	7.6
U	1.1	1.0	1.3	1.5	1.1	1.1	1.3	1.0	1.0	1.3

One approach to defining environmental background is to use the maximum values for the concentrations of metals of environmental concern. Although not commonly done, it is a conservative approach. A more common approach is to define background as the average concentration of the element of interest plus the value of the standard deviation. From the results of this study, the recommended values using both approaches are summarized in Tables 3 and 4, in addition to interelement ratios for those elements which were demonstrated to covary with statistical significance (e.g., Zr vs. Hf, Table 4). Of the 39 minor and trace elements analyzed, 74% (n = 29) vary by less than 10 ppm between the 20 sampled sites (Fig. 1). Of the ten major element oxides considered here, there is a < 3wt% variation between all 20 sites sampled with a < 1 wt%variation observed for 7 of them. All standard deviations (reported at 2σ) are < 1.

X-ray powder diffraction (XRD)

Powder XRD data for sample material is comparatively uniform with respect to the number of minerals present and the relative proportions or abundance of those minerals (Fig. 6). Major minerals detected by powder XRD include illite, chlorite, quartz, calcite, dolomite and feldspar. The major peaks for quartz have values of $d_{(101)} = 3.3435$ Å and $d_{(101)} = 4.2550$ Å. The major peaks for calcite and dolomite are $d_{(104)} = 3.035$ Å and $d_{(104)} = 2.888$ Å respectively. The exact identification of feldspar species is challenging owing to potential peak overlaps and the presence of numerous species such as microcline, orthoclase, albite and intermediate composition plagioclase. Calcian ordered albite is common with the major peak being $d_{(002)} = ~3.18$ Å. Several other peaks at ~ 3.83 Å, 3.70 Å, 3.47 Å, 3.31 Å, 3.24 Å are

wt. % TiO ₂	· · · · ·	SiO ₂	r ² = 0.61	°°° °°°	000 0 8.890 045 0	• • • •		* * * * * * * * * * *	1 ² = 0.67	• • •
wt. % AI ₂ O ₃		r ² = 0.61	SiO ₂	° ° ° ° °	8 0 0 03 03 09 09 0	· · · · ·	· · · · · · · · · · · · · · · · · · ·	· · · · ·	r ² = 0.8	
wt. % Fe ₂ O ₃		·	°, æ «, «, °	SIO, • ************************************	۰ ۰ ۴	**************************************	•		·	*. # 58°
wt. % MnO		9 84 S	* ************************************	° 998° °	SiO ₂ •	· · · · · · · ·	•	* * * \$*a *s; * *		, A *3 • *
wt. % MgO			**************************************	8 8400 80 9 9 9 9	۰ ۲	SiO ₂		* * * * * *		• • • • • • • • • • • • • • • • • • •
wt. %CaO			* * * * * * * * * * * * * * * * * * *	ୢୄୖ୶ୡୣଌୠୄୖ	000 0 0 000 0 0 0 0 0 0 0 0 0 0 0 0 0 0	• • • • • •	SiO ₂	*	· ·	***** *** *
wt. %Na2O				00 80 0 80 80 0 80 80 0 90 80	٠ ٠ ٠ ٠ ٠ ٠ ٠ ٠ ٠ ٠ ٠ ٠ ٠		· · · · · · · · · · · · · · · · · · ·	SiO ₂ • • • • • • • • • • • • • • • • • • •		*** *** *** **
wt. %K ₂ O		r ² = 0.67	r ² = 0.8	° °	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		• • • • •	• • • • • • • •	SiO ₂	• • • • • • •
wt. %P ₂ O ₅			° °°°		**************************************	•••••••	••••	• • • • • • • • • • • • • • • • • • •	••••••	
43	wt. % SiO ₂	wt. % TiO ₂	wt. % Al ₂ O ₃	wt. % Fe ₂ O ₃	wt. % MnO	wt. % MgO	wt. % CaO	wt. % Na ₂ O	wt. % K ₂ O	wt. % P ₂ O ₅

Fig. 2 Major oxide vs. major oxide from all samples collected along the transect in Fig. 1. Little variation with respect to major element chemistry is observed at localities sampled (see summary presented

in Table 3). Positive correlations exist within the dataset with respect to a few major oxides (TiO₂, Al₂O₃, K₂O). Particularly narrow ranges are observed in wt. % Fe₂O₃ and wt. % MnO (highlighted)

consistent with a mixture of ordered microcline, intermediate microcline and orthoclase. A Ca–Mg–Fe rich amphibole (likely actinolite) was identified by a $d_{(020)}$ of ~ 8.44 Å in samples 3,15, and 18. This would be consistent with the mineralogy of likely Canadian-sourced crystalline basement material.

Illite and chlorite are the only clay mineral species identified and representative powder XRD patterns are presented in Fig. 7. Excluding samples 19 and 20, powder XRD patterns for all other samples show $d_{(001)} = 10.01$ Å (± 0.08 Å), $d_{(002)} = 4.99$ Å (± 0.03 Å), and $d_{(003)} = 3.32$ Å (± 0.01 Å) for illite for air-dried treatments and there is no detectable expansion upon ethylene glycol treatment, indicating the mineral phase is illite and not an interstratified illite–smectite mineral. Powder XRD patterns for ripidolite (a variety of chlorite) for all samples show $d_{(001)} = 14.21$ Å (±0.08 Å), $d_{(002)} = 7.10$ Å (±0.03 Å), $d_{(003)} = 4.74$ Å (±0.02 Å), $d_{(004)} = 3.55$ Å (±0.01 Å) and $d_{(005)} = 2.84$ Å (±0.01 Å). A minor peak at approximately 7.63 Å is observed in some XRD patterns (e.g., 14, 19, 20) and this peak is interpreted as the (020) of gypsum.

One-dimension diffraction models using NEWMOD 2, v. 1.1 were made for illite and ripidolite. The best topological match for the illite diffraction pattern observed was a model that had 98% illite with 0.8 K atoms and 0.15 Fe atoms interstratified with 2% dioctahedral smectite with 0.15 Fe atoms using a Reichweite value of 3. Some XRD patterns from samples 19 and 20 show a broad hump that is broadly consistent with an R3 illite with approximately 10–12% dioctahedral smectite. The best topological match for the



Fig. 3 Primitive-mantle (PM) normalized multi-element spidergrams summarizing the trace element characteristics of the till sampled. As shown, all show similar degrees of enrichment and depletion with notable enrichment in the large ion lithophile elements (LILEs), Pb, Hf, and Zr. All sampled tills also display a negative Nb–Ta anomaly, a characteristic also observed in bulk and upper continental crust compositions. Shown for comparison are the PM-normalized signatures of the bulk, upper, middle, and lower continental crust (BCC, UCC, MCC, and LCC, respectively). For discussion see text. Normalizing values from McDonough and Sun (1995). Crustal reservoir composition from Rudnick and Gao (2003)



Fig. 4 Chondrite-normalized rare earth element (REE) profiles for till and crustal reservoirs sampled (from Fig. 3). All till samples display light-REE enrichment with heavy-REE depletion and a negative Eu anomaly. For discussion see text. Normalizing values from Nakamura (1974)

ripidolite diffraction pattern observed was a model that had 2.88 silicon–Fe atoms, 3 hydroxide Fe atoms, and a hydroxide layer value of 0.92.

Transmission electron microscopy (TEM)

The results of a TEM investigation of samples 1 and 4 show that illite, the dominant clay mineral occurs as subhedral to euhedral plates (Fig. 8). The (hk0) faces of illite often exhibit rounding and evidence of mechanical deformation. Grain mount images show that illite particles are commonly a few micrometers to approximately 50 nm in diameter. Results from structural imaging and selected area electron diffraction (SAED) along [001] of illite crystals show that the illite is often highly crystalline. Although present in X-ray powder diffraction patterns, chlorite was not often observed in TEM grain mounts. This may be due to size fractionation where chlorite crystals are larger and fall out of suspension quickly, leaving dominantly illite in the suspensions prepared.

X-ray computed tomography (XCT)

Sample material selected for XCT shows a wide variation in volumes of particles, varying by five orders of magnitude (Fig. 9). Regardless of particle size distribution present, all histograms are skewed toward the fine particle size without other pronounced modes of occurrence. In all examples, larger grains or particles appear to be predominantly matrix supported. The density of the spatial distribution of the grains or clasts is also generally even with random orientations. Some clast clustering is evident in the middle row image of Fig. 9, but there is no evidence of structures which may be expected from deformed tills. The spatial distribution of components observed is therefore consistent with the interpretation of Ekberg et al. (1993) that this unit is a lodgement till.

Reflective spectroscopy

Reflective spectra of till samples are consistent with what would be expected for a material in which a dominant component is carbonate derived, and in which silicate minerals and clay minerals are also present (Fig. 10). The spectra have several distinct features consistent with features known for functional groups. A general positive ramp in the visible and near infrared is apparent in both ambient dry and wet spectra which is typical of silicate-rich geomaterials that are present (e.g., feldspar and quartz). Major features observed include absorptions at ~1454 nm (molecular water), 1900 nm (carbonate ion), 1875 nm (molecular water), ~2170 nm (Al-OH), and ~ 2200 nm (Al-OH). A combined adsorption feature is observed at ~2320 nm which is interpreted as resulting from a combination of features at ~ 2300 nm (Al-OH, Mg-OH), 2330 nm (OH), and 2350 nm (carbonate ion). For wet samples, the 1454 nm (molecular water)



Fig. 5 a-k Trace element variability throughout the till sampled. Correlations in Zr (ppm) vs. Hf (ppm) are attributed to variable proportions of the accessory phase zircon being present, in which variable proportions of magnetite are inferred to account for the co-varia-

tion in V (ppm) vs. Ga (ppm). The correlations depicted in **b-d** are acknowledged here as being leveraged by one data point. For discussion see text

Table 3Maximum, minimum,and average abundances of		SiO ₂	TiO ₂	Al_2O_3	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5
major element oxides (wt. %)	Maximum	46.13	0.47	8.20	5.88	0.07	5.59	14.92	1.00	2.03	0.16
	Minimum	43.18	0.38	7.33	2.90	0.05	4.77	13.13	0.75	1.79	0.11
	Average	44.75	0.43	7.78	3.29	0.06	5.27	14.32	0.90	1.91	0.13
	2SD	0.88	0.02	0.24	0.63	0.00	0.21	0.41	0.06	0.07	0.01

and 1875 nm (molecular water) features are much more pronounced. The features above 2100 nm are notably less intense than those of the ambient dry samples.

Discussion

Bulk chemistry

From both a geochemical and a mineralogical perspective, the glacial till sampled is relatively homogenous. As documented, for major elements, the range of individual components is a few weight percent (at maximum) with Fe₂O₃ (5.88–2.90 wt%) SiO₂ (46.13–43.18 wt%) and CaO (14.92-13.13 wt%) showing the greatest variation. Minor and trace elements either show significant linear trends on X-Y plots, or a simple single population scatter. Powder XRD data also show a modest to minimal variation in both phase diversity and relative abundance of phases, consistent with results from complementary bulk chemical analyses. The relative proportions of the major reflections of illite, ripidolite, quartz, calcite, and dolomite vary by approximately

Table 4	Maximum,	, minimum,	and average	concentrations	of minor an	id trace e	elements re	eported in	this study (p	pm)

	Be	V	Cr	C	Co	Ni	Cu	Zn	Ga	As	Rb
Maximum	1.66	60.40	58.42	1	2.75	34.23	20.43	34.49	10.04	20.95	74.51
Minimum	1.40	50.97	35.87	7	.60	23.62	14.00	11.44	8.62	3.15	60.67
Average	1.55	56.47	42.08	8	.40	27.11	16.02	21.10	9.30	5.46	67.68
2SD	0.11	4.72	8.52	2	.36	4.17	2.78	13.14	0.68	7.58	5.87
	Sr	Y	Zr		Nb	Мо	Sn	Sb	Cs	Ba	La
Maximum	234.20	20.88	173.9	5	6.60	11.92	0.53	0.44	2.42	402.91	24.36
Minimum	209.18	16.95	158.9	1	3.98	2.74	0.12	0.34	1.62	304.20	12.12
Average	222.27	18.23	181.2	3	4.91	4.11	0.18	0.37	2.01	337.06	16.21
2SD	11.68	2.21	69.14	ŀ	1.37	3.88	0.31	0.05	0.32	54.69	4.98
	Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Но	Er
Maximum	55.78	5.08	26.61		5.25	0.91	4.14	0.67	3.97	0.71	1.96
Minimum	31.86	2.37	18.30)	3.87	0.77	3.10	0.53	3.28	0.58	1.65
Average	39.75	3.24	21.10)	4.34	0.84	3.44	0.58	3.51	0.63	1.75
2SD	9.73	1.12	3.46		0.58	0.08	0.46	0.06	0.35	0.08	0.17
	Tm	Yb	Lu	Hf	Та	W	Pb	Th	U	Zr/Hf	V/Ga
Maximum	0.31	2.08	0.31	6.40	0.61	0.74	12.94	7.60	1.71	43.77	6.42
Minimum	0.25	1.72	0.25	3.21	0.45	0.51	10.30	3.65	0.97	38.72	5.87
Average	0.27	1.87	0.27	4.47	0.53	0.61	11.26	5.11	1.22	40.40	6.07
2SD	0.03	0.18	0.03	1.49	0.09	0.12	1.35	1.72	0.39	2.58	0.29



Fig. 6 Representative powder X-ray diffraction patterns of selected samples. Major reflections are labeled for dominant minerals which include quartz, calcite, feldspars and dolomite, illite and ripidolite are labeled



Fig. 7 Representative powder X-ray diffraction patterns of the $< 2 \mu m$ size fraction of selected samples. These patterns are in the ethylene glycol state and indicate that illite and ripidolite are the primary phyllosilicate minerals present. Major reflections are labelled

10–15%. Modeling of illite and ripidolite XRD patterns also suggests that the chemical composition of these minerals is well defined (little variation exists).

X-Y plots of pollutant elements essentially group as single populations and can thus be utilized as distinct geogenic fingerprints for the till. These groupings are also significant with respect to the interpretation of X-Y elemental plots in unknown pollutant samples. Such multi-element variation(s) can be used to demonstrate if elemental concentrations and/ or ratios of suspected pollutant concentrations are similar to, or different from, the geogenic background. This information could then be used to provide some degree of constraint on the potential source(s) of pollutants. Table 5 summarizes the average abundances of environmentally relevant trace metals for the till sampled and compares these to results from recent pollution studies across the region. For many of the elements shown, abundances in the till are present at concentrations of similar orders of magnitude (e.g., 10 s of ppm or less). However, several elements in previous studies are documented to be present at significantly higher concentrations, i.e., above the proposed geogenic background, most notably Pb and Zn.

Elemental ratios of geogenic background concentrations of elements could also be used to compare to additional future geologic references (e.g., the extensive interbedded limestones and shales of the Cincinnatian Series) and may also be of use in modeling sediment mixing between these components. The geochemical and mineralogical composition of the regionally extensive sampled till (90% of the Quaternary cover of Butler County) therefore serves as an important baseline to compare other materials to those from across the area, ones that may have experienced pollution over the past 150 years of industrial activity.

Mineralogy and geologic source: comparisons to previous work

Comprehensive studies in the peer-reviewed literature which focus on the mineralogy of bedrock or glacial tills in south-western Ohio are lacking. The entire Ordovician section of the Cincinnati Arch is recognized as having sparse dolomite and consists of well-preserved fossiliferous limestone and calcareous shales (e.g., Bassarab and Huff 1969; Holland 1993; Jennette and Pryor 1993; Dattilo et al. 2008, 2012). There is somewhat sparse literature on the details of the shales' clay mineralogy or of the bedrock in the region with the most relevant work by Bassarab and Huff (1969) on the Kope and Fairview formation shales and Booth and Osborne (1971) on the insoluble residues in limestones from Hamilton County to the south of the field area considered by this study.

The mineralogy of the till sampled at Peffer Park in Butler County, Ohio, is that which would be expected, being

Fig. 8 Bright field TEM images of the $< 5 \, \mu m$ -size fraction. **a** A platy illite particle with an aggregate of Fe-oxides at the top of the particle. This image was acquired at \times 50,000. **b** A structural image acquired at 1.5millionx approximately along the c-axis taken form the upper left region of the illite particle in a. c The inset selected area electron diffraction pattern indicates that the illite particle is a single crystal and has not deformed as indicated by a lack of streaking



dominated by minerals of regional carbonate rocks (calcite and dolomite) and regional shales (illite, ripidolite, quartz), with some admixture of components likely derived from the Canadian shield (e.g., amphibole from the chemically intermediate-evolved nature of the igneous and metamorphic crystalline basement). Dolomite is interpreted here as being derived dominantly from the Silurian bedrock to the north of the field area (Janssens 1977) with the illite and ripidolite mineralogy observed in the Peffer Park till samples consistent with the region's Ordovician shales. Mineralogical data from glacial tills in northern and western Ohio have been reported (Szabo 2003; Fausey et al. 2000; Haefner 2000). Notably, Fausey et al. (2000) report that clay mineralogy of tills from Preble, Auglaize, Madison, Darke and nearby Preble Counties have clay mineralogy dominated by illite (65–80%) with the second most abundant clay being vermiculite (10–14%), followed by < 5% each of kaolinite and quartz. No vermiculite was observed in the Peffer Park till and the only expandable component identified was R3 illite–smectite, observed in only a few samples.



Fig.9 Top row: MK-2 volume distribution frequency and corresponding sample. Middle row; MK-3 volume distribution frequency and corresponding sample. Bottom row: MK-2 volume distribution

frequency and corresponding sample. All histogram colors correspond to the grains shown in the respective inset 3D image. Note that volume scale changes with sample scale



Fig. 10 Representative reflective spectra of till samples from 350 to 2500 nm with the upper set being ambient air-dry samples and the lower set being wetted evenly with approximately 3 g of water. These spectra thus represent the range that would normally be encountered in hyperspectral remotely sensed images. Major absorption features are identified

This suggests that the clay mineralogy in particular of tills may be more regionally diverse than previously recognized and that systematic investigations using a larger number of samples may be warranted.

Fausey et al. (2000) and Szabo (2003) also report calcite and dolomite as being significant components of tills in northern and western Ohio. Among these studies, there is however a range of values reported for calcite (0.1-11.5%) and dolomite (4–35%). Powder XRD data show that the relative ratio of calcite and dolomite shows little variation in the Peffer Park samples. This suggests that the interpretations of Fausey et al. (2000) and Szabo (2003) that the variation of carbonate minerals in tills in northern Ohio is likely real, although previous workers appear not to have considered multiple samples and so no comment on variability is possible at this stage. Future work on the bulk mineralogy of tills in the region is thus justified and should combine the method(s) used by previous authors who used a Chittick apparatus with powder XRD and quantitative phase analysis to fully understand the variability of carbonate minerals in glacial tills throughout the region.

X-ray computed tomography

The μ CT results presented here indicate a wide range of particle volumes in each of the samples, though distributions were all skewed towards the smaller grain size. The μ CT data likely explain the poorly correlated and highly variable Atterberg limit data collected on the same three samples used for μ CT representative samples. The high variability of the results of these geotechnical tests likely relates to the variable grain size documented in the particle volume histograms. Future, detailed studies involving μ CT and Atterberg limit tests, using numerous samples, may provide future insight into this extent of this variability.

One noteworthy limitation of using μ CT to discern grain size distributions is that grains which are chemically identical or similar to the matrix do not provide sufficient contrast to be easily identified as a discrete component. As such, these volume distributions are inherently biased against lithic material most similar to the matrix of the till. Nonetheless μ CT has proven to be useful to quantify and image textures of the till that otherwise would not be available. These results suggest future work of comparing tills of a variety of origins and environmental conditions is warranted.

Reflective spectroscopy and remote sensing implications

Reflective spectroscopy enables rapid characterization and can be used to compare tills that may be mineralogically similar. The features observed in reflective spectra are consistent with the mineralogical and chemical composition otherwise observed for the till samples. Calcite and dolomite contribute to the carbonate adsorption features. Illite, feldspar and ripidolite contribute to the Al–OH features. Ripidolite contributes to the Mg-OH features. The feature at ~ 350–370 nm is interpreted as noise from the edge of the dish, but is also acknowledged as potentially being a result of Fe–O bonds. The numerous features and overall topology of the reflective spectra of till samples would enable Table the av abund Peffer sedim region

5 Comparison between erage trace element		n	V	Cr	Co	Ni	Cu	Zn	As	Mo	Sb	W	Pb
ances in sampled till at	Average Peffer Park glacial till	20	55	42	8	27	16	21	5	4	<1	<1	11
Park and those in street	Dietrich et al. (2018, street sediment)	14	56	160	9	52	28	374	8	3	2	2	85
al pollution investigations	Dietrich et al. (2018, ballfield sediment)		67	54	9	30	15	76	8	2	<1	<1	2
1 0	Flett et al (2016)	27	24	34	7	38	245	611	4	n.a	n.a	n.a	468
	LeGalley and Krekeler (2013)	15	n.a	28	n.a	14	60	588	n.a	n.a	n.a	n.a	297
	LeGalley et al. (2013)	7	n.a	97	20	63	n.a	1368	n.a	n.a	n.a	n.a	501

All abundances in ppm, "n" refers to the number of samples analyzed in each study

identification in hyperspectral imagery which may be useful for erosion studies, petroleum spill studies and the monitoring of land surface motion in natural areas (e.g., Vrieling 2006; Chabrillat et al. 2019; Pabón et al. 2019; Bachmann et al. 2019). The addition of water to tills significantly changes the topology of the spectra, having implications for hyperspectral remote sensing detection. These spectra thus represent the range that would normally be encountered in hyperspectral remotely sensed images. Hyperspectral imaging using these spectra should also be useful for future investigations of erosion and landslide activity, both of which are common in southwestern Ohio (e.g., Brown 1985; Haneberg 1991, 2000).

Uses in broader contexts

What is the natural geogenic background for southwestern Ohio? For this study, the background was characterized as an abundant near surface geologic material which shows no anthropogenic influence. It is acknowledged here that other potential background candidate materials do exist in the area (the interbedded limestones and shales of the Cincinnatian Series for example), but many of these are problematic in that they have been directly or indirectly exposed to significant anthropogenic pollution for at least 150 years. Additionally, the common soils and silts in fluvial settings and agricultural fields likely suffer an anthropogenic metal pollution from regional coal and manufacturing practices. Therefore, the Peffer Park till provides an excellent environmental comparative material in the context of geogenic comparisons for pollutants. Furthermore, the Peffer Park till data presented here provides a means to compare future investigations on glacial sands, flood plain soils and bedrock throughout southwestern Ohio to gain an improved understanding of the nature of variability in the background material mineralogy, composition, 3D texture, and elemental abundances, including those metals relevant to urban pollution studies.

This is significant because the number of studies investigating urban pollution in the southwest Ohio region is growing (Fernald Environmental Management Project 1998a, b; Turer et al. 2001; Martuzevicius et al. 2004; Mishra et al. 2004; Wojas and Almquist 2007; LeGalley et al. 2013; LeGalley and Krekeler 2013; Tortorello et al. 2013; White et al. 2014; McHugh et al. 2015; Dietrich et al. 2018). This work is expected to continue to grow as the post-industrial cities convert to service and technology-based economies with associated redevelopment. The environmental background values reported here are planned to be used in several ongoing studies in the City of Hamilton (e.g., Gander et al. 2016; Richards and Krekeler 2016) and the City of Middletown (e.g., Osborne et al. 2016). Additionally, this investigation will work to support future environmental investigations in numerous contexts throughout the region (Rech et al. 2018; Lazar et al. 2019).

Although there has been an interest in the metal pollution of Butler County and some urban settings in Ohio, detailed investigations of metal pollution in non-urban environments in the Ohio-Kentucky-Indiana region are not numerous in the peer-review literature compared to other regions of the USA. Investigations of metal pollution in Ohio rivers (Evans and Gottgens 2007; Matisoff and Eaker 1992; Bradley et al. 1998; Lyons et al. 2006; Tully 2013) have been carried with fewer investigations of wetland, lake, and river environments (Lopez et al. 2010; Gbolo and Lopez 2015; Lazar et al. 2019). Having a well-characterized reference material will support future investigations of nearby lake environments (e.g., Brookville Lake, Hueston Woods Lake), the extensive agricultural region to the immediate north of the study site, and preserved lands throughout the region.

There are also broad implications for improving characterization, and advancing knowledge, of local and regional glacial stratigraphy, structure, and competency. Currie et al. (2018b) recently produced a revised bedrock topographic map for the Oxford and College Corner Quadrangles, Butler and Preble Counties, OH, with work aimed at resolving details of glacial stratigraphy including tills, sand and gravel units and complexities associated with water production across the region. The mineralogical, geochemical and textural results on the Peffer Park till presented here thus support these ongoing investigations. Furthermore, glacial tills have been of general interest in Ohio for both pragmatic geotechnical reasons (Brockman and Szabo 2000; Weatherington-Rice et al. 2000), but also within the context of improving understanding of the region's glacial history (e.g., Szabo and Totten 1992, 1995; Ekberg et al. 1993). Specifically, Szabo (2003) systematically investigated tills in northern Ohio and found that there was a large regional variation in tills, but distinct trends in mineralogy, such as carbonate content declining from till plains to towards the Allegheny plateau, and a "constant" illite–kaolinite ratio. However, Szabo (2003) did not characterize multiple samples in the way the present investigation has. Thus, there was no extensive investigation of the potential variability within a single sample site. The interpretations of the trends in the Szabo (2003) study are thus based on limited sample populations.

The data presented here on the Peffer Park till of Butler County in southwest Ohio demonstrates an unexpected homogeneity in the chemical composition and mineralogy. It is well recognized that glacial stratigraphy, even at the scale of several meters, can be extremely complex. The integrated application of ICP-OES and ICP-MS for bulk chemical characterization, SEM, TEM and X-ray CT for mineralogical and 3D component distribution, coupled with the spectral reflectance via reflective spectroscopy may be a valuable tool for improving stratigraphic correlations and/or differentiating between units. It is acknowledged here that this may not be appropriate for clast-rich tills, but certainly demonstrates a potential for tills with finer particle distributions and/or for matrix material derived from clast-rich tills.

The hypothesis stated earlier is therefore rejected and it is suggested that the results indicate that the Peffer Park till contains a critical comparative material for Butler County and surrounding areas. The mineralogy and chemical composition show little variation and are now well characterized such that investigators can use the till as a direct comparative for southwestern Ohio, or as an analog for other regions which have been glaciated in the past. The results of this study also provide, or enable, an experimental material for investigations involving, but are not limited to, pollution interaction, hydrogeology, weathering, soil and geotechnical investigations. To our knowledge, no such reference till exists with its components characterized to the extent they have been here.

Conclusions

The results of this study, which comprehensively document for the first time the mineralogy, texture, bulk composition, spectral characteristics, and 3D distribution of components in a regionally extensive Wisconsin-aged glacial till, have broad implications. Unexpectedly, the glacial till from Peffer Park, Oxford, Ohio, sampled has a remarkably low variation with respect to geochemical, mineralogical, and sedimentological composition. With respect to bulk chemical composition, the major element oxides of the 20 tills samples along $a \sim 60$ m transect vary by less than ~ 3 wt. %, with seven of the major element oxides varying by less that 1 wt. % (Ti, Al, Mn, Mg, Na, K, and P). Bulk trace element characteristics highlight the till's geochemical affinity to the Earth's bulk and upper continental crust reservoirs with a characteristic enrichment in the large ion lithophile elements (e.g., Rb, Th, U), an enrichment in the light rare earth elements (e.g., La, Ce), and a relative depletion in the heavy rare earths (e.g., Yb, Lu). As with major element signatures, trace element signatures are surprisingly consistent with 29 of the trace (and minor) elements analyzed varying by less than 10 ppm between sample sites (representing 74% of the analytes). From XRD analysis, the till's mineralogy is characterized by quartzo-feldspathic materials in addition to calcite, dolomite and clay minerals (illite, chlorite) and minor amphibole. The dominance of silicate and carbonate minerals is confirmed by TEM and reflective spectroscopy.

The geochemical and mineralogical composition of the till serves as an important baseline to compare glacial sand silt and clay and soils that may have otherwise be polluted from over 150 years of industrial activity. Given the increasing number of studies focused on characterizing and identifying sources of pollution in southwest Ohio, this work also enables the use of important environmental, geogenic, background reference material for multiple aspects of the study. The dataset reported here therefore serves as a crucial reference for extensive post-industrial areas not only in and around Butler County, Ohio, but also across the Midwest.

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