Organic Matter Biomarker Fingerprinting of Glacial Deposits

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
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Abstract

The goal of this thesis was to test the applicability of biomarker analyses to better understand the glacial stratigraphic record of the Hudson Bay Lowlands and Oak Ridges Moraine. A biomarker analysis conducted on three geologic deposits from the Hudson Bay Lowlands showed that they can be differentiated based on organic matter (OM) inputs and stage of diagenesis, relating to paleoclimate and depositional environments. In the second study, a biomarker analysis was applied to samples from ten deposits in the Oak Ridges Moraine. These deposits were differentiated based on OM inputs relating to paleovegetation. Additionally, reincorporation and post-deposition alteration led to sample heterogeneity confirming the current understanding of glacial depositional processes and environments. This thesis shows that biomarker analyses can effectively differentiate and contextualize geologic deposits based on OM inputs and stage of diagenesis. This in turn will provide a more robust understanding of the stratigraphic record.
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Chapter 1: Introduction

1.1. Organic matter biomarkers

Carbon in the natural environment is distributed between interconnected carbon pools consisting of the ocean, atmosphere, biota, and soil (Janzen 2004). Oceans, the atmosphere, and biota contain approximately 39 000, 785, and 400 to 600 Pg of carbon, respectively (Intergovernmental Panel on Climate Change 2000, Intergovernmental Panel on Climate Change 2001, Janzen 2004). Soils contain approximately 1500 to 2000 Pg of carbon in various forms ranging from recent litter to old and altered compounds (Amundson 2001, Janzen 2004). Based on these values, soil organic matter (OM) accounts for approximately three times more carbon than living organisms (Janzen 2004) and is comprised of organic molecules from plants, bacteria, fungi, and their respective degradation products, to name a few (Weete 1976, Hedges and Mann 1979, Hedges et al. 1988, Otto et al. 2005). Specific OM compounds (biomarkers) have been used to elucidate OM sources to soil and its stage of diagenesis (Otto et al. 2005, Feng et al. 2007) but has also been used for identifying climatically-forced shifts in vegetation (Brincat et al. 2000, Xu et al. 2009) and for characterizing geologic deposits (Parnell et al. 2007). Tracing the identity and quantity of OM back to the time at which it was deposited provides insight into the types of organisms present at that time (Eglinton and Hamilton 1967, Weete 1976, Baas et al. 2000). Similarly, the degree to which the OM is oxidized or degraded provides information about that the extent of diagenesis (Ertel and Hedges 1985).

A biomarker is an organic compound that has a similar carbon skeleton to its precursor natural product compound (Simoneit 2005); it can therefore be traced back to its biogenic origin. Biomarkers can be used as tracers for geological (Ternois et al. 2001, Parnell et al. 2007) and environmental processes (Brincat et al. 2000, Otto et al. 2005), and may provide valuable
information about the past environments. The next section of this Introduction provides an overview of biomarker measurements and how they are used to study OM sources and stage of diagenesis.

1.2. Sources and diagenesis of organic matter using biomarkers

1.2.1. Sources of free and bound lipids

Various organisms have different biosynthetic pathways and anatomical structures, and the presence of a biomarker can therefore be traced back to their biogenic origin (Simoneit 2005). Straight-chain lipids, such as \( n \)-alkanes, \( n \)-alkanols, and \( n \)-alkanoic acids provide insight into possible OM sources (Eglinton and Hamilton 1967, Weete 1976). Specifically, odd-numbered long-chain (≥ \( C_{20} \)) \( n \)-alkanes and even-numbered long-chain \( n \)-alkanols and \( n \)-alkanoic acids are derived from leaf waxes and are therefore used as a biomarker of vascular plants (Eglinton and Hamilton 1967, Bianchi 1995, Otto et al. 2005). Odd-numbered mid-chain lipids with maximum at \( C_{23} \) and \( C_{25} \) originate from submerged/floating plants (Ficken et al. 2000) and Sphagnum mosses (Baas et al. 2000, Nott et al. 2000). Short-chain (< \( C_{20} \)) lipids, on the other hand, are indicative of microbial organisms (Weete 1976, Otto et al. 2005). That being said, \( n \)-alkanoic acids ranging between \( C_{12} \) and \( C_{18} \) have been shown to come from plants and microbes, so some biomarkers are not always organism-specific (Weete 1976, Harwood and Russell 1984). Additionally, compounds such as brassicasterol (Kanazawa et al. 1971), dinosterol (Shimizu et al. 1976), and long-chain (\( C_{37} \) to \( C_{39} \)) alkenones (Volkman et al. 1980) are found in only aquatic organisms and can be used as a tracer for aquatic OM sources.

Bound lipids are another class of compounds that can be obtained from sediment samples, and may provide information about the amount of OM input from cutin and suberin. Cutin is a leaf wax found in vascular plant cuticles (Holloway 1982, Otto and Simpson 2006b),
and suberin is found in vascular plant roots (Kolattukudy and Espelie 1989, Otto and Simpson 2006b). Suberin-derived OM is characterized by, for example, α,ω-alkanedioic acids and ω-hydroxyalkanoic acids ranging between C$_{20}$ and C$_{32}$ (Otto and Simpson 2006b). Cutin-derived OM, on the other hand, is characterized by hydroxyalkanoic acids with carbon lengths of C$_{14}$, C$_{15}$, and C$_{17}$ (Otto and Simpson 2006b).

1.2.2. Sources of lignin-derived phenols

Lignin is a polymer found in higher land plants and accounts for approximately one-third of woody biomass (Donaldson 2001). Lignin-derived phenols are a class of compounds that include: vanillyl (V), syringyl (S), and cinnamyl (C) monomers. Ratios of S/V and C/V have been used to identify the type of vascular plant from which the lignin originates (Hedges and Mann 1979). Lignin phenols comprised of V monomers (V = vanillin, acetovanillone, and vanillic acid) are believed to originate from gymnosperm wood, while lignin phenols that contain both V and S monomers (S = syringaldehyde, acetosyringone, and syringic acid) likely originate from angiosperm wood (Hedges and Mann 1979). The presence of C monomers (C = p-coumaric acid and ferulic acid) indicates that the lignin is of non-woody origin (Hedges and Mann 1979). As such, a plot of S/V versus C/V can separate vascular plant inputs into four distinct regimes (i.e. woody gymnosperms, woody angiosperms, non-woody gymnosperms, and non-woody angiosperms) and can be used to identify the botanical source of lignin in different samples (Figure 1.1).

1.2.3. Diagenesis of lignin-derived phenols

The degree of oxidation of lignin-derived phenols can also provide valuable information regarding the stage of diagenesis (Ertel and Hedges 1985, Hedges et al. 1988, Otto and Simpson 2006a). In particular, oxidation of vanillyl and syringyl aldehyde (Al) monomers to their
corresponding phenolic acid (Ad) monomers has been shown to increase with progressive biodegradation (ten Have and Teunissen 2001) and photo-oxidation of lignin (Feng et al. 2011). The degree to which oxidation has occurred serves as a degradation parameter (Ertel and Hedges 1985, Hedges et al. 1988, Opsahl and Benner 1995). Ad/Al ratios for vanillyl and syringyl monomers (denoted at (Ad/Al)v and (Ad/Al)s, respectively) for fresh angiosperms and conifer wood are typically around 0.1 to 0.2, while that for non-woody tissues are around 0.2 to 1.6 (Hedges and Mann 1979, Hedges et al. 1988, Otto and Simpson 2006a). In addition, Otto et al. (2006a) reported (Ad/Al) ratios of 0.2 to 0.5 and 0.8 to 4.2 for plant samples and soils, respectively, which is consistent with previous studies (Ertel and Hedges 1984, Ertel and Hedges 1985, Goni and Hedges 1992). Increased Ad/Al ratios in mineral horizons suggest that lignin is more degraded in mineral horizons than in organic horizons (Sanger et al. 1996). Lastly, in a study of North Atlantic Ocean sediments, (Ad/Al)v and (Ad/Al)s ranged from 0 to 10 and from 0.3 to 12, respectively (Xu et al. 2009). Therefore, stage of diagenesis has been shown to vary depending on age and the depositional environment.

1.3. Elucidation of paleoclimate and depositional events

Biomarker analysis has been shown to be useful in the elucidation of paleovegetation (Brincat et al. 2000). Brincat (2000) found that vegetation shifts from the Last Glacial Maximum (21 000 years ago) into the Holocene (12 000 years ago) were characterized by a shift in the distribution of n-alkanes. Sediments belonging to the Holocene were characterized by n-alkanes with a maximum at C27, which is indicative of forest vegetation, while those belonging to the Last Glacial Maximum were characterized by a maximum at C29, which is indicative of herbaceous vegetation (Brincat et al. 2000). Such a shift was corroborated by palynological analysis: pollen grain concentrations of present-day forest vegetation increased in sediment
belonging to the Holocene, confirming this shift in vegetation (Brincat et al. 2000). Biomarker compositions have also been shown to characterize geologic deposits. For instance, Canadian Arctic and Baffin Bay samples were characterized by higher relative concentrations of long (C_{28}) triaromatic steroids compared to short (C_{20} and C_{21}) counterparts, indicating less thermal maturity because long triaromatic steroids are more susceptible to alteration (Riolo et al. 1986, Parnell et al. 2007). On the other hand, the Greenland sample was characterized by lower relative concentrations of long to short triaromatic steroids, suggesting greater thermal maturity (Parnell et al. 2007). This study showed that the provenance of the Baffin Bay sample was from Canadian Arctic (Parnell et al. 2007). They further showed that sediment at Orphan Knoll (off the coast of Newfoundland) originated from northwest Greenland and that it was transported approximately 3000 km (Parnell et al. 2007). Marine sediments from Orphan Knoll were also analyzed by Xu et al. (2009), and it was shown that increased gymnosperm biomarkers were correlated with climate cooling between 958 000 – 840 000 years ago. Poor correlations with magnetic susceptibility and Gamma Ray Attenuation suggest that ice rafted and non-ice rafted debris from eastern Canada or even southern Greenland may both have transported terrigenous OM during the study period (Xu et al. 2009). Geologic processes may therefore be important in the transport and deposition of OM (Parnell et al. 2007).

It has also been shown that mineralogy may dictate the preservation of biomarkers (Marshall et al. 2009). Marshall et al. (2009) showed that deposits rich in black shale preserved OM derived from primary production from bacterial and algal sources. Carbonate-rich units, however, did not preserve this fresh OM and only n-alkanes were preserved (Marshall et al. 2009). The degree to which a biomarker analysis may be useful can be limited by the geologic processes taking place. For instance, Ternois (2001) showed that the concentration of n-alkanes,
n-alkanols, and n-alkanoic acids in marine sediments was elevated in glacial periods due to the erosion of sediment containing terrigenous OM and the transport of this material out to sea. On the other hand, these concentrations were lower in interglacial sediments (Ternois et al. 2001). The erosion and transport of sediment containing OM may also cause OM reincorporation (Meckler et al. 2008). The amount of OM reincorporation has been estimated based on the reincorporation of ancient palynomorphs (pollen grains, spores, etc; Meckler et al. 2008). If these ancient palynomorphs exist in younger sediment, the concentration will be a representation of the extent of OM reincorporation (Meckler et al. 2008).

1.4. Gas chromatography-mass spectrometry analysis of biomarkers

Gas chromatography-mass spectrometry (GC-MS) is the analytical workhorse of typical biomarker analyses (Simoneit 2005, Medeiros and Simoneit 2007). GC is a separation technique that separates gas phase compounds based on their respective adsorption to a stationary phase (Rohrschneider 1966, McReynolds 1970). By separating highly complex mixtures, one is able to analyze individual molecules provided that sufficient separation has been achieved. In GC, the mixture of compounds is volatilized to the gas phase and transported through the column by a gaseous mobile phase, such as hydrogen, helium, or nitrogen (Skoog et al. 2007). The speed that compounds travel through the column is dependent on the interaction between each analyte and the stationary phase. The chemical composition of a stationary phase dictates what analytes it is best at separating. For instance, a common stationary phase of poly(dimethylsiloxane) separates hydrocarbons, but the addition of a mere 5% diphenyl by composition to the stationary phase can increase the selectivity for aromatics (Skoog et al. 2007). Due to strong adsorption of polar compounds to the poly(5%-diphenyl-95%-dimethylsiloxane) stationary phase, the extract is derivatized to convert polar functional groups into compounds that are amenable to GC
A common derivatization is the conversion of reactive hydrogen atoms (e.g. attached to oxygen or nitrogen groups) to their trimethylsilyl derivatives using \(N,O\)-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine (Horning et al. 1969, Butts 1970, Otto et al. 2005). Stationary phases must be thermally stable in the temperature ranges used and be chemically inert (modification of the stationary phase must not occur throughout the course of an analysis; Skoog et al. 2007).

MS is a technique that identifies organic molecules (Pavia et al. 2009), and it can also be used as an analytical detector for trace level quantification (Woods et al. 2011). Molecules are ionized before they are introduced into the MS. There are different types of ion sources ranging from hard to soft. Hard sources may cause analyte molecules to break or fragment, whereas soft sources cause less fragmentation (Skoog et al. 2007). Electron ionization (EI) is an example of a hard source technique that is used commonly with GC-MS, while matrix-assisted laser desorption-ionization (MALDI) and electrospray ionization (ESI) are soft methods (Pavia et al. 2009). Quadrupole and time-of-flight (TOF) mass analyzers are both frequently used in MS. In EI with a quadrupole mass analyzer for example, gaseous molecules are ionized at the ion source. Ions are then accelerated between four parallel rods with a potential difference of 5 to 10 V (Skoog et al. 2007). Only ions with certain mass-to-charge ratios will pass to the ion transducer (where ions are converted to an electric signal), while other ions will be neutralized by the rods (Skoog et al. 2007). The electrical signal then allows total ion current (TIC) or selected ion monitoring (SIM) chromatograms to be obtained, but SIM has lower limits of detection and therefore increased sensitivity (Pavia et al. 2009).

The inherent limitation of a biomarker analysis is that only what is extracted, separated, and detected can be analyzed. Therefore, several extraction or chemolytic methods must be used
to target different classes of compounds. Solvent extraction, base hydrolysis, and CuO oxidation are all complementary techniques to one another because they extract different compounds (Hedges and Mann 1979, Otto et al. 2005, Otto and Simpson 2006b), but these three techniques do not represent all of the OM in a sample. For instance, to characterize fresh microbial inputs, phospholipid fatty acid analysis can also be performed (Frostegard and Baath 1996). After solvent extraction, base hydrolysis, and CuO oxidation, Otto and Simpson (2007) reported that 34.6 % of the soil OM was extracted, showing that such treatments only extract part of the total OM. Additionally, of the OM extracted, only the OM that travels the entire column will be detected. Compounds that are not volatilized or still adsorbed to the stationary phase at the end of the analysis will not be detected. For instance, it has been reported that the GC-MS response to OM equated to only 17 % of the extracted compounds being detected (Otto and Simpson 2007). Compounds are quantified by integrating the area under the chromatographic peak, and relating this area to the area and known concentration of a standard. The detection limits of GC-MS range in magnitude between ng to fg depending on the analytes response and type of MS instrument and operation mode (Simoneit 2005).

1.5. The geologic processes that give rise to the study areas

Glacial advances and retreats result in the formation of geologic deposits and landforms, as shown in the Hudson Bay Lowlands (HBL; Chapter 2) and the Oak Ridges Moraine (ORM; Chapter 3). Glacial advances erode and transport pre-existing sediment and sediment is deposited subglacially, i.e. under the ice as till (Figure 1.2; Menzies and Shilts 2002). Additionally, sediment can be deposited in a glaciolacustrine environment, whereby glacial sediment is deposited on the lake floor. Knowing the stratigraphy (layering) of glacial deposits is key to hydrostratigraphic assessments for quantitative hydrogeological modeling (e.g. Howard
et al. 1995, Gerber and Howard 2002, Meriano et al. 2009, Eyles and Meriano 2010). Furthermore, the stratigraphy provides information for reconstructions of depositional settings and paleoclimate (Boyce and Eyles 2000).

1.5.1. The Hudson Bay Lowlands (Chapter 2)

The importance of understanding and identifying stratigraphic units on the regional scale in the HBL arises from two principal concerns. During the Last Glacial Maximum (~ 22 000 years ago; Mix et al. 2001), the HBL was at the geographic centre of the three kilometer thick Laurentide Ice Sheet (Dyke et al. 1989). By identifying and relating different deposits of this region with their respective ages, it may be possible to gain further understanding of glacial advances and retreats in the region. The resulting stratigraphy can then be traced back to depositional processes and to the climate at the time of deposition. This knowledge may help explain glacial processes in the HBL and elsewhere under the Laurentide Ice Sheet. From a more economic standpoint, it is important to understand this region because it is home to economic deposits, such as diamonds (Janse and Sheahan 1995). Being able to identify different deposits, and relating these deposits with the same deposit located elsewhere (on the regional scale) may lead to more specific and cost-effective exploration (i.e. if diamonds are found in a particular deposit, then they may be found in the same deposit, but at a different geographic location). The number and ages of deposits in the HBL relating to glacial and deglacial events over the last 100 000 years is under debate (Thorleifson et al. 1992). In a study conducted by Shilts (1982), it was noted that there could be as many as seven tills and six interglacial cycles. A decade later, it was suggested that two of the tills were of pre-Sangamon origin (deposited prior to Oxygen Isotope Stage 5e), and two or three tills were of post-Sangamon (see Thorleifson et al. 1992 for a major review). Techniques used have either resulted in nonfinite ages
radiocarbon dating on peat, marine shells, etc) or unrealistic reconstructions of previous geologic events (Thorleifson et al. 1992, Allard et al. 2012). In the HBL study (Chapter 2), three post-Sangamon tills were selected and analyzed: the Severn, Sachigo, and Rocksand tills, which are of late to early Wisconsin origin (Figure 1.3; Dyke 2004, Stokes et al. 2012).

1.5.2. The Oak Ridges Moraine (Chapter 3)

The ORM is another very important geologic setting, but for a much different reason than the HBL. The stratigraphy, or layering, of the ORM is of great importance to residents of south-central Ontario because the ORM dictates groundwater flow behaviours in the region (Howard et al. 1995). Identifying and relating the stratigraphic units found in the ORM with their respective ages will help to understand the hydrogeologic role of the ORM and to identify environmentally sensitive areas (Howard et al. 1995, Meriano et al. 2009, Eyles and Meriano 2010). The layers range in age from approximately 12,500 to 135,000 years of age and reach depths of approximately 300 metres below ground surface (See Figure 1.4; Eyles 2002, Eyles 2004). The stratigraphy of the ORM is important to understand because the deposits range in porosity and therefore permeability of water (Sharpe et al. 1999, Meriano et al. 2009). These deposits, therefore, dictate groundwater flow behaviours in the region based on the relative sequencing of aquifers (rock with high permeability allowing water to flow) and aquitards (rock with low permeability preventing water to flow). Deposits such as the ORM sediment (also known as the Oak Ridges Aquifer Complex), Thorncliffe Formation, and Scarborough Formation are more permeable (Figure 1.4), so they allow groundwater and any contaminants contained therein to be transported more readily (Howard et al. 1995, Boyce and Eyles 2000, Meriano et al. 2009). Deposits such as Halton Till and Sunnybrook Formation are less permeable, and so, they hinder groundwater movement acting as aquitards. The layering of these deposits, whether the deposit
be an aquifer or aquitard, dictate groundwater movement and velocity. A thorough understanding of the hydrostratigraphy of the ORM is essential for land use planning and well head protection.

1.6. Objectives of this study

Current geologic approaches to identifying and characterizing stratigraphic units in the HBL and ORM have led to poor regional identification of stratigraphic units in both cases (Kassenaar and Wexler 2006, Allard et al. 2012). These regions are important for reasons ranging from academic, economic, and public policy pursuits. In an attempt to identify geologic deposits across the HBL and ORM, biomarker analyses were conducted on glacial sediment samples to identify OM sources and stage of diagenesis. Differences in OM compositions are a reflection of different vegetation and depositional environments and we therefore hypothesize that such compositions can be used to identify a particular deposit. It is therefore suggested that OM composition may provide a fingerprint for each geologic deposit. The objective of these two studies was to characterize the OM found within subsurface geologic deposits; specifically, the purpose of this thesis was to:

1. Determine the OM composition and stages of diagenesis of three samples from specific sites in the HBL, belonging to three known deposits. The OM composition is a reflection of the types of organisms present at the time of deposition and the stage of diagenesis should be, in part, a reflection of the age of each deposit. We hypothesize that OM should therefore be able to differentiate the three deposits based on paleoenvironments.

2. Characterize ten different deposits from the ORM on the basis of OM composition and stage of diagenesis. The OM composition and stage of diagenesis should be useful in
fingerprinting different deposits (we hypothesize that one deposit should have the same OM inputs and be in the same stage of diagenesis irrespective of its location and depth). This fingerprint should then be able to locally and regionally identify deposits over the study area, providing insight into the stratigraphy of the ORM.

To accomplish these objectives, three samples from the HBL were subjected to solvent extraction, base hydrolysis, and CuO oxidation. Extracts were subsequently identified and quantified using GC-MS to differentiate OM sources and stage of diagenesis. These results are found in Chapter 2. Forty-nine samples from the ORM were then subjected to solvent extraction and CuO oxidation and were also analyzed through GC-MS. These results are found in Chapter 3. The overall goal of this thesis is to determine the validity of using OM biomarkers as a tool for characterizing different stratigraphic units in glacial deposits.
1.7. References


Eyles, N. 2004. Toronto rocks. Fitzhenry & Whiteside Limited, Markham, ON.

Eyles, N. 2002. Ontario rocks: three billion years of environmental change. Fitzhenry & Whiteside Limited, Markham, ON.


1.8. Figures

Figure 1.1. Plot of syringyl/vanillyl (S/V) versus cinnamyl/vanillyl (C/V) showing separation of different vascular plant inputs: wa = woody angiosperm, a = non-woody angiosperm, wg = woody gymnosperm, g = non-woody gymnosperm. Modified from Hedges and Mann (1979).
Figure 1.2. Glacial processes involved in the erosion, transport, and deposition of sediment.
Figure 1.3. Stratigraphic column for the major Hudson Bay Lowland tills.
Figure 1.4. Stratigraphic units of the Oak Ridges Moraine, Southern Ontario, and their corresponding ages. Modified from Eyles (2002).
Chapter 2: Biomarker analysis of glacial tills from the Hudson Bay Lowlands, Canada: An elucidation of depositional environments

2.1. Abstract

The Hudson Bay Lowlands (HBL) is the world’s third largest wetland and is home to a wealth of economic deposits. During the Last Glacial Maximum, approximately 22,000 years ago, the HBL was at the geographic centre of the three kilometer thick Laurentide Ice Sheet. The stratigraphy of this region has not yet been fully delineated because of a poor understanding of glacial tills with their respective ages, and ice flow directions leading to uncertainty in the dynamics of the Laurentide Ice Sheet. Here, organic geochemical biomarkers are used to analyze the organic matter (OM) source and stage of diagenesis in three HBL glacial tills of late (Sachigo and Severn) to early Wisconsin age (Rocksand). Solvent extraction, base hydrolysis, and cupric oxide oxidation were performed to isolate and quantify free lipids, bound lipids, and lignin-derived phenols, respectively. Lipid biomarker patterns reflect higher Sphagnum-derived inputs to the Severn and Rocksand tills relative to the Sachigo till. Furthermore, the Severn till contained the most suberin-derived OM, while the Sachigo till had the least. Lastly, the OM within the Severn till is dominated by inputs from non-woody gymnosperms and non-woody angiosperms, whereas Sachigo and Rocksand tills show inputs from both woody and non-woody gymnosperms and angiosperms. Acid-to-aldehyde ratios of lignin-derived phenols suggest that the Severn till has undergone less diagenesis in comparison to Sachigo and Rocksand. Overall, the biomarkers relate to the global paleoclimate and depositional environments of the three tills.

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1 Samples were collected by Nick Eyles. Laboratory work and calculations were performed by Pui Sai Lau. Data analysis was conducted by Nicholas M. Battram and Myrna J. Simpson. This chapter was written by Nicholas M. Battram, Nick Eyles, and Myrna J. Simpson.
The results of this study suggest that biomarkers are able to differentiate the OM within three glacial tills and this may provide greater resolution to the current understanding of the HBL stratigraphy.

2.2. Introduction

Successive glacial advances and retreats may dictate the stratigraphy of many regions (Barrie and Conway 1999). The Hudson Bay Lowlands (HBL) is the world’s third largest wetland (Riley 1982) and is the result of these glacial advances and retreats (Thorleifson et al. 1992, Allard et al. 2012). The Laurentide Ice Sheet covered approximately $12.6 \times 10^6 \text{ km}^2$ of North America (Andrews et al. 1983), and the HBL is at the geographic centre of this former ice sheet (Dyke et al. 1989, Thorleifson et al. 1992, Dyke 2004). Understanding of the dynamics of the ice sheet is still constrained by a lack of knowledge of the regional glacial stratigraphy which reflects a complex relationship between ice flowing from opposing source areas in Keewatin and Quebec-Labrador (Thorleifson et al. 1992). As a consequence, the changing dynamics of the ice sheet and the relationship with paleoclimate records from the Arctic and North Atlantic oceans is debated with several opposing models (Thorleifson et al. 1992; Kleman et al. 2010; Allard et al. 2012; Stokes et al. 2012). This uncertainty has a direct economic impact in Canada as it limits the attractiveness of the HBL for mineral exploration programs in areas of thick glacial sediments containing multiple tills of unknown age and affinity, despite the presence of known kimberlite pipes (diamonds; Janse and Sheahan 1995) for example.

Lack of agreement as to the Wisconsin glacial history of the HBL is a major data gap in understanding of the Laurentide Ice Sheet which is of global significance given that it was the dominant control on eustatic sea levels during the 100 000 year duration of the last glacial cycle. Tills are exposed in a restricted number of outcrops along prominent river exposures and are
differentiated on the basis of different ice flow directions indicated by clast fabric analyses, the orientation of surface landforms such as flutes (Boulton and Clark 1990), striations (mainly on bedrock along the east coast of Hudson Bay; Veillette et al. 1999) together with analysis of amino acids (isoleucine epimerization) which provides a measure of diagenesis and thus age (see Thorleifson et al. 1992 for a major review). Major limitations are imposed by uncertainty surrounding precisely what till unit is being sampled in exposures and core, at sites distant from specific well-studied type sections. Moreover, all tills are found superposed stratigraphically i.e., the Severn rests on Sachigo which in turn rests on the Rocksand suggesting some degree of cannibalization has occurred resulting in textural and perhaps geochemical overlap between the tills. $^{230}$Th/U dating of wood and a thermoluminescence study of marine sediments suggests the HBL was ice free during the last interglacial which ended at about 100 000 years ago (Forman et al. 1987; Allard et al. 2012). An early phase of ice sheet growth is variably dated to early Wisconsin Oxygen Isotope Stages (OIS) 5b or 4 (Kleman et al. 2010) or earlier during OIS 5d at about 110 000 years ago (Stokes et al. 2012). Early ice is thought to have flowed northwestward across Hudson Bay and James Bay from Quebec and Labrador but according to some the resulting till (the Rocksand till) may in fact be younger (Kleman et al. 2010). Subsequent later Wisconsin ice flows (OIS 3, 2) recorded by the Sachigo and Severn tills rotated in direction anticlockwise toward the southwest, south and eventually southeast during the Last Glacial Maximum (~ 22 000 years ago; Dyke et al. 1989, Mix et al. 2001) possibly indicating the increasing influence of ice moving eastward from the Keewatin sector (Dyke 2004) thereby displacing Quebec and Labrador ice southwards depositing the Sachigo and Severn tills. This is suggestive of what is now known as ‘flow switching’ of component ice streams within the ice sheet (e.g., Greenwood et al. 2012; Winsborrow et al. 2012). A major uncertainty is the configuration of this sector of the ice sheet after deposition of the Rocksand till i.e., during the
mid-Wisconsin. Amino acid analysis of reworked marine shell fragments in tills and other sediments suggest that the HBL may have experienced a mid-Wisconsin deglacial episode at around 35 000 years ago (Andrews et al. 1983) and other ice-free episodes are depicted in the model of Kleman et al. (2010) during OIS 5 and OIS 3 at about 80 000 and 60 000 years ago, respectively. Stokes et al. (2012), on the other hand, identified a single ice free episode at 80 000 years ago followed by almost continued growth of the ice sheet. It is possible that Keewatin and Labrador ice masses were not confluent then and at other times allowing brief deglacial phases in the HBL and local flooding by marine waters. The central challenge in both paleoenvironmental analysis and mineral exploration is to differentiate tills in outcrop and core which are known to contain much reworked sediment and thus overlap in their physical properties. However, whereas incorporation of older material in tills is a problem in lithostratigraphic analyses, it may also ultimately provide a geochemical means of discriminating these tills based on their varying organic matter (OM) content.

Organic geochemical analysis using biomarkers have been used to gain insight into past depositional environments (Brincat et al. 2000, Ternois et al. 2001), but to the best of our knowledge, has yet to be applied to sediments from the HBL. An OM biomarker is an organic compound that can be traced back to its biogenic origin due to the preservation of the carbon skeleton of the natural product precursor compound (Simoneit 2005). Biomarker studies have been able to examine the organic geochemistry of glacial sediments (Brincat et al. 2000, Parnell et al. 2007, Marshall et al. 2009). For instance, one study on glacial sediments from a Lake Baikal core showed an increase in the ratio of C$_{27}$ to C$_{31}$ $n$-alkanes, derived specifically from forest and herbaceous vegetation, respectively (Brincat et al. 2000). This shift was attributed to a change in vegetation patterns from herbaceous to forest dominated as the temperature rose from
the Last Glacial Maximum (Brincat et al. 2000) into the Holocene (~ 12 000 years ago; Dyke 2004, Tornqvist and Hijma 2012). This biomarker shift was also corroborated by an increase in the concentration of pollen grains of present-day forest vegetation (Brincat et al. 2000). Changes in depositional environments and paleoclimate have also been elucidated using OM biomarkers. Increased concentrations of terrigenous \( n \)-alkanes, \( n \)-alkanols, and \( n \)-alkanoic acids have been detected in marine sediments from a core taken from the Sea of Okhotsk corresponding to glacial periods due to the erosion and transport of terrigenous OM by ice in the winter (and melting in the summer), in addition to atmospheric circulation (Ternois et al. 2001). A study of the São Francisco Craton showed that bacterial and algal biomarkers in samples rich in black shale were preserved due to rapid remineralization (as suggested by the presence of glendonite) of these biomarkers; in carbonate-rich samples however, such biomarkers were not preserved and only \( n \)-alkanes were preserved (Marshall et al. 2009). This suggests that the mineralogy of a sample may be important in OM protection and preservation (Marshall et al. 2009). Another study was able to successfully resolve Baffin Bay and Canadian Arctic samples from Greenland samples (Parnell et al. 2007). Baffin Bay and Canadian Arctic samples were characterized by higher relative concentrations of long (C\(_{28}\)) triaromatic steroids, indicating less thermal maturity compared to the Greenland samples (Parnell et al. 2007). Long triaromatic steroids are more susceptible to alteration than their short (C\(_{20}\) and C\(_{21}\)) counterparts which results in an increase in the relative concentration of short triaromatic steroids with increased maturity (Riolo et al. 1986, Parnell et al. 2007). Collectively, these studies have been able to resolve different OM inputs in terms of location, age, and even paleoclimate (Brincat et al. 2000, Ternois et al. 2001, Parnell et al. 2007), and such an approach may hold valuable clues as to the history of the HBL. Hence, the objective of this study was to characterize the biomarker compositions of three tills representing major depositional episodes within the HBL region. The three glacial tills studied
were Sachigo (late Wisconsin), Severn (youngest; late Wisconsin), and Rocksand (oldest; early Wisconsin). Solvent extraction and chemolytic methods were performed to release free and bound lipids, as well as to release any lignin-derived phenols from within the sample (Otto et al. 2005). Free lipids provide information regarding the inputs from microbial (Weete 1976) and plant sources of OM (Eglinton and Hamilton 1967, Tulloch 1976), in addition to OM degradation proxies (Zhu et al. 2011). Bound lipids provide information on suberin- (from roots and bark) and cutin-derived (from leaf cuticles) OM from vascular plants (Otto and Simpson 2006b). Lastly, lignin-derived phenols allow woody and non-woody sources and angiosperm and gymnosperm sources to be differentiated (Hedges and Mann 1979) and provide insight about the stage of diagenesis (Ertel and Hedges 1985). The overall goal is to determine if biomarker signatures can be used to differentiate different till types within the HBL.

2.3. Methods

2.3.1. Sampling and carbon analysis

Three samples were collected from different sites within the HBL (Figure 2.1). A sample from the Sachigo till was collected from the east bank of Gods River (56° 09’ 25.12” N 92° 29’ 23.68” W) and is thought to be of late Wisconsin age (Stokes et al. 2012). A sample from the Severn till was collected from the south bank of the Niskibi River (56° 13’ 01.78” N 88° 51’ 46.57” W) and is believed to be the youngest of the three tills and of late Wisconsin age (Dyke 2004, Stokes et al. 2012). Lastly, a sample from the Rocksand till was collected from the west bank of the Severn River (54° 58’ 16.77” N 88° 58’ 30.92” W) and is the oldest of the three samples and of early Wisconsin age (Stokes et al. 2012). The samples were obtained from beneath the surface of unweathered material and there are no indications of recent OM inputs.
Carbon content was determined using a LECO SC-444 (University of Guelph, Guelph, Ontario, Canada). Organic carbon (OC) contents of the Sachigo, Severn, and Rocksand samples were found to be 0.21 %, 0.35 %, and 0.16 %, while inorganic carbon contents were found to be 4.84 %, 5.75 %, and 3.64 %, respectively.

2.3.2. Organic matter biomarker extraction and quantification

Solvent extraction was used to isolate free (unbound) compounds (Otto et al. 2005). Samples (~ 20 g) were sequentially sonicated for 15 min in 15 mL of three different solvents of varying polarity: (i) dichloromethane (DCM), (ii) DCM/methanol (MeOH) (1:1; v/v), and (iii) MeOH. Samples were centrifuged and supernatants collected. Combined extracts were filtered, concentrated by rotary evaporation, and dried under nitrogen in glass vials. Following solvent extraction, non-polar and polar compounds were separated by column chromatography (Feng et al. 2010). Dried extracts were dissolved in n-hexane and loaded onto a silicic acid column. Following the addition of n-hexane to elute non-polar compounds, DCM:MeOH (1:1; v/v) was added to the column to elute polar compounds. Eluted fractions were dried under nitrogen in glass vials.

Base hydrolysis was performed on the air-dried soil residues from the solvent extraction stage (Otto and Simpson 2006b). Samples (~ 6 g) were refluxed with 20 mL of 1 M methanolic KOH for 3 hrs. After cooling, the supernatants were collected, while the remaining residues were sonicated twice in DCM/MeOH (1:1; v/v). The combined supernatants were centrifuged, and the supernatants were acidified to pH 1, followed by concentration by rotary evaporation. Distilled water was added to the extracts, and a liquid–liquid extraction with diethyl ether was then performed. The ether phase was dried with anhydrous Na₂SO₄. Extracts were concentrated by rotary evaporation and dried under nitrogen in glass vials.
Cupric oxide (CuO) oxidation was performed on the air-dried residues from the base hydrolysis stage (Hedges and Ertel 1982, Otto and Simpson 2006a). Teflon-lined bombs were loaded with each sample (~ 6 g), 1 g DCM-rinsed CuO, 100 mg ammonium iron (II) sulfate hexahydrate [Fe(NH$_4$)$_2$(SO$_4$)$_2$•6H$_2$O], and 15 mL 2 M NaOH. The headspace was purged with nitrogen, and the bombs were heated to 170 °C for 2.5 hrs. The supernatants were collected, and the remaining solids were washed twice with distilled water. The supernatants and washes were combined and centrifuged. The new supernatants were decanted and acidified to pH 1. They were then left in the dark for an hour to avoid the polymerization of cinnamic acids. Samples were then centrifuged, and the supernatants were liquid-liquid extracted with diethyl ether. The combined ether phases were dried with Na$_2$SO$_4$, concentrated by rotary evaporation, and dried under nitrogen in glass vials.

Prior to identification and quantification using gas chromatography – mass spectrometry (GC-MS), solvent extracts and CuO oxidation products were converted to their trimethylsilyl (TMS) derivatives using N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine at 70 °C for 1.5 hrs. The base hydrolysis extracts were derivatized with diazomethane in ether at 40 °C, followed by derivatization with BSTFA and pyridine.

GC-MS analysis was performed on an Agilent model 6890N GC coupled to an Agilent model 5973 quadrupole mass selective detector (Otto et al. 2005). Separation was achieved on a HP-5MS fused-silica capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness) with He as the carrier gas. The oven was held at 65°C for 2 min, and then the temperature was increased to 300°C at a rate of 6°C/min, with a final isothermal hold at 300°C for 20 min. 2μL of each sample was injected in splitless mode at an injection temperature of 280°C using an Agilent 7683 autosampler. The mass spectrometer was operated in electron ionization (EI) mode at 70 eV and
scanned from 50 to 650 Da. Data was processed using Agilent Chemstation G1701DA software, and compounds were identified by comparison of mass spectra to commercial mass spectral libraries and standard compounds. Perdeuterated tetracosane (C\textsubscript{24}D\textsubscript{50}), oleic acid (TMS), and ergosterol (TMS) were used as external standards for solvent extraction, while oleic acid (methylated and/or TMS) was used for base hydrolysis, and vanillic acid (TMS) for CuO oxidation. These biomarker methods have been shown to detect as much as 5% of the total OC in a soil sample with ~10% relative standard error (Otto and Simpson 2007). Duplicate analysis of CuO oxidation products with HBL samples was found to be ~14% or less and is consistent with previous studies with soil OM (Otto and Simpson 2007).

2.4. Results and discussion

2.4.1. Composition and sources of solvent extractable aliphatic compounds

Solvent extractable biomarkers may identify OM sources from microbial (Weete 1976, Otto et al. 2005) and plant sources (Eglinton and Hamilton 1967, Otto et al. 2005). The combined solvent extractable lipids of the three tills contained primarily: \textit{n}-alkanes, \textit{n}-alkanols, and \textit{n}-alkanoic acids of various carbon lengths (Table 2.1), which is consistent with both microbial and plant sources. Aquatic (lacustrine and/or marine) biomarkers, such as brassicasterol (Kanazawa et al. 1971, Ternois et al. 2001), dinosterol (Shimizu et al. 1976), and long-chain (C\textsubscript{37}-C\textsubscript{39}) alkenones (Volkman et al. 1980) were not detected, even though suggested ice flow directions come from Hudson Bay and James Bay and reincorporation of aquatic biomarkers was expected (Dyke et al. 1982, Fisher et al. 1985, Menzies et al. 2012). The total \textit{n}-alkane concentration was highest for the Sachigo till, followed by Severn and Rocksand (Table 2.1). The Carbon Preference Index (CPI) is a parameter used for the preservation of OM (Meyers and Ishiwatari 1993). The CPI for \textit{n}-alkanes (CPI\textsubscript{alk}) is a measure of the specificity for
odd-numbered \(n\)-alkanes compared to even-numbered, and as the \(n\)-alkanes undergo diagenesis, this specificity is decreased, resulting in a lower \(\text{CPI}_{\text{alk}}\) value (Meyers and Ishiwatari 1993). The \(\text{CPI}_{\text{alk}}\) was 1.37 for Sachigo, 3.23 for Severn, and 4.37 for Rocksand (Table 2.1). These values do not correspond with the proposed ages of these tills and may be due to the variation in the types of alkanes observed. Differences in the \(n\)-alkane distribution (Eglinton and Hamilton 1967, Nott et al. 2000) may reflect varying sources of OM to sediments. For example, the \(n\)-alkane distribution ranged from \(C_{22}\) to \(C_{35}\) at Sachigo and from \(C_{21}\) to \(C_{33}\) at Severn and Rocksand. Exclusively long-chain (\(\geq C_{20}\)) \(n\)-alkanes were detected across all three sites suggesting inputs from vascular plants (Eglinton and Hamilton 1967, Bianchi 1995, Otto et al. 2005). Vascular plants are characterized by the abundance of long-chain \(n\)-alkanes with maxima (\(C_{\text{max}}\)) at \(C_{27}\), \(C_{29}\), and \(C_{31}\) (Eglinton and Hamilton 1967). The \(C_{\text{max}}\) for the three tills was \(C_{27}\) and is consistent with inputs from vascular plants. Submerged and/or floating plants (Ficken et al. 2000) and \textit{Sphagnum} mosses (Baas et al. 2000, Nott et al. 2000) are characterized by mid-chain \(n\)-alkanes with \(C_{\text{max}}\) at \(C_{23}\) and \(C_{25}\). \textit{Sphagnum} mosses are known to be a principal contributor to \textit{Sphagnum}-dominated peat (Ficken et al. 1998, Baas et al. 2000, Nott et al. 2000, Nichols et al. 2006, Xu et al. 2010, Schellekens and Buurman 2011). Ice flow comes from Hudson Bay and James Bay (Menzies et al. 2012, Dyke et al. 1982, Fisher et al. 1985), but the lack of biomarkers that are indicative of aquatic sources suggests that \textit{Sphagnum} may be a more likely source of the observed \(C_{23}\) \(n\)-alkanes. Alternatively, it is possible that aquatic biomarker concentrations were below detection limits or they were simply not preserved within the stratigraphic record (Marshall et al. 2009). The proxy, \(C_{23}/(C_{23} + C_{29})\) has been used to examine the relative inputs from \textit{Sphagnum} (\(C_{23}\)) in relation to vascular plants (\(C_{29}\); Nichols et al. 2006, Schellekens and Buurman 2011). The \(C_{23}/(C_{23} + C_{29})\) ratio for the Sachigo till is 0.20, while Severn and Rocksand tills have ratios of 0.44 and 0.40 respectively, suggesting higher relative inputs from
Sphagnum-derived OM at the time of deposition at both Severn and Rocksand tills. Other \( n \)-alkane parameters were tested but provided little insight in differentiating the tills (Table 2.1). Such parameters have been shown to differentiate between grass/broad leaf- and conifer-derived OM (\( C_{29}/C_{27} + C_{29} + C_{31} \); Lei et al. 2010) and between grass and tree tissues (\( C_{31}/C_{29} \); Schwark et al. 2002, Bai et al. 2009).

The total \( n \)-alkanol concentration was highest at Rocksand, followed by Severn and Sachigo (Table 2.1). Short-chain \( n \)-alkanols (< \( C_{20} \)) typically originate from microbial sources (Weete 1976) and long-chain \( n \)-alkanols (\( \geq C_{20} \)) from vascular plants (Tulloch 1976, Bianchi 1995). The \( n \)-alkanol distribution ranged from \( C_{16} \) to \( C_{30} \) in each till, and the \( C_{\text{max}} \) was \( C_{28} \) in the Sachigo and Severn tills, while it was \( C_{22} \) in the Rocksand till, further supporting high inputs from vascular plants. The total quantity of short-chain \( n \)-alkanols was lowest for the Severn till, and was higher for the Sachigo and Rocksand tills. As such, these short-chain \( n \)-alkanol microbial biomarkers were likely preserved from the time of deposition as it is unlikely that microbial activity was high after deposition due to the depth and lack of nutrients in the tills.

The total \( n \)-alkanoic acid concentration was highest for Sachigo, followed by Rocksand and Severn (Table 2.1). Like \( n \)-alkanols, short-chain \( n \)-alkanoic acids (< \( C_{20} \)) typically originate from microbial sources (Weete 1976) and long-chain \( n \)-alkanoic acids (\( \geq C_{20} \)) from vascular plants (Tulloch 1976, Bianchi 1995). Carbon lengths ranged from \( C_{12} \) to \( C_{24} \) at Sachigo, from \( C_{12} \) to \( C_{22} \) at Severn, and from \( C_{12} \) to \( C_{20} \) at Rocksand; additionally, the \( C_{\text{max}} \) was \( C_{16} \) at all three sites, indicating possible microbial inputs. The CPI for \( n \)-alkanoic acids (\( \text{CPI}_{\text{aoic}} \)) shows the specificity for even-numbered \( n \)-alkanoic acids at each site: \( n \)-alkanoic acids are more reactive than their \( n \)-alkane and \( n \)-alkanol counterparts, and as they undergo diagenesis, their specificity for even-numbered chain lengths are decreased, resulting in lower \( \text{CPI}_{\text{aoic}} \) values (Meyers and
Ishiwatari 1993). The CPI$_{\text{aoic}}$ was 18.6 at Sachigo, 24.0 at Severn, and 13.2 at Rocksand. This suggests that Severn (youngest; late Wisconsin) is the least altered because it has the highest specificity for even-numbered $n$-alkanoic acids, while Rocksand (oldest; early Wisconsin) has the lowest value, 13.2, indicating that it is more diagenetically altered.

2.4.2. Composition and sources of bound lipids

Bound lipids serve as useful biomarkers for vascular plants, specifically from suberin (roots and bark) and cutin (leaf cuticles; Otto and Simpson 2006b). The base hydrolysis extracts contained $\alpha,\omega$-alkanedioic acids and $\omega$-hydroxyalkanoic acids (Table 2.2). $\alpha,\omega$-Alkanedioic acids and $\omega$-hydroxyalkanoic acids ranging between $C_{20}$ and $C_{32}$ originate from suberin, which is a biopolymer found in the roots of vascular plants (Kolattukudy and Espelie 1989, Otto and Simpson 2006b). The lowest total $\alpha,\omega$-alkanedioic acid concentration was observed at Sachigo, while the highest was observed at Severn. $\alpha,\omega$-Alkanedioic acids ranged between $C_{24}$ and $C_{28}$ at each site with exclusively even-numbered chain lengths present, indicating inputs from suberin (Kolattukudy and Espelie 1989, Otto and Simpson 2006b). $\omega$-Hydroxyalkanoic acids ranged from $C_{16}$ to $C_{28}$ at Sachigo and Severn and from $C_{12}$ to $C_{28}$ at Rocksand and in both cases compounds were exclusively even-numbered. However, only $\omega$-hydroxyalkanoic acids ranging between $C_{20}$ and $C_{28}$ are indicative of suberin inputs (Kolattukudy and Espelie 1989, Otto and Simpson 2006b). The $\alpha,\omega$-alkanedioic acids and $\omega$-hydroxyalkanoic acids suggest that higher suberin inputs were observed at Severn, while decreasing inputs were observed at Rocksand and Sachigo, respectively. Cutin, on the other hand, is a polymeric wax found in leaf cuticles (Holloway 1982, Otto and Simpson 2006b). $\omega$-Hydroxyalkanoic acids ranging between $C_{16}$ and $C_{18}$ are indicative of suberin- or cutin-derived OM (Otto and Simpson 2006b). OM inputs originating from either suberin or cutin were low at Sachigo and Severn, while such inputs were
more significant at Rocksand. The lack of cutin-derived OM at these sites may be due to low inputs at the time of deposition or from the degradation of cutin (Otto and Simpson 2006b). In fact, suberin is believed to be more resistant to degradation compared to cutin (Kolattukudy 1981, Nierop and Verstraten 2003, Otto and Simpson 2006b).

2.4.3. Composition, sources, and diagenesis of CuO oxidation products

CuO oxidation products serve as biomarkers for different vascular plant classes, i.e. woody versus non-woody tissues and gymnosperm versus angiosperm sources (Hedges and Mann 1979, Otto and Simpson 2006a). The lignin monomers obtained with CuO oxidation can be grouped into three classes of compounds to illustrate further differences between the three glacial tills: vanillyl (vanillic acid, vanillin, and acetovanillone), syringyl (syringic acid, syringaldehyde, and acetosyringone), and cinnamyl units (p-coumaric acid and ferulic acid; Figure 2.2a). The vanillyl monomers were the most abundant units at all of the sites sampled. This may be the result of an accumulation of vanillyl monomers, as they have been shown to be more resistant to biodegradation compared to syringyl and cinnamyl monomers (Hedges et al. 1988, Goñi et al. 1993). By plotting the ratio of syringyl units to vanillyl units (S/V; Figure 2.2b) and cinnamyl units to vanillyl units (C/V), OM originating from angiosperm and gymnosperm and from woody and non-woody sources can be separated into four separate regions (Hedges and Mann 1979). The CuO oxidation results (Figure 2.2b) suggest that the lignin-derived phenols in the Severn sample originate from a mixture of non-woody angiosperms and gymnosperms. Sachigo and Rocksand, however, received OM inputs from a mixture of sources, i.e. woody and non-woody tissues of both angiosperms and gymnosperms.

Lignin-derived phenols also provide insight into the stage of OM diagenesis. Over time, aldehyde functional groups are oxidized to carboxylic acids (ten Have and Teunissen 2001) and a
ratio of the acid-to-aldehyde (Ad/Al) is often used as a degradation parameter (Ertel and Hedges 1985, Hedges et al. 1988, Opsahl and Benner 1995). There was a discrepancy between the Ad/Al ratios of vanillyl [(Ad/Al)\textsubscript{v}] and syringyl [(Ad/Al)\textsubscript{s}] monomers: specifically, Sachigo and Rocksand have higher (Ad/Al)\textsubscript{v} ratios than Severn but lower (Ad/Al)\textsubscript{s} ratios (Figure 2.2c). Vanillyl monomers, however, are more resistant to oxidation (Hedges et al. 1988, Opsahl and Benner 1995) and are more consistent with the ages of the tills. Severn has the lowest (Ad/Al)\textsubscript{v} ratio, suggesting preservation of vanillyl units at this site; Severn is thought to be the youngest till and is of late Wisconsin age. The lignin in the Sachigo and Rocksand tills, however, is at an advanced stage of oxidation and diagenesis which is consistent with late and early Wisconsin origins, respectively.

2.5. Implications for organic matter fingerprinting using biomarkers

The biomarkers observed in this study show differences in OM composition between the three tills and are consistent with environmental conditions at the time of deposition. The \textit{n}-alkane data suggests that \textit{Sphagnum} inputs vary between locations; specifically, the Severn and Rocksand tills received more relative \textit{Sphagnum} inputs compared to the Sachigo till. Increased \textit{Sphagnum} inputs to the Rocksand till coincide with warmer temperatures during the Sangamon interglacial period (OIS 5e; Petit et al. 1999, Stuiver and Grootes 2000), and possibly increased primary productivity of organisms (Dorrepaal et al. 2004, Gunnarsson 2005, Breeuwer et al. 2008) prior to incorporation of sediment within the Rocksand till (Table 2.3). Severn was deposited in the late Wisconsin, and as this till was being deposited, it could have reincorporated sediment and OM from the Rocksand till, leading to an elevated \textit{Sphagnum} parameter as well. Sachigo was deposited following colder conditions earlier in the late Wisconsin (Stokes et al.
It therefore follows that the climate in the time leading up to deposition of Sachigo may have been too cold for \textit{Sphagnum} to be as productive in the region (Table 2.3).

Suberin-derived OM concentrations appear to follow this same trend: the Severn till contained the most suberin-derived material, which may have resulted from the migration of vascular plant species northward into the study area as the Laurentide Ice Sheet retreated during periods of warmer temperatures (Webb et al. 2004). This likely led to increased vascular plant inputs and subsequent preservation. Suberin is hypothesized to be more resistant to biodegradation than cutin in the environment (Kolattukudy 1981, Nierop and Verstraten 2003, Otto and Simpson 2006b) which may explain the observed trends in this study. The Rocksand till also had a higher concentration of suberin compared to Sachigo. Based on the lignin-phenol distribution, Sachigo and Rocksand have lower C/V ratios than Severn and received mixed inputs from angiosperms and gymnosperms (woody and nonwoody alike), while Severn received inputs from nonwoody angiosperms and gymnosperms (Hedges and Mann 1979). Therefore, the OM compositions of the three samples provide insight into OM sources (e.g. paleovegetation) that serve to differentiate the Sachigo, Severn, and Rocksand tills.

The degree of OM diagenesis is consistent with the proposed ages of the HBL sediments examined in this study. For example, OM diagenesis may result in a loss of specificity in the preference for even- versus odd-chain length \(n\)-alkanoic acids, resulting in lower CPI$_{aoic}$ values (Meyers and Ishiwatari 1993). The Severn till, which is youngest of the three, had the highest CPI$_{aoic}$ value, indicating that the \(n\)-alkanoic acids at this site have the highest specificity for even-numbered chain lengths. The proposed lack of OM diagenesis in the Severn till is corroborated by the lowest relative degree of oxidation of vanillyl lignin-derived phenols in comparison to the other two sites (Table 2.3). The Rocksand till had the lowest CPI$_{aoic}$ value and the Sachigo till
had the highest \((Ad/Al)_{v}\), which both suggest that the OM in these two tills are the most altered of the three studied. The difficulty in explaining the history of Sachigo and Rocksand with regards to the degree of diagenesis is complicated by environmental uncertainties. First, the amount of oxidation (Ertel and Hedges 1985) that took place prior to the deposition of this material may have varied between Sachigo and Rocksand. In addition to biotic degradation, abiotic processes cannot be excluded as a possible cause of diagenesis. One study showed that the photo-oxidation of lignin did not substantially change the composition of litter OM at the surface, but an increase in the \((Ad/Al)_{v}\) ratios in pine needles and mineral soil samples was observed (Feng et al. 2011). The \((Ad/Al)_{v}\) ratio of the mineral soil sample increased with photo-oxidation, but did not increase in other samples, suggesting less side chain oxidation in S than V phenols in that study (Feng et al. 2011). Photo-oxidation can also occur upon exposure to light in aquatic environments (Opsahl and Benner 1995) and on surface soils/sediment (Feng et al. 2011), but it is unlikely that the increases in oxidation observed by Feng et al. (2011) would have as great of magnitude in this study given that photo-oxidation is likely limited after deposition. In a study of freeze-thaw cycles, a slight increase in the \((Ad/Al)_{v}\) over time (~ 50 % increase from 0 to 7 freeze-thaw cycles) was observed for grass-amended soil samples (Feng et al. 2007). No such trends were observed for non-amended and lignin-amended soil samples (Feng et al. 2007). Given the successive glacial advance and retreat of the Laurentide Ice Sheet in the HBL (Thorleifson et al. 1992, Dyke 2004, Kleman et al. 2010), we hypothesize that the discrepancy between the ages of the Sachigo and Rocksand tills and their respective stage of diagenesis may arise from freeze-thaw cycles (Feng et al. 2007). Another uncertainly is attributed to the proposed age of the Rocksand till varying by about 30 000 years (the duration of Oxygen Isotope Stage 5; Stokes et al. 2012), and so, uncertainty in the age itself makes such a correlation more difficult. Nonetheless, both the CPI_{soil} and the degree of oxidation of the vanillyl lignin-derived
phenols suggest that the OM of the Sachigo (late Wisconsin) and Rocksand (early Wisconsin) tills has experienced increased diagenesis in comparison to Severn (youngest; late Wisconsin; Table 2.3).

2.6. Conclusions

In contrast to characterizing tills based on the previously-discussed geologic techniques, this study shows that: (i) a biomarker analysis was able to differentiate tills based on OM source and stage of diagenesis and (ii) the quantity of particular biomarkers related to the depositional environments. Although aquatic biomarkers were not detected, this does not preclude an aquatic environment from existing in this HBL historically. Evidence has shown that the erosion, transport, and deposition of sediment containing terrigenous OM may dilute marine biomarker concentrations below detectable levels (Villanueva et al. 1997). Alternatively, such biomarkers may not have been preserved in HBL sediments. Having said this, analysis of organic geochemical biomarkers has the potential to test competing stratigraphic models of the number of marine intervals in the HBL and associated ice sheet volume minima in the region (Kleman et al. 2010, Stokes et al. 2012). All tills analyzed in the present study are found superposed stratigraphically i.e., the Severn rests on Sachigo which in turn rests on the Rocksand indicating that some cannibalization may have occurred from the oldest to youngest till resulting in possible geochemical overlap between all three tills. Nonetheless, this study clearly demonstrates that biomarker analyses can differentiate the type of OM within these sediments. The detected OM biomarkers and the stage of diagenesis corresponded to global paleoclimate, paleovegetation, and approximate ages of the tills. This confirms that biomarkers can differentiate tills where conventional lithostratigraphic techniques cannot be used. Future work in this field could benefit from an expanded program of sampling and analysis across the HBL. Specifically, the
applicability of using OM biomarkers would be more robust if more geological deposits were analyzed across numerous geographic sites. The biomarker approach has shown that the three glacial tills can be characterized by their OM compositions. Inputs from Sphagnum and vascular plants, in addition to the degradation of lignin-derived phenols, provide valuable insight into the biogeochemical processes that have occurred at each site and can lead to the characterization of a particular deposit based on its depositional environment.
2.7. References


### 2.8. Tables


<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>Sachigo (mg/g OC)</th>
<th>Severn (mg/g OC)</th>
<th>Rocksand (mg/g OC)</th>
</tr>
</thead>
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<td></td>
<td></td>
</tr>
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<td>n.d.</td>
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<tr>
<td>Short c</td>
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<tr>
<td>Long d</td>
<td>0.344</td>
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<tr>
<td>Total</td>
<td>0.418</td>
<td>0.505</td>
<td>0.855</td>
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</table>
Table 2.1 continued.

<table>
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<tr>
<th>Molecular Formula</th>
<th>Sachigo (mg/g OC)</th>
<th>Severn (mg/g OC)</th>
<th>Rocksand (mg/g OC)</th>
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<tr>
<td>n-Dodecanoic acid</td>
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<sup>a</sup> Not detected (n.d.): the compound was not detected.
<sup>b</sup> CPI<sub>alk</sub> = (Σ odd-number chain length n-alkanes)/(Σ even-number chain length n-alkanes).
<sup>c</sup> Short = Σ n-alkanols ranging from C₁₆ – C₁₉.
<sup>d</sup> Long = Σ n-alkanols ranging from C₂₀ – C₃₀.
<sup>e</sup> CPI<sub>anoi</sub> = (Σ even-number chain length n-alkanoic acids)/(Σ odd-number chain length n-alkanoic acids).
Table 2.2. Compounds identified in the base hydrolysis extract of samples from the Sachigo, Severn, and Rocksand tills (reported in mg/g OC).

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>Sachigo (mg/g OC)</th>
<th>Severn (mg/g OC)</th>
<th>Rocksand (mg/g OC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha,\omega )-Alkanedioic acids</td>
<td>( \alpha,\omega )-Tetracosanodioic acid</td>
<td>( \alpha,\omega )-C(<em>{24})H(</em>{50})O(_2)</td>
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<tr>
<td>( \alpha,\omega )-Hexacosanodioic acid</td>
<td>( \alpha,\omega )-C(<em>{26})H(</em>{54})O(_2)</td>
<td>0.294</td>
<td>0.331</td>
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<tr>
<td>( \alpha,\omega )-Octacosanodioic acid</td>
<td>( \alpha,\omega )-C(<em>{28})H(</em>{58})O(_2)</td>
<td>0.178</td>
<td>0.190</td>
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<tr>
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<td>0.805</td>
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<tr>
<td>( \omega )-Hydroxyalkanoic acids</td>
<td>( \omega )-Hydroxydodecanoic acid</td>
<td>( \omega )-C(<em>{12})H(</em>{24})O(_3)</td>
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<table>
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<th>Summations</th>
<th>Suberin</th>
<th>Suberin or Cutin</th>
<th>Suberin and Cutin</th>
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<td>Suberin</td>
<td>0.643</td>
<td>0.829</td>
<td>0.741</td>
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<td>Suberin or Cutin</td>
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<td>0.002</td>
<td>0.284</td>
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<tr>
<td>Suberin and Cutin</td>
<td>0.644</td>
<td>0.831</td>
<td>1.025</td>
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\(^a\) Not detected (n.d.): the compound was not detected.

\(^b\) Suberin = \( \Sigma \omega \)-hydroxyalkanoic acids C\(_{20}\) – C\(_{32}\) + \( \alpha,\omega \)-alkanedioic acids C\(_{20}\) – C\(_{32}\); Suberin or Cutin = \( \Sigma \omega \)-hydroxyalkanoic acids C\(_{16}\) and C\(_{18}\); Suberin and Cutin = \( \Sigma \) Suberin + Cutin + Suberin or Cutin (taken from Otto and Simpson 2006b).

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<th>Till</th>
<th>OIS</th>
<th>Climatostratigraphic Units</th>
<th>Ice Flow</th>
<th>OM Source</th>
<th>OM diagenesis</th>
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<td>SEVERN</td>
<td>OIS 2</td>
<td>Late Wisconsin</td>
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<tr>
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<td>- Reworking of the Rocksand till</td>
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<tr>
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<td>- Inputs from non-woody gymnosperms and angiosperms</td>
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<td>- Highest CPI\textsubscript{aoic}</td>
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2.9. Figures

Figure 2.1. Map of the Hudson Bay Lowlands identifying the sampling locations along the Ontario-Manitoba border. Modified from Thorleifson (1992).
Figure 2.2. (a) plot of total monomer concentration for the lignin-derived phenols at each site (b) plot of S/V versus C/V (S = \( \sum \) syringyl units; V = \( \sum \) vanillyl units; C = \( \sum \) cinnamyl units), where “wa” denotes woody angiosperms, “wg” woody gymnosperms, “a” non-woody angiosperms, and “g” non-woody gymnosperms (modified from Hedges and Mann 1979); (c) plot of the acid-to-aldehyde ratios for vanillyl (Ad/Al)_v and syringyl units (Ad/Al)_s.
Chapter 3: Organic matter biomarker characterization of subsurface geologic deposits in the Oak Ridges Moraine, Canada

3.1. Abstract

The stratigraphy of the Oak Ridges Moraine (ORM) dictates the groundwater discharge and recharge of this regional aquifer, and continued urbanization northward originating from the Greater Toronto Area may negatively impact groundwater quality. Uncertainty in the regional stratigraphy of the ORM has made the identification of environmentally sensitive areas challenging. To better define the stratigraphy of this region, a borehole drilling campaign was conducted at eight sites across the ORM, which resulted in a total of forty-nine samples that have been linked to ten different geologic deposits. Biomarker analyses were used to characterize organic matter (OM) composition and stage of diagenesis of the forty-nine samples. Solvent extraction and cupric oxide oxidation were used for the determination of free lipids and lignin-derived phenol biomarkers, respectively. The solvent extracts contained primarily: \(n\)-alkanes, \(n\)-alkanols, and \(n\)-alkanoic acids, and \(n\)-alkane degradation proxies were shown to vary as a function of geologic deposit. A conifer biomarker, nonacosan-10-ol, was detected in the samples and concentrations were consistent with hemispheric temperatures over the last 135 000 years and with known conifer migration over the last 21 000 years. Lignin-derived phenol data suggested that the OM in these geologic deposits may have experienced reincorporation and post-deposition alteration to varying extents. The biomarker analysis conducted in this study was able to provide differentiation amongst the geologic deposits by providing details about OM

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\(^2\) Samples were collected and mineralogical and carbon data was provided by Rick Gerber and Mike Doughty. Solvent extraction was performed by David M. Wolfe, and CuO oxidation and calculations were performed by Nicholas M. Battram. Data analysis and writing were conducted by Nicholas M. Battram and Myrna J. Simpson.
composition and stage of diagenesis with respect to depositional environments and large-scale glacial processes. The results of this study may improve the current understanding of the stratigraphy of the ORM by identifying the biomarker fingerprint of aquifers and aquitards to ultimately implement more effective land- and water-use policies in the Greater Toronto Area.

3.2. Introduction

Groundwater is the world’s largest source of freshwater after frozen ice and snow (Shiklomanov 2000), but urbanization (Howard et al. 1995) and excessive usage of groundwater (Aeschbach-Hertig and Gleeson 2012) pose threats to this resource. The Oak Ridges Moraine (ORM) is part of a major regional aquifer and is considered a vital source of drinking water for the Greater Toronto Area. This glacial moraine is situated north of the Greater Toronto Area and covers approximately 1400 km\(^2\), spanning east from the Niagara Escarpment for over 140 km to Rice Lake, south of Peterborough (Figure 1; Howard et al. 1995). In addition, the ORM offers other benefits such as a habitat for wildlife, a supply of aggregates (i.e. sand, gravel, etc that is mined for construction purposes), and a setting for recreation (Howard et al. 1995, Eyles 2004, Kassenaar and Wexler 2006). The Greater Toronto Area and the nearby ORM are currently experiencing rapid population growth and urbanization. This urbanization is a threat to the quality of water resources, and it is of concern on the regional scale in south-central Ontario because the ORM is north of Canada’s largest city, Toronto (Howard et al. 1995). In addition, the application of fertilizers to agricultural, park, and residential land within the ORM threatens the quality of groundwater because fertilizers may leach into this resource (Howard and Livingstone 2000). Pesticides are also applied to the aforementioned land, but biodegradation and retention by soils mitigates the threat of pesticides leaching into the groundwater (Howard and Livingstone 2000). Furthermore, insufficient knowledge regarding the location and extent of stratigraphic units that determine the regional hydrogeology presents a risk to this groundwater
resource (Gerber and Howard 2002). The area was formed over the past 135 000 years through successive glacial advances and retreats (Eyles 2004). However, the exact stratigraphy, or geologic layering, of the ORM is highly complex and must be determined through a multi-faceted approach of borehole data, seismic profiling, and sediment analysis (Sharpe et al. 2003). This complexity has led to difficulty in determining the hydrogeology of the region because stratigraphic units have varying degrees of permeability for water and contaminants contained therein in comparison to one another. The stratigraphy and permeability are important for understanding the recharge and discharge behaviour of groundwater within the ORM (Howard et al. 1995, Sharpe et al. 2003). Consequently, the hydrogeology must be delineated for the development of accurate land- and water-use policies in this region (Howard et al. 1995, Gerber and Howard 2002, Meriano and Eyles 2003, Kassenaar and Wexler 2006, Meriano and Eyles 2009).

In the 1970’s, the groundwater flow in the region was recognized as important for the recharging of this system (Haefeli 1970). However, hydrogeological relationships between the aquifer and nearby aquifers were difficult to define based on water well records (Sibul et al. 1977, Turner 1977). This was in part due to the majority of the wells penetrating less than 75 m (only one-third the thickness) of the glacial sediments of the ORM (Howard et al. 1995). Research has since expanded the techniques used to identify stratigraphic units and to understand their hydrogeology. For example, the physical characteristics of borehole samples (i.e. sand, silt, boulder, etc) have been compared to exposed outcrops with similar characteristics for identification (Eyles et al. 1983, Boyce et al. 1995). In a study by Boyce et al. (1995), thirty-six boreholes were drilled north of Pickering, Ontario. Lithofacies (i.e. sand vs. gravel, degree of consolidation, etc) in the core samples were compared with outcrops at West Duffins Creek, Rouge River, Rouge River, and the Lake Ontario shoreline to determine their identity.
Additionally, ice flow direction data (e.g. boulder striations) were analyzed at these outcrops to determine glacial advance directions and origin (Boyce et al. 1995). This is one example of the work that has been conducted to understand the regional stratigraphy within the ORM (i.e. the identity, origin, and vertical and horizontal extent of geologic deposits). Borehole geophysics, seismic reflection, and ground penetrating radar have also been used to determine the horizontal and vertical extent of various deposits (Boyce et al. 1995, Pugin et al. 1999, Sharpe et al. 2003). Sharpe et al. (2003) showed that geophysical and sedimentological data was able to provide aquifer dimensions and the degree to which nearby aquifers are connected by delineating the stratigraphic architecture. For instance, along Grasshopper Park Road on the south slope of the ORM, tunnel channel sediments with high permeability were shown to be kilometers long, hundreds of meters wide, and tens of meters thick (Sharpe et al. 2003). Lastly, hydrogeological studies have been conducted to relate the geology with groundwater flow behaviour (Gerber and Howard 1996, Gerber and Howard 2002). Gerber and Howard (2002) showed that 60 % of the entire groundwater discharge of this system flows along the south flank of the ORM. Only less than 25 % of the entire groundwater discharge from this basin flows within the ORM boundary, illustrating the importance of the regional hydrogeology outside the defined boundary of the ORM (Gerber and Howard 2002). Meriano et al. (2009) conducted a hydrogeological study on the south slope of the ORM and showed that approximately 850 tonnes of chloride from road deicing salt was transported to Frenchman’s Bay during the 2004-2005 salting season. Eyles and Meriano (2010) further showed that Frenchman’s Bay receives 26 % of road salt applied to the watershed, but it only covers 1.3 % of its area. The work of Meriano et al. (2009) and Eyles and Meriano (2010) show the importance of understanding the stratigraphy of the ORM and what can be learned from sufficient subsurface data. Due to the complexity of the ORM however, the vertical and horizontal extent of each geologic deposit is yet to be entirely defined (Barnett et al.
A biomarker approach has yet to be applied to the ORM and may provide further insight into the identity and extent (i.e. horizontal and vertical) of each geologic deposit.

Biomarkers are organic matter (OM) compounds that have a similar structural core to their precursor compound and are therefore indicative of their biological origin (Streibl and Herout 1969, Simoneit 2005). Biomarkers have been used for the reconstruction of past climate and vegetation patterns (Villanueva et al. 1997, Brincat et al. 2000, Ternois et al. 2001). Brincat et al. (2000) showed that shifts in vegetation from herbaceous to forest coincided with the start of the Holocene (~ 12 000 years ago; Dyke 2004, Tornqvist and Hijma 2012). Such a shift in vegetation was represented by a change in the relative abundance of C_{27} versus C_{31} n-alkanes (used as biomarkers for forest and herbaceous vegetation, respectively) and was confirmed by an increase in the concentration of pollen grains characteristic of current forest vegetation (Brincat et al. 2000). Higher relative concentrations of terrigenous, plant-derived long-chain n-alkanes, n-alkanols, and n-alkanoic acids have been detected in sediments from the Sea of Okhotsk belonging to glacial periods compared to interglacial periods, suggesting that the erosion and transport of sediment containing OM by ice may result in increased terrigenous OM inputs to marine sediments during glacial periods (Villanueva et al. 1997, Ternois et al. 2001). Biomarkers have also been used to distinguish samples from Greenland, Baffin Bay, and the Canadian Arctic (Parnell et al. 2007). This study demonstrated that Newfoundland coastal sediments originated from northwest Greenland and were transported approximately 3000 km (Parnell et al. 2007). The reincorporation of plant-derived n-alkanes during ice advances coincided with the presence of debris (e.g. sediment and OM) transported by ice that served to dilute marine biomarkers, decreasing marine biomarker concentrations by the incorporation of sediment and terrigenous OM (Villanueva et al. 1997). The erosion, transport, and
reincorporation of sediment containing \(n\)-alkanes may therefore result in multiple generations of OM being incorporated into glacier-transported sediments (Marshall et al. 2009). Lastly, biomarker analysis of glacial tills confirmed that three deposits from the Hudson Bay Lowlands could be differentiated based on OM inputs and stage of diagenesis (Chapter 2).

Biomarkers have been used to examine paleoclimate (i.e. climate and resulting vegetation; Villanueva et al. 1997, Brincat et al. 2000, Ternois et al. 2001) and sediment transport and deposition (Villanueva et al. 1997, Parnell et al. 2007). Biomarkers may therefore provide further insight into the identification of stratigraphic units (Marshall et al. 2009) and subsequently improve the understanding of the hydrogeology of the ORM. Here, we employ biomarker characterization of ten geologic deposits sampled from different locations within the ORM. We specifically targeted unbound lipids which provide information about microbial-derived (Weete 1976) and plant-derived OM (Eglinton and Hamilton 1967, Tulloch 1976). Additionally, cupric oxide (CuO) oxidation was used to obtain signatures of vascular plant-derived OM (i.e. gymnosperm versus angiosperm and woody versus non-woody sources; Hedges and Mann 1979a) and the stage of diagenesis (Ertel and Hedges 1985). The overall objective of this study is to characterize OM composition and stage of diagenesis to differentiate each geologic deposit found within the ORM.

3.3. Methods
3.3.1. Sampling

Forty-nine samples were obtained from borehole drilling at eight sites across the ORM between January 13 and January 19, 2010 (Figure 3.1). The eight sites were: Credit Valley Conservation, High Park, Earl Bales, Queensville, Ballantrae, Uxbridge, Purple Woods, and Rice Lake from west to east (Figure 3.1). The combination of geographic location (i.e. site) and depth
result in a sample representing a particular geologic deposit. These depths, however, vary as a function of geographic location due to large-scale glacial processes involved in the formation of these deposits (Sharpe et al. 1999, Gerber and Howard 2002). Different locations, therefore, require different depths to sample a given deposit. The forty-nine samples represent ten geologic deposits that (i) range in age from 13 000 to 135 000 years (Eyles 2004) and (ii) range in depth from approximately 4 to 173 metres below ground surface (Table 3.1). The ten deposits (and their suggested ages) include the Halton Till (HT; 13 000 years), Upper Newmarket Till (UNT; 13 000 to 25 000 years old), Oak Ridges Aquifer Complex (ORAC; 13 300 years ago), Inner Newmarket Sediment (INS; 20 000 years ago), Tunnel channel (Channel; 20 000 years ago), Lower Newmarket Till (LNT; 18 000 to 20 000 years ago), Thorncliffe Formation (TF; 30 000 to 50 000 years ago), Sunnybrook Drift (Su; 45 000 years ago), Scarborough Formation (Scar; 60 000 to 100 000 years ago), and York Till (YT; 135 000 years ago; Boyce et al. 1995, Eyles 2004, Kassenaar and Wexler 2006). The samples at the various sites were collected using a CME75 drill rig equipped with PQ size (external and internal diameter of 122.6 mm and 85 mm, respectively) hydraulic rotary coring equipment. This equipment creates a continuous core of the soil and rock units encountered. Drilling mud was used as a coolant for the diamond drill bit. It was also used to keep the borehole open and lubricated so the drilling equipment functioned properly. During drilling, the core was removed from the core barrel in 1.524 m increments and placed in protective PVC plastic sleeves. Samples of select sections of the core were placed in zip-lock plastic bags and transported to the laboratory for analysis. Prior to placement within the plastic bags, any skin of drilling mud on the surface of the sample core was removed. Mineralogical data was also obtained for select samples. For example, the amount of amphibole calcic hornblende, iron oxide, and titanite are shown for selected samples and their respective stratigraphic units (Appendix Figure A1, A2, and A3, respectively).
3.3.2. Total carbon and biomarker analyses

Carbon contents were determined using a LECO SC-444 S & C analyzer (University of Guelph Agriculture and Food Laboratory, Guelph, Canada). Inorganic carbon contents were determined by ashing for 3 hours prior to analysis, and organic carbon contents were determined by subtracting the inorganic carbon from the total carbon (Table 3.1).

Samples were first subjected to solvent extraction that served to liberate unbound lipids (Otto et al. 2005). Samples (~ 20 g) were sonicated sequentially with 15 mL of dichloromethane, dichloromethane: methanol (1:1; v/v), and methanol for 15 min. Samples were then centrifuged, and the supernatants were collected and filtered. Extracts were then concentrated by rotary evaporation and dried in glass vials.

Air-dried residues from solvent extraction were then subjected to CuO oxidation to characterize lignin-derived phenols (Hedges and Ertel 1982, Otto and Simpson 2006). Samples (~ 10 g) were added to a Teflon-lined bomb with 1 g CuO, 100 mg ammonium iron (II) sulphate hexahydrate [Fe(NH₄)₂(SO₄)₂·6H₂O] and 15 mL of 2 M NaOH. The headspace was purged with nitrogen, and the bombs were heated to 170 °C for 2.5 hours. Supernatants were collected, and the remaining solids were washed twice with distilled water. The supernatants and the two washes were combined, centrifuged, acidified to pH 1, and left to sit in the dark for 1 hour. Samples were then centrifuged, liquid-liquid extracted with diethyl ether, and dried with anhydrous Na₂SO₄. Extracts were concentrated by rotary evaporation and dried in glass vials.

Solvent extracts and CuO oxidation products were derivatized with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine at 70 °C for 1.5 hours. Tetracosane and derivatized dodecanoic acid were used as external standards for the solvent extracts and derivatized vanillic acid for the CuO oxidation products.
3.3.3. Identification and quantification

Gas chromatography – mass spectrometry (GC-MS) was used to separate and identify the various compounds in the solvent extracts and CuO oxidation products (Otto et al. 2005). An Agilent model 5973 quadrupole mass selective detector was placed downstream of an Agilent model 6890N gas chromatograph (Otto 2005). Helium was used as the carrier gas through a HP-5MS fused-silica capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness). The GC oven was operated at 65 °C for 2 min and the temperature was increased at a rate of 6 °C/min to a final temperature of 300 °C (held for 20 min). An Agilent 7683 autosampler was used to inject 1 μL of sample in splitless mode at an injection temperature of 280 °C. The spectrometer scanned between 50 and 650 Dalton and was operated in electron ionization (EI) mode at 70 eV. Lastly, Agilent Chemstation G1701EA software was used to identify compounds by comparison with commercially available mass spectra and standards.

3.4. Results and discussion

3.4.1. Solvent extractable compounds

The solvent extractable compounds observed in this study included: *n*-alkanes, *n*-alkanols, and *n*-alkanoic acids (See Figure 3.2; Appendix Table A1). Long-chain lipids (with maxima at C<sub>27</sub>, C<sub>29</sub>, and C<sub>31</sub>) are believed to originate from the waxes of vascular plants (Eglinton and Hamilton 1967, Bianchi 1995, Otto et al. 2005) and mid-chain lipids (C<sub>23</sub> and C<sub>25</sub>) from submerged and floating aquatic macrophytes (Ficken et al. 2000) and *Sphagnum* mosses (Baas et al. 2000, Nott et al. 2000). Short-chain lipids (< C<sub>20</sub>) typically arise from microbes (Harwood and Russell 1984, Volkman et al. 1998). The Carbon Preference Index for *n*-alkanes (CPI<sub>alk</sub>) is a measure of the specificity for odd- versus even-numbered chain lengths (Meyers and Ishiwatari 1993). A CPI greater than two indicates fresh inputs, while lower than two indicates older OM (Tuo and Li 2005, Pautler et al. 2010). Average CPI<sub>alk</sub> values for each deposit were
below two, consistent with the presence of older OM (Figure 3.2). Additionally, the ratio of high molecular weight (HMW) $n$-alkanes ($C_{27}$, $C_{29}$, $C_{31}$, $C_{33}$) to HMW $n$-alkanols ($C_{24}$, $C_{26}$, $C_{28}$, $C_{30}$) has been used as a degradation proxy because $n$-alkanes are typically more resistant to degradation than $n$-alkanols (Zhu et al. 2011). According to the data in Figure 3.2, a decrease in the CPI$_{alk}$ was generally associated with an increase in the ratio of HMW-alkanes/HMW-alkanols. Most of the deposits had approximately equal proportions of $n$-alkanes and $n$-alkanols, indicating that degradation or preservation of both homologues were comparable; ORAC and Su, however had higher relative concentrations of $n$-alkanes than $n$-alkanols, indicating increased degradation in these deposits compared to the others (Zhu et al. 2011). These degradation proxies may serve to differentiate deposits from one another. Additional $n$-alkane, $n$-alkanol, and $n$-alkanoic acid data can be found in the Appendix Table A1. The terrestrial/aquatic ratio (TAR) is used to differentiate between OM of terrestrial and aquatic origin (Bourbonniere and Meyers 1996) and it varied between stratigraphic units. Parameters that differentiate between grasses/broad leaf- and conifer-derived OM ($C_{29}/C_{27} + C_{29} + C_{31}$; Lei et al. 2010) and between grass and tree tissues ($C_{31}/C_{29}$; Schwark et al. 2002, Bai et al. 2009) were also tested, but did not vary between stratigraphic units.

One biomarker that was observed to vary amongst the ten deposits was nonacosan-10-ol which is found in conifer needles (Kolattukudy and Walton 1973, Caldicott and Eglinton 1975, Matas et al. 2003). Lower average concentrations of nonacosan-10-ol were detected in the HT, UNT, and ORAC (Figure 3) and correspond to the migration of conifer species out of south-central Ontario and to the northwest based on pollen data and climate estimates over the last 21 000 years (Shuman et al. 2002, Webb et al. 2004). The highest concentrations of nonacosan-10-ol were observed in INS, LNT, and TF. Ages for these deposits have been suggested to be 20 000 to 50 000 years old, and may correspond to Marine Isotope Stage 3 (Eyles 2004, Kassenaar
and Wexler 2006). Lower concentrations were also detected in the Su and Scar, which may correspond to Marine Isotope Stage 4 around 60,000 and in YT, which may correspond to Marine Isotope Stage 6 around 135,000 years ago (Pisias et al. 1984, Martinson et al. 1987, Stuiver and Grootes 2000, Eyles 2004).

3.4.2. CuO oxidation products

Lignin-derived phenols obtained through CuO oxidation are helpful for differentiating vascular plant sources (Hedges and Mann 1979a) and stage of oxidation (Ertl and Hedges 1985). For instance, angiosperms and gymnosperm sources and woody and non-woody sources can be differentiated from one another based on the relative proportion of particular lignin-derived phenols (Hedges and Mann 1979a). The eight lignin derived phenols detected in this study belong to three classes of monomers: vanillyl (V: vanillin, acetovanillone, and vanillic acid), syringyl (S: syringaldehyde, acetosyringone, and syringic acid), and cinnamyl (C: ferulic acid and p-coumaric acid). Angiosperms contain syringyl units and non-woody vascular plants contain cinnamyl units, and so a plot of S/V and C/V (Figure 3.4) can be used to differentiate OM from different botanical sources (Hedges and Mann 1979a). The vast majority of samples have received inputs from a mixture of all four sources (i.e. woody and non-woody gymnosperms and angiosperms). Particular samples, however, have received OM from exclusively woody gymnosperms, exclusively non-woody gymnosperms, and exclusively non-woody angiosperms (Figure 3.4). Samples from the same stratigraphic units did not cluster together, but rather, the majority of samples regardless of the deposit, were localized in the centre between all four regimes (OM contribution from woody and non-woody angiosperms and gymnosperms). The ratio of acid-to-aldehyde for syringyl and vanillyl units [(Ad/Al)\textsubscript{s} and (Ad/Al)\textsubscript{v}, respectively] are commonly used as degradation proxies because aldehyde functional groups are oxidized to acids with increasing degradation (ten Have and Teunissen 2001). A plot
of \((Ad/Al)\textsubscript{v}\) versus \((Ad/Al)\textsubscript{s}\) for samples where both the acid and the aldehyde were detected shows that ratios are generally less than 5 (Figure 3.5). Exceptions to this however, are observed where \((Ad/Al)\textsubscript{v}\) ratios range upwards of 24 because of the high concentrations of vanillic acid observed. Furthermore, such ratios could not be calculated for some samples because vanillin was not detected.

3.4.2.1. Comparison of samples at varying depths from the same borehole site

We hypothesize that the same stratigraphic units will have the same lignin-derived OM composition because these biomarkers reflect terrestrial inputs and may provide high resolution for elucidating OM signatures amongst various geologic deposits. To test this hypothesis, a comparison was first made among deposits at one particular site. Two samples from Purple Woods belonging to TF, Purple Woods (111 m) and Purple Woods (134 m), had the same CuO oxidation signatures as one another (Figures 3.4 and 3.5; Appendix Table A2): the S/V, C/V, \((Ad/Al)\textsubscript{v}\), and \((Ad/Al)\textsubscript{s}\) ratios for these two samples were within the error of each other, even though these samples were separated by approximately 20 m. Two other samples at this site, Purple Woods (11 m) and Purple Woods (80 m), belonging to the LNT, showed very similar but non-identical lignin-phenol signatures. Syringyl monomers were not detected in either sample, and this limited the calculation of S/V and \((Ad/Al)\textsubscript{s}\) ratios. Vanillin was not detected in either sample, and so an undefined \((Ad/Al)\textsubscript{v}\) was calculated. The absence of syringyl monomers and vanillin was consistent between the two samples; however, their C/V ratios were different, indicating some degree of OM heterogeneity. INS samples at Rice Lake were highly heterogeneous based on the S/V, C/V, \((Ad/Al)\textsubscript{v}\), and \((Ad/Al)\textsubscript{s}\) ratios (Figures 3.4 and 3.5; Appendix Table A2). These samples account for approximately 60 m of the core at this site, and so the depths of these samples were quite different. For example, the \((Ad/Al)\textsubscript{s}\) ratio of samples collected at Rice Lake at different depths were quite variable. In fact, these values were only
obtained for deeper deposits: the ratios were 0.97 ± 0.47 at Rice Lake (100 m), and 1.18 ± 0.22 at Rice Lake (114 m). Such a difference between samples of the same deposit suggests OM heterogeneity and is corroborated by the high relative standard errors of many samples. Furthermore, lignin-derived phenol data of Channel samples, Queensville (14 m), Queensville (21 m), and Queensville (82 m), were variable as well. C/V values ranged between not being detected at Queensville (82 m) and 0.92 ± 0.21 at Queensville (21 m); S/V ratios ranged between not being detected at Queensville (82 m) and 0.27 ± 0.07 at Queensville (21 m) (Figure 3.4; Appendix Table A2). It is therefore evident that a comparison of lignin-derived phenols may not be able to correlate, or relate, samples of a common deposit with one another due to sample heterogeneity.

3.4.2.2 Comparison of samples at varying depths from different borehole sites

A comparison of lignin-derived phenol data of the same deposit but at different sites showed differentiation between deposits. Due to the lack of lignin-derived phenols in each of the ORAC samples, C/V, S/V, (Ad/Al)_s, and (Ad/Al)_v parameters could not be calculated at Purple Woods (16 m), Ballantrae (17 m), and Ballantrae (25 m) irrespective of its site or depth (Appendix Table A2). While such parameters could not be calculated, the lack of lignin-derived phenols in this deposit differentiates it from other deposits, and so it may aid in the identification of ORAC samples. A comparison of HT at different sites, however, showed differences in their respective lignin-derived phenol parameters. Two samples belonging to HT were collected at High Park (4 m) and at Earl Bales (5 m), which are located approximately 20 km apart. We hypothesize that similar CuO oxidation signatures should be observed between the two samples because they should have received similar OM inputs and experienced the similar geologic processes; such signatures are quite different between the two sites however. The lignin-derived phenol ratios [C/V, S/V, (Ad/Al)_s, or (Ad/Al)_v] were quite variable (Figures 3.4 and 3.5;
Appendix Table A2). This variability was also observed for the LNT samples. While the CuO oxidation signatures of the two LNT samples collected at Purple Woods were quite similar, a comparison of LNT samples across different sites showed that the signatures at Ballantrae, Earl Bales, Purple Woods, and Rice Lake were highly variable (Figures 3.4 and 3.5; Appendix Table A2). Therefore, even when samples at the same site and of the same deposit showed similar lignin-derived phenol signatures, a comparison at different sites may not. This prevents a regional correlation from being made based explicitly on biomarker data, likely due to OM heterogeneity.

3.4.2.3. Evidence for organic matter reincorporation

Analysis of samples based on CuO oxidation signatures is complicated by samples having OM compositions very similar to the underlying material. For instance, Rice Lake (151 m) and Rice Lake (166 m) belong to TF and have average C/V ratios of 0.47 ± 0.12 and 0.47 ± 0.06 and S/V ratios of 0.33 ± 0.07 and 0.38 ± 0.04, respectively. This is very similar to the ratios for that of YT at Uxbridge. Uxbridge, however, is the only site at which YT was sampled. As glaciers advance, the underlying sediments and the OM present therein are eroded and transported, and as glaciers retreat, sediments and OM are subglacially deposited (Menzies and Shilts 2002). Because of the large-scale process involved and differing rates of erosion, varying degrees of the underlying material can be reincorporated at any particular time and place (Menzies and Shilts 2002). It is possible that material from the YT may have eroded and may have been reincorporated into the TF at this site, since the YT is lower in the stratigraphic record (Eyles 2002, Eyles 2004). Reincorporation of OM has been shown to result from ice-transported sediments (Villanueva et al. 1997), and multiple generations of OM coexisting in one deposit (Marshall et al. 2009) may result in a heterogeneous OM composition for that particular deposit. Additionally, OM heterogeneity of samples may have led to the high relative standard errors
observed. This may have also limited an OM composition of Channel samples, for instance, from being identified (Section 3.4.2.1). This is expected given that the process by which tunnel channels are created is large-scale and catastrophic (Russell et al. 2003). While the drainage of the Laurentide Ice Sheet is now thought to have been episodic (Shaw 1996), the filling of channels is generally poorly understood (Russell et al. 2003). The amount of OM reincorporation has been estimated based on the amount of extinct or highly altered pollen grains, spores, and dinocysts (Meckler et al. 2008). Their findings suggest that OM reincorporation could complicate bulk parameters and biomarkers by contributing older material of different composition (Meckler et al. 2008). The heterogeneity of the samples in this study are consistent with Meckler et al. (2008) and what is currently known about the ORM (i.e. uncertainty in the origin of deposits; Kassenaar and Wexler 2006).

3.4.2.4. Evidence for post-deposition alteration

Another prominent observation from the CuO oxidation data was the high (Ad/Al)_v ratios. One particular Channel sample collected from Queensville Deep (21 m) had an (Ad/Al)_v ratio of 23.71 ± 6.43 (Figure 3.5; denoted A). The (Ad/Al)_v ratios may be skewed by increased vanillic acid concentrations. Increased concentrations of vanillic acid may serve as an indicator for the degree of diagenesis (Ertel and Hedges 1985, Hedges et al. 1988, Opsahl and Benner 1995), but we hypothesize that it may also result from the preservation of vanillic acid monomers after oxidation from vanillin. Vanillyl monomers have been shown to be more resistant to degradation than syringyl and cinnamyl monomers (Hedges et al. 1988, Goñi et al. 1993) and we hypothesize that the environment within such geologic deposits may not be conducive to the degradation of vanillic acid. Another sample with a characteristically high (Ad/Al)_v ratio is the Earl Bales (13 m), which belongs to LNT (Figure 3.5; denoted B). The formation of Channel and LNT may result in OM reincorporation due to the catastrophic release of meltwater and the
advance of glaciers, respectively. In addition to these particular samples with \((\text{Ad/Al})_v \geq 10\), some samples had undefined \((\text{Ad/Al})_v\) ratios due to the absence of vanillin. There were numerous samples where vanillic acid was detected, but vanillin was not, ultimately leading to undefined \((\text{Ad/Al})_v\) ratios (and hence such data points are not presented in Figure 3.5). Lignin oxidation before glacial erosion (Hedges and Mann 1979a) and transport through aquatic systems (Haddad et al. 1992) to a marine setting is possible (Hedges and Mann 1979b). Furthermore, reincorporation may have been followed by subsequent oxidation via freeze-thaw cycles (Feng et al. 2007) and photo-oxidation (Feng et al. 2011) with both processes limited to before deposition. Freeze-thaw cycles have been shown to cause an increase of approximately 30 to 50% in both the \((\text{Ad/Al})_v\) and \((\text{Ad/Al})_s\) ratios of sediments after seven freeze-thaw cycles (Feng et al. 2007). It was suggested that freeze-thaw cycles may accelerate lignin oxidation (Feng et al. 2007), and so this may partially explain our observed Al/Al ratios given the cyclic nature of temperature fluxes over the past 135,000 years (Martinson et al. 1987, Stuiver and Grootes 2000), but such oxidation would be limited after deposition. Photo-oxidation has also been shown to enhance lignin oxidation (Opsahl and Benner 1995, Feng et al. 2011). This process however would only occur in areas exposed to light, such as in open water (Opsahl and Benner 1995) or on the surface of sediment (Feng et al. 2011). Such oxidation may occur (Opsahl and Benner 1995, Feng et al. 2011), especially in a glacial environment where erosion and reincorporation of sediment may bring sediment back to the surface (Menzies and Shilts 2002) or where glacial lakes form from meltwater (Gilbert 1997). Photo-oxidation, however, would also be limited after deposition. The high \((\text{Ad/Al})_v\) ratios (and in some samples, the presence of vanillic acid but not vanillin) suggests enhanced oxidation of lignin with time. Due to the biomarker data and the mechanisms involved in the formation of the ORM, OM reincorporation and post-deposition alteration may provide reasons as to why regional correlations of deposits are difficult.
3.5. Conclusions

This study has shown that depositional environments and processes in the ORM can be investigated based on OM composition and stage of diagenesis, but there is nonetheless some degree of uncertainty in defining the stratigraphy of the ORM. This observation is consistent with what is currently known about the ORM: large-scale and even catastrophic geologic processes leading to the formation of the ORM have resulted in a highly complex geologic system that needs to be fully understood in order to accurately model hydrogeological processes (Sharpe et al. 2003). Due to the sample heterogeneity arising from OM reincorporation, future work should focus on locations where the stratigraphy is better defined (i.e. stratigraphic units with defined boundaries). Such sites would be located closer to Lake Ontario where outcrops have visually provided a wealth of knowledge in this regard (Eyles 2004). If the stratigraphy was well known and biomarker analysis was applied, then basic fingerprints to which other samples could be compared could be used. Once known stratigraphic units were characterized, more robust comparisons could be made. This study has shown that OM source can be used to differentiate various deposits present in the ORM and that OM stage of diagenesis can help explain depositional processes. While some deposits could be regionally correlated, others could not due to OM heterogeneity. Depositional environments, however, were consistent with hemispheric temperatures and the resulting vegetation in the region. OM heterogeneity was consistent with the large-scale erosion and depositional processes involved in the formation of these deposits. The results of this study, however, may aid in understanding and resolving the history and stratigraphy of the ORM, which will ultimately provide insight into environmentally and hydrogeologically sensitive areas.
3.6. References


Eyles, N. 2004. Toronto rocks. Fitzhenry & Whiteside Limited, Markham, ON.

Eyles, N. 2002. Ontario rocks: three billion years of environmental change. Fitzhenry & Whiteside Limited, Markham, ON.


### 3.7. Tables

Table 3.1. Depth (metres below ground surface; mbgs), stratigraphic unit, inorganic carbon (IC), and organic carbon (OC) of the samples from the Oak Ridges Moraine.

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<tr>
<th>Site</th>
<th>Depth (midpoint; mbgs)</th>
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<th>Stratigraphic Unit Acronym</th>
<th>IC (%)</th>
<th>OC (%)</th>
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3.8. Figures

Figure 3.1. Map of the study area, indicating the sites at which samples were cored. Modified from Howard et al. (1995).
Figure 3.2. Average Carbon Preference Index for $n$-alkanes ($\text{CPI}_{\text{alk}}$) and the ratio of high molecular weight (HMW) $n$-alkanes to HMW $n$-alkanols for each deposit. $\text{CPI}_{\text{alk}} = (\Sigma \text{odd-numbered } n\text{-alkanes})/ (\Sigma \text{even-numbered } n\text{-alkanes})$. HMW $n$-alkanes $= \Sigma C_{27}, C_{29}, C_{31}, C_{33}$, while HMW $n$-alkanols $= \Sigma C_{24}, C_{26}, C_{28}$, and $C_{30}$.
Figure 3.3. Average concentrations of nonacosan-10-ol, a conifer biomarker, for the various geologic deposits in the ORM. Values are reported in μg/g of organic carbon (OC).
Figure 3.4. Plot of S/V versus C/V (S = Σ syringaldehyde, acetosyringone, and syringic acid; V = Σ vanillin, acetovanillone, and vanillic acid; C = Σ ferulic acid and p-coumaric acid) for each sample. Four regimes indicate possible vascular plant sources: woody angiosperm (wa), non-woody angiosperm (a), woody gymnosperm (wg), and non-woody gymnosperm (g). Note: undefined S/V and C/V ratios preclude particular samples from being plotted. Adapted from Hedges and Mann (1979a).
Figure 3.5. Vanillyl and syringyl acid-to-aldehyde [(Ad/Al)v and (Ad/Al)s] ratios of all the samples. Note: undefined (Ad/Al)v and (Ad/Al)s preclude particular samples from being plotted.
Chapter 4: Conclusions

4.1. Summary

Biomarker analyses were conducted to characterize organic matter (OM) source and stage of diagenesis to differentiate, or fingerprint, various glacial geologic deposits. Solvent extraction and chemolytic methods were performed to release unbound lipids (Otto et al. 2005), bound lipids (Otto and Simpson 2006b) and lignin-derived phenols (Hedges and Ertel 1982, Otto and Simpson 2006a) respectively. In the first study (Chapter 2), three glacial tills from the Hudson Bay Lowlands (HBL) were analyzed using biomarker analyses by gas chromatography-mass spectrometry. This study found that glacial tills could be differentiated based on OM source and stage of diagenesis, and that OM composition could be related to past depositional environments (i.e. paleoclimate and paleovegetation) and approximated ages. It also served as a proof-of-concept study which suggested that this approach may be used to characterize glacial tills.

In the second study (Chapter 3), the same biomarker approach was conducted on forty-nine samples from the Oak Ridges Moraine (ORM). These samples were collected from a drilling campaign at eight different sites and at various depths across the ORM. These samples were categorized into ten different geologic deposits. In this study, OM sources were related to paleoclimate and paleovegetation, which served to differentiate the ten geologic deposits based on OM composition and to fingerprint the deposits to some degree. Lignin-derived phenols, however, suggested that OM reincorporation and post-deposition alteration were at least partially responsible for sample heterogeneity.
4.1.1. Summary of the Hudson Bay Lowlands project (Chapter 2)

Three tills (Sachigo, Severn, and Rocksand) were differentiated from one another based on OM sources and stage of diagenesis. The solvent extract was dominated by lipids consistent with vascular plant (Eglinton and Hamilton 1967, Otto et al. 2005) and microbial sources (Harwood and Russell 1984, Volkman et al. 1998). Although inferred ice flow directions pass through Hudson Bay and James Bay (Dyke et al. 1982, Fisher et al. 1985, Menzies et al. 2012), aquatic biomarkers were not detected likely due to the concentrations of such biomarkers being decreased by the presence of ice-transported sediment and terrigenous OM (Villanueva et al. 1997) or due to a lack of preservation (Marshall et al. 2009). The $n$-alkane data suggested that Sphagnum-derived inputs may be more prominent in the Severn and Rocksand tills compared to Sachigo. This is consistent with warmer temperatures in the Sangamon interglacial period leading up to the deposition of the Rocksand till (Stuiver and Grootes 2000) and possibly an increase in productivity of Sphagnum species (Dorrepaal et al. 2004, Breeuwer et al. 2008). Severn likely reincorporated some of the Rocksand till, resulting in increased Sphagnum inputs as well. Furthermore, Severn received the most suberin input (from vascular plant roots and bark; Kolattukudy and Espelie 1989, Otto and Simpson 2006b) and received input from non-woody gymnosperms and non-woody angiosperms (Hedges and Mann 1979, Otto and Simpson 2006a). Sachigo and Rocksand however, received input from both woody and non-woody gymnosperms and angiosperms. Vanillyl lignin-derived phenols in the Severn till were least oxidized, and this is consistent with Severn being the youngest (late Wisconsin) of the three tills studied (Dyke 2004, Stokes et al. 2012). Vanillyl lignin-derived phenols found in Sachigo (late Wisconsin) and Rocksand (early Wisconsin) underwent greater oxidation, consistent with their increased ages (Stokes et al. 2012). These three tills were characterized and differentiated based on OM sources and stage of diagenesis, and as such may serve as a fingerprint for each deposit.
4.1.2. Summary of the Oak Ridges Moraine project (Chapter 3)

Ten deposits were sampled at eight different sites across the ORM, which resulted in a total of forty-nine samples being collected. The solvent extract contained $n$-alkanes, $n$-alkanols, and $n$-alkanoic acids. The loss of specificity for odd-numbered $n$-alkanes (Tuo and Li 2005, Pautler et al. 2010) and higher ratios of high molecular weight $n$-alkanes to that of $n$-alkanols (Zhu et al. 2011) suggest that these OM components have experienced varying degrees of diagenesis. A conifer biomarker, nonacosan-10-ol, was also detected in each deposit and their concentrations varied with hemispheric temperatures (Stuiver and Grootes 2000) and the migration of paleovegetation (Shuman et al. 2002, Webb et al. 2004). Greatest concentrations were detected in deposits ranging in age from approximately 20 000 to 50 000 years old. Geologic deposits younger than ~ 20 000 years of age had lower relative concentrations of nonacosan-10-ol. This was likely a result of conifer migration out of the study area and to the northwest (Shuman et al. 2002, Webb et al. 2004) due to increasing temperatures (Stuiver and Grootes 2000). Deposits older than ~ 50 000 years of age had lower concentrations of nonacosan-10-ol, consistent with colder glacial paleoclimate (Stuiver and Grootes 2000). The relatively high standard error associated with the solvent extract and lignin-derived phenol data indicated that the OM was indeed heterogeneous. Such heterogeneity likely stems from glacial reincorporation of older sediments (Menzies and Shilts 2002). Furthermore, vanillyl lignin-derived phenols experienced considerable oxidation, which is likely a reflection of its age but post-depositional processes as well (e.g. freeze-thaw cycles; Feng et al. 2007). The biomarker data of this study is consistent with paleovegetation (Shuman et al. 2002, Webb et al. 2004) and the known geologic processes giving rise to geologic deposits (Menzies and Shilts 2002).
4.2. Limitations and future work

While biomarker analyses are widely-used to characterize OM (Otto et al. 2005, Parnell et al. 2007, Marshall et al. 2009, Pautler et al. 2010), the applicability of such an analysis is limited by the geologic setting that it is used to study. Geologic processes without known parameters, such as erosion and depositional rates (Menzies and Shilts 2002), may result in complex biomarker signatures. The work presented in this thesis has shown some success in using such an approach to characterizing geologic deposits and explaining depositional environments, but there remains opportunity for further research. Future studies should address the following limitations:

1. The limited dataset (3 samples) in the HBL study lacked replication, and so a future study could involve collecting additional samples from each of the Sachigo, Severn, and Rocksand tills. A biomarker analysis could then be conducted on these samples using the same method as described in Chapter 2, and the resulting fingerprints could be compared to the original samples. This study would address the reproducibility of such a fingerprint.

2. OM heterogeneity in the ORM samples limited a distinct fingerprint for specific stratigraphic units from being determined based on all extraction techniques used, as was done in the HBL study. Future work would benefit from retrieving samples from borehole drilling at a location where stratigraphic units were known with greater certainty. Such sites would be located closer to Lake Ontario (Eyles 2004), where outcrops have provided insight into the stratigraphy. Borehole samples are often compared to such outcrops in order to identify the deposit (Boyce et al. 1995). Drilling at an outcrop would allow “standards” to be obtained. If a stratigraphic unit was known with certainty, the OM composition could then be determined and could
be used for comparison purposes, much in the same way that cored samples are visually inspected against outcrop standards.

3. While the ages of each deposit in the ORM are known with some degree of certainty based on previous studies (Boyce et al. 1995, Eyles 2004). The erosion, transport, and deposition of sediment containing OM may often lead to older OM being reincorporated into younger deposits (Menzies and Shilts 2002, Marshall et al. 2009). Isolation of biomarkers for compound specific radiocarbon isotope analysis could provide insight into the age of each particular biomarker (Eglinton et al. 1996) and into the possibility of OM reincorporation. In the case of OM reincorporation, radiocarbon isotope signatures of particular biomarkers would appear older, and would lend further credence to OM reincorporation.

4. *n*-Alkanes originate from many sources, and while chain length often provides insight into biogenic origin, some chain lengths are derived from multiple organisms. Compound specific stable isotope analysis, however, may be able to differentiate inputs from cyanobacteria versus photosynthetic bacteria and from C₃ versus C₄ plants (Schidlowski et al. 1983). For example, C₃ plants are believed to have more depleted δ¹³C values ranging between -23 to -34 ‰ (Benner et al. 1987, Hayes 2001). C₄ plants, however, are less depleted than C₃ plants and have δ¹³C values ranging between -6 to -23 ‰ (Benner et al. 1987, Hayes 2001).

5. The complexity of sediment extract sometimes resulted in the coelution of compounds. Multi-dimensional chromatography allows for separation of compounds in one column, and then the compounds are further separated upon injection into the second column (Gorecki et al. 2004). This technique would therefore allow for the separation of coeluting compounds, so that they could better identified and quantified.
This set of proposed studies would improve the current knowledge of geologic deposits, their subsurface extent, and their depositional processes. Furthermore, employing advanced techniques, such as isotope analysis and multi-dimensional chromatography may provide greater insight into the age of OM and more specific OM sources.

4.3. Conclusions

The results of these studies suggest that geologic deposits can be characterized and differentiated based on OM inputs and stage of diagenesis. Specifically, OM inputs can be related to the paleoclimate and paleovegetation, and the stage of diagenesis may be consistent with age. The inherent difficulty in applying a biomarker analysis to geologic deposits, however, is a result of the depositional processes involved in the formation of the deposit itself. Variations in erosion and depositional rates dictate the degree of OM reincorporation, complicating the biomarker signatures of geological deposits. Nonetheless, this thesis has shown that a biomarker analysis has potential for differentiating geologic deposits and the elucidation of depositional environments and processes.
4.4 References


Eyles, N. 2004. Toronto rocks. Fitzhenry & Whiteside Limited, Markham, ON.


## Appendices

Table A1. Average concentrations of solvent extractable lipids for the samples of each stratigraphic unit (measured in μg/g OC).

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<td>3725.06 ± 340.12</td>
<td>2680.67 ± 253.33</td>
<td>6287.49 ± 252.01</td>
<td>5138.94 ± 218.39</td>
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<td>Total</td>
<td>5649.26 ± 303.16</td>
<td>4019.32 ± 347.09</td>
<td>2894.92 ± 257.17</td>
<td>6766.89 ± 262.25</td>
<td>6160.72 ± 251.38</td>
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<tr>
<td>HMW n-alkanes $^c$</td>
<td>1026.87 ± 24.27</td>
<td>1084.50 ± 218.34</td>
<td>881.41 ± 148.19</td>
<td>1624.56 ± 142.11</td>
<td>1351.26 ± 108.67</td>
</tr>
<tr>
<td>TAR $^d$</td>
<td>1.19 ± 0.30</td>
<td>4.73 ± 1.73</td>
<td>7.01 ± 2.22</td>
<td>4.15 ± 0.83</td>
<td>1.99 ± 0.36</td>
</tr>
<tr>
<td>C$<em>{29}/$(C$</em>{27}$+C$<em>{29}$+C$</em>{31}$)</td>
<td>0.36 ± 0.02</td>
<td>0.36 ± 0.16</td>
<td>0.36 ± 0.13</td>
<td>0.35 ± 0.07</td>
<td>0.36 ± 0.06</td>
</tr>
<tr>
<td>C$<em>{31}$/C$</em>{29}$</td>
<td>0.69 ± 0.06</td>
<td>0.74 ± 0.41</td>
<td>0.74 ± 0.34</td>
<td>0.66 ± 0.15</td>
<td>0.70 ± 0.14</td>
</tr>
<tr>
<td>C$<em>{23}/$(C$</em>{23}$+C$_{29}$)</td>
<td>0.54 ± 0.06</td>
<td>0.46 ± 0.18</td>
<td>0.35 ± 0.16</td>
<td>0.57 ± 0.09</td>
<td>0.51 ± 0.10</td>
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</tbody>
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<table>
<thead>
<tr>
<th>n-alkanols</th>
<th>HT</th>
<th>UNT</th>
<th>ORAC</th>
<th>INS</th>
<th>Channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short</td>
<td>604.69 ± 138.75</td>
<td>193.48 ± 45.71</td>
<td>814.54 ± 157.28</td>
<td>517.04 ± 200.00</td>
<td>622.66 ± 111.18</td>
</tr>
<tr>
<td>Long</td>
<td>897.39 ± 107.47</td>
<td>1266.38 ± 175.53</td>
<td>174.05 ± 54.64</td>
<td>2882.38 ± 310.88</td>
<td>1912.42 ± 127.05</td>
</tr>
<tr>
<td>Total</td>
<td>1502.08 ± 175.50</td>
<td>1462.85 ± 181.38</td>
<td>988.59 ± 166.51</td>
<td>3399.42 ± 369.66</td>
<td>2535.08 ± 168.83</td>
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<tr>
<td>HMW n-alkanols $^e$</td>
<td>586.81 ± 91.65</td>
<td>801.18 ± 164.47</td>
<td>126.18 ± 33.27</td>
<td>1784.42 ± 268.69</td>
<td>1222.32 ± 109.52</td>
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<table>
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<th>n-alkanoic acids</th>
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<th>UNT</th>
<th>ORAC</th>
<th>INS</th>
<th>Channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short</td>
<td>210.71 ± 29.94</td>
<td>243.39 ± 45.46</td>
<td>708.41 ± 150.76</td>
<td>664.60 ± 81.79</td>
<td>582.24 ± 58.22</td>
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<tr>
<td>Long</td>
<td>289.64 ± 32.46</td>
<td>150.84 ± 45.24</td>
<td>265.65 ± 94.52</td>
<td>628.22 ± 136.54</td>
<td>479.79 ± 38.25</td>
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<tr>
<td>Unsaturated $^f$</td>
<td>16.94 ± 9.82</td>
<td>20.71 ± 13.08</td>
<td>500.67 ± 167.85</td>
<td>130.72 ± 27.95</td>
<td>116.14 ± 14.37</td>
</tr>
<tr>
<td>Total</td>
<td>517.29 ± 45.24</td>
<td>414.95 ± 65.46</td>
<td>1474.72 ± 244.62</td>
<td>1423.54 ± 161.60</td>
<td>1178.18 ± 71.13</td>
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Table A1 continued.

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<tr>
<th></th>
<th>LNT</th>
<th>TF</th>
<th>Su</th>
<th>Scar</th>
<th>YT</th>
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<tr>
<td>Short</td>
<td>552.85 ± 67.02</td>
<td>380.53 ± 29.31</td>
<td>2223.07 ± 316.19</td>
<td>1375.70 ± 227.32</td>
<td>36.43 ± 10.09</td>
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<tr>
<td>Long</td>
<td>4733.94 ± 149.93</td>
<td>3930.23 ± 130.02</td>
<td>8667.65 ± 964.42</td>
<td>4153.89 ± 236.41</td>
<td>371.97 ± 33.96</td>
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<tr>
<td>Total</td>
<td>5286.80 ± 164.23</td>
<td>4310.76 ± 133.28</td>
<td>10890.72 ± 1014.93</td>
<td>5529.59 ± 327.97</td>
<td>408.40 ± 35.43</td>
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<tr>
<td>HMW n-alkanes</td>
<td>1268.80 ± 76.46</td>
<td>1180.92 ± 73.46</td>
<td>2409.97 ± 530.78</td>
<td>912.27 ± 74.30</td>
<td>102.46 ± 15.78</td>
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<tr>
<td>TAR</td>
<td>3.18 ± 0.51</td>
<td>4.23 ± 0.51</td>
<td>1.91 ± 0.58</td>
<td>1.04 ± 0.24</td>
<td>4.10 ± 1.57</td>
</tr>
<tr>
<td>C_{29}/(C_{27}+C_{29}+C_{31})</td>
<td>0.35 ± 0.04</td>
<td>0.36 ± 0.05</td>
<td>0.36 ± 0.17</td>
<td>0.37 ± 0.07</td>
<td>0.33 ± 0.10</td>
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<tr>
<td>C_{31}/C_{29}</td>
<td>0.66 ± 0.08</td>
<td>0.72 ± 0.11</td>
<td>0.79 ± 0.47</td>
<td>0.67 ± 0.14</td>
<td>0.70 ± 0.28</td>
</tr>
<tr>
<td>C_{23}/(C_{23}+C_{29})</td>
<td>0.53 ± 0.08</td>
<td>0.50 ± 0.08</td>
<td>0.45 ± 0.19</td>
<td>0.58 ± 0.14</td>
<td>0.53 ± 0.22</td>
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<td><strong>n-alkanols</strong></td>
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<tr>
<td>Short</td>
<td>398.04 ± 43.99</td>
<td>427.95 ± 51.05</td>
<td>2180.01 ± 809.25</td>
<td>272.69 ± 52.88</td>
<td>50.58 ± 15.27</td>
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<tr>
<td>Long</td>
<td>2403.53 ± 218.98</td>
<td>2914.09 ± 185.28</td>
<td>1177.49 ± 171.20</td>
<td>713.08 ± 119.42</td>
<td>356.46 ± 31.65</td>
</tr>
<tr>
<td>Total</td>
<td>2801.57 ± 223.35</td>
<td>3342.04 ± 192.19</td>
<td>3357.49 ± 827.16</td>
<td>985.76 ± 130.61</td>
<td>407.04 ± 35.14</td>
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<tr>
<td>HMW n-alkanols</td>
<td>1515.32 ± 186.12</td>
<td>1882.73 ± 158.60</td>
<td>690.98 ± 98.61</td>
<td>493.46 ± 111.80</td>
<td>232.18 ± 26.96</td>
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<td><strong>n-alkanoic acids</strong></td>
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<td></td>
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<tr>
<td>Short</td>
<td>446.76 ± 39.81</td>
<td>405.04 ± 33.26</td>
<td>1330.93 ± 382.73</td>
<td>181.90 ± 22.76</td>
<td>88.13 ± 11.52</td>
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<tr>
<td>Long</td>
<td>389.48 ± 37.34</td>
<td>410.45 ± 41.54</td>
<td>440.57 ± 109.50</td>
<td>61.69 ± 19.29</td>
<td>79.16 ± 7.77</td>
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<tr>
<td>Unsaturated</td>
<td>120.27 ± 27.81</td>
<td>118.25 ± 32.07</td>
<td>369.39 ± 251.22</td>
<td>34.38 ± 15.89</td>
<td>57.13 ± 28.68</td>
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<tr>
<td>Total</td>
<td>956.51 ± 61.26</td>
<td>933.74 ± 62.13</td>
<td>2140.88 ± 470.72</td>
<td>277.97 ± 33.81</td>
<td>224.43 ± 31.87</td>
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</tbody>
</table>

\[ a \] Short = \( \sum \) n-alkanes, n-alkanols, or n-alkanoic acids < C_{20}  \
\[ b \] Long = \( \sum \) n-alkanes, n-alkanols, or n-alkanoic acids \( \geq \) C_{20}  \
\[ c \] High molecular weight (HMW) n-alkanes = \( \sum \) C_{27}, C_{29}, C_{31}, C_{33} n-alkanes  \
\[ d \] Terrestrial/Aquatic Ratio (TAR) = (C_{27} + C_{29} + C_{31})/(C_{15} + C_{17} + C_{19})  \
\[ e \] HMW n-alkanols = \( \sum \) C_{24}, C_{26}, C_{28}, C_{30} n-alkanols  \
\[ f \] Unsaturated = \( \sum \) unsaturated n-alkanoic acids
Table A2. Lignin-derived phenol ratios of selected samples.

<table>
<thead>
<tr>
<th>Stratigraphic Unit</th>
<th>Sample</th>
<th>C/V</th>
<th>S/V</th>
<th>(Ad/Al)ₐ</th>
<th>(Ad/Al)ᵥ</th>
</tr>
</thead>
<tbody>
<tr>
<td>TF</td>
<td>Purple Woods (111 m)</td>
<td>0.93 ± 0.27</td>
<td>0.46 ± 0.14</td>
<td>1.03 ± 0.22</td>
<td>2.24 ± 0.92</td>
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<tr>
<td></td>
<td>Purple Woods (134 m)</td>
<td>0.84 ± 0.22</td>
<td>0.49 ± 0.13</td>
<td>0.99 ± 0.38</td>
<td>2.56 ± 0.93</td>
</tr>
<tr>
<td></td>
<td>Rice Lake (151 m)</td>
<td>0.47 ± 0.12</td>
<td>0.33 ± 0.07</td>
<td>1.02 ± 0.23</td>
<td>4.08 ± 1.52</td>
</tr>
<tr>
<td></td>
<td>Rice Lake (166 m)</td>
<td>0.47 ± 0.06</td>
<td>0.38 ± 0.04</td>
<td>3.54 ± 0.52</td>
<td>1.88 ± 0.23</td>
</tr>
<tr>
<td>LNT</td>
<td>Ballantrae (29 m)</td>
<td>1.11 ± 0.21</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<tr>
<td></td>
<td>Earl Bales (13 m)</td>
<td>0.46 ± 0.04</td>
<td>0.23 ± 0.06</td>
<td>0.31 ± 0.31</td>
<td>13.64 ± 11.14</td>
</tr>
<tr>
<td></td>
<td>Purple Woods (11 m)</td>
<td>0.14 ± 0.04</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<td></td>
<td>Purple Woods (80 m)</td>
<td>0.77 ± 0.32</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>INS</td>
<td>Rice Lake (39 m)</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<td>Rice Lake (66 m)</td>
<td>0.39 ± 0.04</td>
<td>0.05 ± 0.01</td>
<td>n.d.</td>
<td>3.38 ± 0.54</td>
</tr>
<tr>
<td></td>
<td>Rice Lake (100 m)</td>
<td>0.46 ± 0.20</td>
<td>0.31 ± 0.09</td>
<td>0.97 ± 0.47</td>
<td>n.d.</td>
</tr>
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<td>Rice Lake (114 m)</td>
<td>0.51 ± 0.04</td>
<td>0.31 ± 0.03</td>
<td>1.18 ± 0.22</td>
<td>1.81 ± 0.39</td>
</tr>
<tr>
<td>Channel</td>
<td>Queensville (14 m)</td>
<td>0.33 ± 0.05</td>
<td>0.26 ± 0.06</td>
<td>0.08 ± 0.03</td>
<td>n.d.</td>
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<tr>
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<td>Queensville (21 m)</td>
<td>0.92 ± 0.21</td>
<td>0.27 ± 0.07</td>
<td>0.11 ± 0.06</td>
<td>23.71 ± 6.43</td>
</tr>
<tr>
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<td>Queensville (82 m)</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>Uxbridge (29 m)</td>
<td>0.43 ± 0.07</td>
<td>0.19 ± 0.02</td>
<td>0.19 ± 0.04</td>
<td>5.08 ± 0.59</td>
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<tr>
<td>ORAC</td>
<td>Ballantrae (17 m)</td>
<td>n.d.</td>
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<td>n.d.</td>
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<td>Ballantrae (25 m)</td>
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<td>n.d.</td>
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<tr>
<td>HT</td>
<td>Earl Bales (5 m)</td>
<td>1.11 ± 0.10</td>
<td>0.08 ± 0.01</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>High Park (4 m)</td>
<td>0.21 ± 0.05</td>
<td>0.36 ± 0.09</td>
<td>1.92 ± 0.31</td>
<td>1.95 ± 0.75</td>
</tr>
<tr>
<td>YT</td>
<td>Uxbridge (79 m)</td>
<td>0.41 ± 0.07</td>
<td>0.41 ± 0.05</td>
<td>0.75 ± 0.20</td>
<td>3.48 ± 0.76</td>
</tr>
<tr>
<td></td>
<td>Uxbridge (83 m)</td>
<td>0.39 ± 0.06</td>
<td>0.34 ± 0.05</td>
<td>0.97 ± 0.18</td>
<td>2.10 ± 0.49</td>
</tr>
</tbody>
</table>
Figure A1. Amount of amphibole calcic hornblende (%) for select samples from the Oak Ridges Moraine.
Figure A2. Amount of iron oxide (%) for select samples from the Oak Ridges Moraine.
Figure A3. Amount of titanite (%) for select samples from the Oak Ridges Moraine.