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Organic matter biomarker analysis as a potential chemostratigraphic tool for Late Pleistocene tills from the Hudson Bay Lowlands, Canada

Nicholas M. Battram, Nick Eyles, Pui Sai Lau, Myrna J. Simpson *

Department of Physical and Environmental Sciences, University of Toronto, 1265 Military Trail, Toronto, ON M1C 1A4, Canada

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ABSTRACT

During the Last Glacial Maximum approximately 22,000 years ago, the Hudson Bay Lowlands (HBL) lay at the center of the 3 km thick Laurentide Ice Sheet. During the course of the last glacial cycle HBL was crossed by ice from the west (the Keewatin sector) and from the east (Labrador sector) but the relative influence of the outflow centers is debateable because of continuing uncertainty surrounding the age and stratigraphic position of lithologically-similar tills in different areas. This study examines the use of organic matter (OM) biomarkers to analyze OM sources in HBL tills. These tills are believed to be of late Wisconsin age (Sachigo, Severn) and an older possibly early Wisconsin deposit (Rocksand Till) and biomarkers may provide insights into source materials and degree of diagenesis. 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 indicate higher *Sphagnum*-derived OM to the Severn and Rocksand tills relative to the Sachigo Till consistent with subglacial reworking and incorporation of peat. OM within the Severn Till is dominated by OM derived from non-woody gymnosperms and non-woody angiosperms whereas Sachigo and Rocksand tills have both woody and non-woody gymnosperms and angiosperms derived OM. Furthermore, the Severn Till contained the most suberin-derived OM, while the Sachigo Till had the least. Acid-to-aldehyde ratios of lignin-derived phenols suggest that the Severn Till has undergone less diagenesis in comparison to Sachigo and Rocksand confirming that it is likely the youngest of the three tills. This study highlights that biomarker analysis is an important chemostratigraphic tool that may distinguish till deposits and provides insight into paleovegetation and paleoclimate in the HBL prior to glacial incorporation of OM into till. This information facilitates paleoenvironmental analyses to be extended into preglacial and interstadial episodes where no stratigraphic record exists.

1. Introduction

The Laurentide Ice Sheet (LIS) was 12.6×10^6 km^2 in extent during the Last Glacial Maximum (c. 22,000 years before present (ybp)) when ice was in excess of 3 km thick over the Hudson Bay Lowlands (HBL), the geographic center of the ice sheet (Dyke et al., 2002; 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 west and east of Hudson Bay respectively (Thorleifson et al., 1992). As a consequence, the changing dynamics of the ice sheet and the relationship with higher resolution paleoclimate records from the Arctic and North Atlantic oceans is debated with several opposing interpretations (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 poorly known age and affinity, despite the presence of known kimberlite pipes. The central challenge in both paleoenvironmental analysis and mineral exploration is to differentiate tills in outcrop and core. This paper has the objective of reporting results of OM biomarker analysis from several tills in the HBL to test the efficacy of using OM biomarkers to differentiate such deposits.

Lack of agreement as to the Wisconsin glacial history of the HBL results in a major data gap in understanding of the LIS 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. The HBL acts as a large depocenter for marine and glacial sediments and Wisconsin tills are of considerable thickness (often in excess of 50 m). Drilling by the Ontario Geological Survey in the Fort Severn area identify that glacial sediment cover on bedrock is as much as 250 m in thickness. HBL tills are mostly massive and fine-textured as a result of the subglacial reworking of pre-existing silty and sandy sediment typical of so-called 'deformation tills' (Benn and Evans, 2010). Large rock clasts are few in

* Corresponding author. Tel.: +1 416 287 7234; fax: +1 416 287 7279.
E-mail address: myrna.simpson@utoronto.ca (M.J. Simpson).

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HBL tills and they commonly contain lenses and rafts of pre-existing sediment that were only partially incorporated and homogenized subglacially under the ice sheet as a soft 'deformable bed'.

HBL tills are exposed in a restricted number of outcrops along rivers and are differentiated on the basis of different ice flow directions indicated by clast fabric analyses, 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) and 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 however by uncertainty surrounding precisely what till unit is being sampled in exposures and cores at sites distant from specific well-studied type sections. Moreover, since all tills are found superposed stratigraphically i.e., the Severn rests on Sachigo which in turn rests on the Rocksand some degree of cannibalization and incorporation of older material is likely resulting in textural and perhaps geochemical overlap between deposits. ^{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 ybp (Forman et al., 1987; Allard et al., 2012). An initial phase of ice sheet growth has been dated to early Wisconsin Oxygen Isotope Stages (OIS) 5b or 4 (Kleman et al., 2010) or even earlier during OIS 5d at about 110,000 ybp (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) could in fact be younger (Kleman et al., 2010, their Fig. 8). Subsequent later Wisconsin ice flows (OIS 3, 2) are recorded by the Sachigo and Severn tills and record an anticlockwise rotation of ice flow direction toward the southwest, south and eventually southeast during the LGM possibly perhaps indicating the increasing influence of ice moving eastward from the Keewatin sector (see Fig. 5 in Dyke et al., 2002) displacing Quebec and Labrador ice southwards and depositing the Sachigo and Severn tills. This is possibly 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 continuing uncertainty is the precise configuration of the Hudson Bay sector of LIS 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 experienced a deglacial episode at around 35,000 years ago (Andrews et al., 1983) and additional 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 ybp respectively (see also Ross et al., 2012; Trommelen, 2013; Dubé-Loubert et al., 2013 for additional discussion). Stokes et al. (2012) on the other hand, identify a single ice free episode at 80,000 ybp 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. Because of the uncertainty, the use of organic geochemical methods, such as OM biomarkers, may provide unique insights into the geologic history of the HBL.

An OM biomarker is an organic compound that can be traced back to its biogenic source due to the preservation of the carbon skeleton of the natural product precursor compound (Simoneit, 2005). Analysis of biomarkers has been used to examine the organic geochemistry of a range of glacial, glaciolacustrine and glaciomarine sediments giving rise to important findings on past vegetation types, sediment or meltwater sources, paleoclimate and age (e.g., Brincat et al., 2000; Ternois et al., 2001; Parnell et al., 2007; Marshall et al., 2009) but has not to our knowledge yet been applied to the terrestrial glacial deposits such as tills of the LIS anywhere in North America. Consequently, there is potential to develop OM biomarker analysis for use as a chemostratigraphic tool for differentiating till deposits in regions such as the HLB. The objective of this study was to investigate the use of OM biomarker analysis to assist with the differentiation of stratigraphic units within the HBL.

2. Materials and methods

2.1. Sampling and carbon analysis

The three HBL tills analyzed in our study are the Severn Till (~ late Wisconsin); Sachigo Till (found below the Severn but also considered late Wisconsin in age; Thorleifson et al., 1992); and the Rocksand Till (~ earliest Wisconsin) collected from type sites along rivers (Fig. 1; Thorleifson et al., 1992). Severn Till was collected from the south bank of the Niskibi River (56° 13′ 01.78″ N 88° 51′ 46.57″ W), Sachigo Till from the east bank of Gods River (56° 09′ 25.12″ N 92° 29′ 23.68″ W) and Rocksand Till from the west bank of the Severn River (54° 58′ 16.77″ N 88° 58′ 30.92″ W). All samples were obtained from unweathered material exposed by excavation and there are no indications of recent OM inputs and were kept refrigerated until analyzed. We collected four random samples (~3 Kg each) from each site. Samples were air-dried and then ground into a fine powder. Preliminary solvent extraction analyses revealed that lipid biomarkers did not vary considerably (standard error ranged between 1.8-9.7% for *n*-alkanes, *n*-alkanols, and *n*-alkanolic acids) and suggested that after grinding, sample heterogeneity was not problematic with respect to biomarker extractions. As such, 250 g from each of the 4 random samples was combined into a 1Kg composite sample for each site. Using a composite sample enabled the use of a sequential biomarker extraction protocol (see Section 2.2) as well as replication of biomarker extractions (each biomarker was extracted in triplicate per composite sample).

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.

2.2. Biomarker extraction and quantification

Solvent extraction and chemolytic methods were performed on the composite till samples to release free and bound lipids, as well as to release any lignin-derived phenols from within the sample (Otto et al., 2005; Otto and Simpson, 2007). Biomarker extractions were performed in triplicate. 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 into the stage of diagenesis (e.g., Ertel and Hedges, 1985).

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 h. 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,