Journal of Archaeological Science: Reports 7 (2016) 155–168

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

The characterisation of amber from deposit sites in western and northern Canada

Jennifer Poulin *, Kate Helwig

Canadian Conservation Institute, 1030 Innes Rd., Ottawa, Ontario K1B 4S7, Canada

ARTICLE INFO

Article history:
Received 26 October 2015
Received in revised form 22 March 2016
Accepted 23 March 2016
Available online xxxx

Keywords:
Amber
FTIR
Py-GC–MS
Resinite
Thule
Amber beads

ABSTRACT

For years, the recovery of amber beads and other objects with amber components from archaeological sites in Canada has raised questions concerning the deposit site sources for this highly traded material. Objects found at one site may have originated elsewhere, thus, the accurate characterisation of amber could aid in establishing trade. In this investigation, 12 distinct amber specimens from 11 deposit sites in Canada were studied in order to determine their subclass and other distinguishing chemical features. The ambers were analysed using Fourier transform infrared spectrometry (FTIR) in combination with pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS), using a thermal separation probe (TSP) to perform the pyrolysis and sample introduction. Analysis of the amber from the 11 deposits in Canada showed that they represent three different classes: Class Ib (based on *regular*-labdanes), Class Ic and Class Id (both based on *enantio*-labdanes). Different forms were found within the Class Ib and Ic ambers, based on the presence and absence of self-crosslinking and free succinic acid. The techniques identified polymeric crosslinking in three subclasses. These include self-crosslinking of communol and communic acid moieties in two Class Ib (form 2) ambers, self-crosslinking of ozol and ozic acid moieties in one Class Ic (form 2) amber and succinylation of the Class Id ambers. Other important characteristics were discovered, including the presence of free succinic acid in six Class Ib (form 1) ambers and one Class Ic (form 1) amber, the presence of diagenetic analogues of both dehydroabietic acid and callitrisic acid in all Class Ib (form 1) ambers, and the attachment of non-polymerisable terpenoids to the macromolecular structures of two Class Ib ambers and one Class Id amber. Amber beads recovered from three Thule sites in the Canadian arctic were characterised and compared to the 12 reference specimens. The beads from site TkAu-1 (Ellesmere Island) were found to originate from the local deposit at Lake Hazen. However, beads from the QeJu-1 (Cornwallis Island) and OkRn-1 (Banks Island) sites closely matched amber specimens from the major deposit at Cedar Lake (Manitoba). This may indicate movement of the Cedar Lake amber to the arctic via trade.

1. Introduction

Canada is rich with amber deposits of varying geological age and subclass. Distinguishing among amber from various Canadian locations is of interest both in the understanding of the organic geochemistry of the deposits, and also in the study of early decorative objects produced by Aboriginal people using these materials. A significant number of amber objects have been recovered from archaeological sites in Canada, particularly in the north. The characterisation of Canadian amber is required to learn more about how this material was used and potentially traded by early people (Wright and Carlson, 1987; Morrison, 1983, 1991).

The Canadian amber included in the current study includes deposit sites from western and northern Canada. The locations of the deposit sites are depicted in Fig. 1. Although these sites contain some of the most abundant Canadian amber deposits presently known, there are also small deposits of amber in many other locations in Canada (McAlpine and Martin, 1969; McKellar and Wolfe, 2010; Poinar et al., 1999; Tappert et al., 2013).

Although there are currently five classes of amber described in the international classification system developed by Anderson et al. (1992), most amber analysed to date is categorised in Class I, having macromolecular structures based on polymers of *regular* or *enantio* labdanoid diterpenes (Anderson and LePage, 1995). Three sub-categories of Class I amber (Class Ia, Class Ib and Class Ic) were initially defined (Anderson et al., 1992; Anderson, 1994), and a fourth (Class Id) was added based on work published from our current project (Poulin and Helwig, 2012). Presently, the class descriptions include:

- Class Ia: resinites based on labdanoid diterpenes having a *regular* configuration, including communic acid, communol and biformene, and incorporating significant amounts of succinic acid. Baltic amber is the only Class Ia resin to date.
- Class Ib: resinites based on labdanoid diterpenes having a *regular*

* Corresponding author.
E-mail addresses: jennifer.poulin@canada.ca (J. Poulin), kate.helwig@canada.ca (K. Helwig).

http://dx.doi.org/10.1016/j.jasrep.2016.03.037
2352-409X/

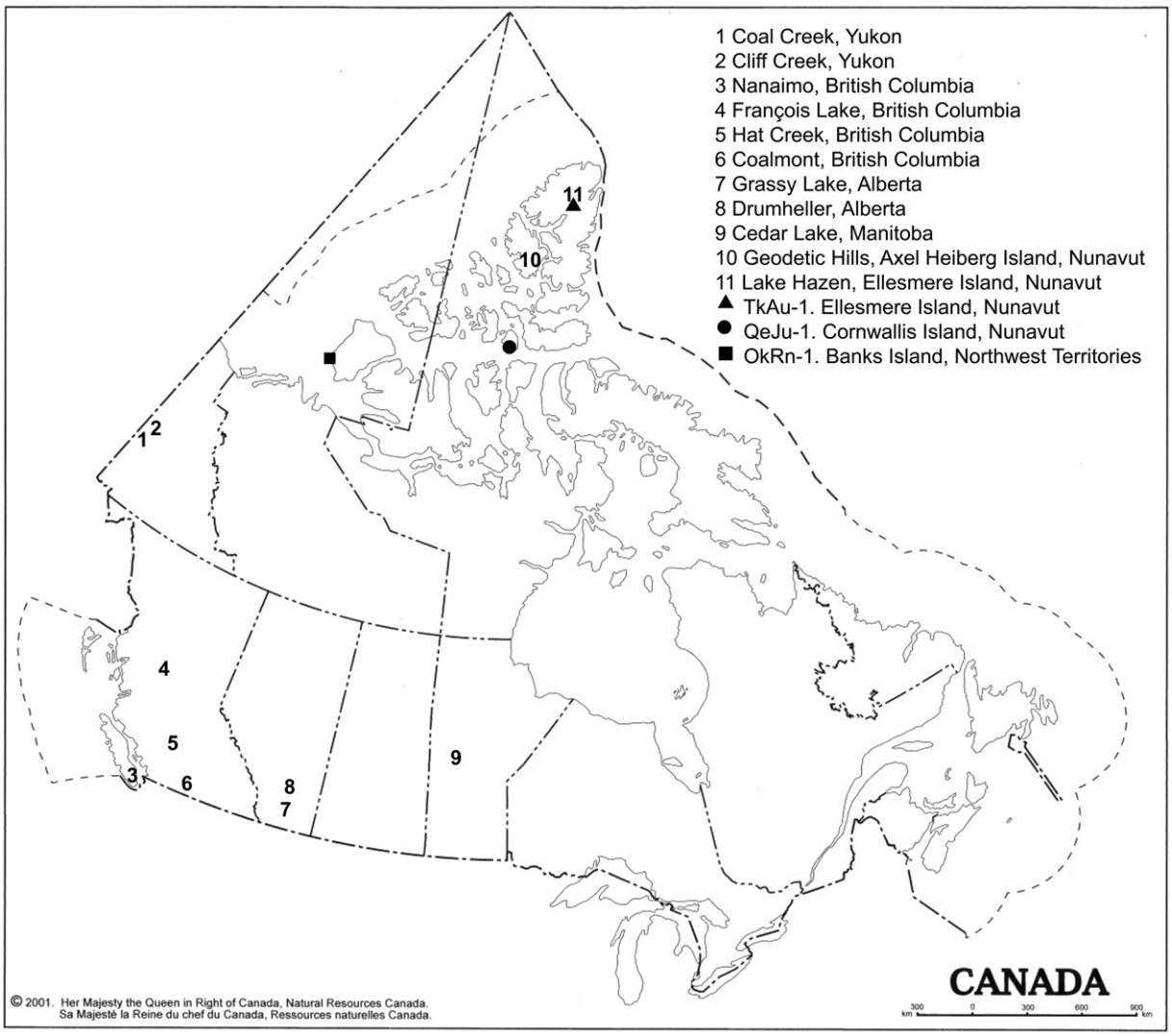

Fig. 1. Locations of amber deposits and archaeological sites included in this study. Map provided by Natural Resources Canada.

configuration, including communic acid, communol and biformene, with the absence of succinic acid.
- Class Ic: resinites based on labdanoid diterpenes having an *enantio* configuration, including ozic acid, ozol and *enantio* biformene, with the absence of succinic acid.
- Class Id: resinites based on labdanoid diterpenes having an *enantio* configuration, including ozic acid, ozol and *enantio* biformene, and incorporating significant amounts succinic acid. Currently, Class Id resinite has only been identified from Canadian deposits.

Based on the work presented in this study, there are subtleties in the sub-classes that are not addressed by the current class descriptions. Molecular structures of the labdanoid monomers in Class I amber are depicted in Fig. 2. Polymerisation occurs from the side chain double bonds when the precursors are exposed to light and air (Clifford and Hatcher, 1995). It has been shown that in addition to polymerisation, certain ambers are also capable of forming stabilising crosslinkages via auxiliary compounds (succinylation in Class Ia and Class Id ambers; Poulin and Helwig, 2014) and through self-crosslinking (Class Ib ambers from Grassy lake and Cedar Lake; Poulin and Helwig, 2015).

In addition to the polymer matrix, amber also contains non-polymerisable compounds such as low molecular weight organic acids, monoterpenes, and diterpenes (abietanes and pimaranes). Previously thought to be free within the macromolecular structure, recent studies have shown that a portion of the terpenoids are bound to the polymeric structure in certain ambers (Poulin and Helwig, 2015). The composition and abundance of these non-polymerisable compounds varies widely among amber samples – even within samples from the

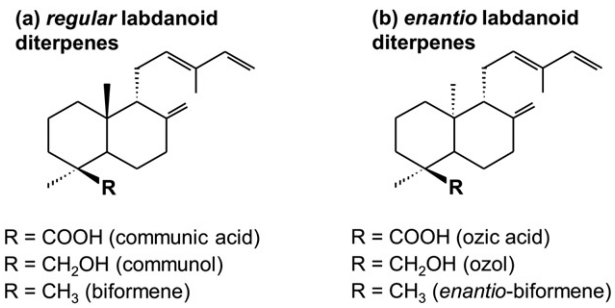

Fig. 2. Molecular structures of labdanoid diterpenes of Class I ambers.