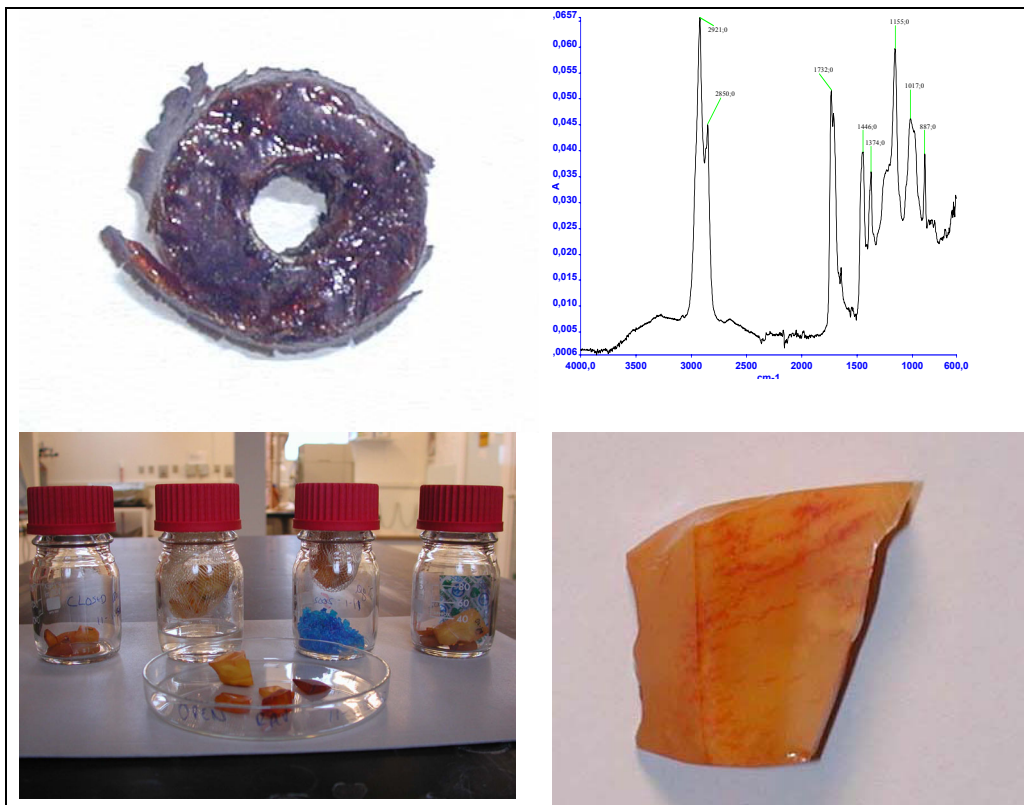# Degradation and inhibitive conservation of Baltic amber in museum collections

Yvonne Shashoua, PhD
March 2002

NATIONALMUSEET

Degradation and inhibitive conservation of Baltic amber in museum collections

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Acknowledgements

1. Abstract

Degradation and inhibitive strategy for Baltic amber in museum collections

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Degradation and inhibitive conservation for Baltic amber in museum collections

1. Abstract

A survey completed in March 2000 suggested that the National Museum of Denmark had more than 17,000 pieces of amber in its collections, making the collections amongst the most significant in Europe. Most of the amber is the Baltic form, and at least 50 million years old. The survey also concluded that 45% of amber objects in the National Museum's collections exhibit deterioration. Around 25% have degraded to such an extent that immediate conservation is necessary; it has been estimated that this would require approximately 8 years work

Degradation of amber in the National Museum collections is manifested by disintegration and loss of surface structure, accompanied by considerable changes in optical properties and in texture. To date, preservation of degrading amber has focused on active conservation approaches such as the application of polymeric materials for impregnating and consolidating fragile examples. Although such treatments may have been effective at consolidating and supporting fragmentary amber surfaces at the time of application, the conservation materials themselves have now deteriorated with time.

Based on the undesirable results of early active conservation treatments, the possibilities for an alternative preservation strategy were investigated. Inhibitive conservation techniques involve controlling the environments in which objects are placed during storage, display and transport, with the aim of slowing those chemical reactions which cause or accelerate deterioration. The study described investigated the factors which influenced deterioration of Baltic amber. Model material was thermally aged in environments which varied relative humidity and oxygen levels to replicate the real-time ageing process.

Findings from all analytical and examination techniques employed in this research project, indicated that the environment in which new Baltic amber is stored, influenced the rate and extent of deterioration. In general, the ageing environments which involved enclosing amber in a container, thereby creating a controlled microclimate, were measurably more effective at inhibiting discolouration, weight loss, degradation of chemical and physical properties than those which exposed samples to the variations of an open environment. Findings from weight loss and discolouration measurements, ATR-FTIR spectroscopy and LV-SEM also suggested that the presence of oxygen, generally thought to be the sole cause of deterioration of amber, was not the only factor in the deterioration mechanism. The presence of water vapour was also important to the rate and extent of deterioration. Further research is required to define the role of water in amber's degradation mechanism.

2. Introduction and background to the research project

Amber collections in the National Museum of Denmark
A survey completed in March 2000 suggested that the National Museum of Denmark has more than 17,000 pieces of amber in its collections (Jensen and Jensen, 2000). The collections are amongst the largest in Europe. Most of the amber is the Baltic form, and at least 50 million years old. It is generally accepted that Baltic amber originated from a vast 'amber forest' in Scandanavia at the beginning of the Tertiary period. It was redistributed first by the glaciation of northern Europe and then by postglacial rivers. As a result, Baltic amber is now found on the east coast of England, eastern parts of the Netherlands, throughout southern Scandanavia, northern Germany, Poland and in Russia down to the Black Sea (Beck, 1986).

After its original use, usually as jewellery or other decorative pieces, amber is likely to be buried for many years in earth or under water in a bog. As a consequence, most of the archæological amber in the National Museum originates from one of these two places. Amber may also be washed up on coasts by seawater and polished by the action of small pebbles and sand, however it usually has another origin.

The Museum's amber collection is of interest to archæologists since amber jewellery refects the economic, social, religious and other cultural beliefs of the peoples who made and wore it. Archæobiologists are more interested in insects and microorganisms trapped during formation of amber. Archæobotanists study the plant source of the amber. For these reasons, it is important that the collections are preserved for study and enjoyment of future generations.

Condition of amber collections
The survey completed in March 2000 also concluded that 45% of amber objects in the National Museum's collections exhibit deterioration. Around 25% have degraded to such an extent that immediate conservation is necessary; it has been estimated that this would require approximately 8 years work (Jensen and Jensen, 2000). The environment in which amber objects were found, greatly influenced their condition and appearance. Amber found in bogs was in better condition than those from dry archæological sites. Only 4% of amber objects originating in a bog exhibited a high degree of degradation in comparison with 40% of objects buried in dry earth. Amber found in dry earth frequently had a thick, pale coloured surface crust which cracked and subsequently crumbled. Bog-found amber was dark brown in colour, and either exhibited no surface crust film or very little.

Degradation of amber in the National Museum collections is manifested by disintegration and loss of surface structure, accompanied by considerable changes in optical properties and in texture (Figure 2.1). Concern for the poor condition exhibited by many of the pieces and the risk of further damage has resulted in restricted access to the collection by curators and students and has reduced the opportunities to display and loan these pieces.

Figure 2.1 Degradation typical of that observed in Baltic amber collections in The National Museum of Denmark. The surfaces have flaked and separated from the body of the piece. Cracks may be observed in the surface .

Conservation of Baltic amber

Once amber objects are registered in museum collections or accessioned, the institution becomes responsible for their long term preservation, until the end of their useful lifetime; that point is reached, arguably, when the object ceases to have a recognizable form or meaning (Bradley, 1994).

Conservators consider two approaches to conservation when planning treatment for any degraded object; they are known as active and inhibitive. Active conservation treatments are those involving practical activities applied as necessary   to individual objects to limit further deterioration and repair damage. They include adhering broken sections, cleaning surfaces and filling missing areas to strengthen objects weakened by deterioration.

To date, practice and research   into the preservation of degrading amber has focused on active conservation approaches such as the application of polymeric materials for impregnating and consolidating fragile examples.   Conservation methods used between 1870 and the 1980s aimed to consolidate and stabilize the fragmented surfaces of deteriorated amber objects, thereby facilitating handling.

The earliest polymeric materials used in the consolidation process were based on aqueous solutions of natural products, such as gelatin, isinglass and agar-agar, sometimes softened by including glycerin in the formulation. The mixture was applied, sometimes warm, to the surface and was often hardened or cross-linked using phenol or formalin. An early treatment to inhibit dehydration of newly excavated

amber involved immersion of pieces in a warm aqueous solution of gelatin to which glycerin and phenol had been added.

Tree resins such as dammar, insect resins, such as shellac, blown or oxidized oils and waxes were applied to surfaces either instead of the aqueous treatments or in addition to them. Vacuum was often applied to facilitate impregnation of treatments. After 1965, natural consolidants were replaced with solvent-based synthetics, including Bedacryl 122X diluted with xylene (Villemos, 1976). Paraloid B72 (poly (ethyl-methyl methacrylate)) has been widely used as a consolidant, since it contains different chemical groups to those found in amber and therefore, does not interfere with analysis by Fourier Transform Infrared spectroscopy (Thickett, 1995).

Although such treatments may have been effective at consolidating and supporting fragmentary amber surfaces at the time of application, the conservation materials themselves have now deteriorated with time. Shrinkage, embrittlement and discolouration of the polymeric materials are visible today; in many cases the degrading material has damaged the structure and appearance of the original surface of the amber object (Figure 2.2). This is a highly undesirable outcome for a conservation treatment. In addition, it is extremely difficult, if at all possible, to reverse the long-term damage caused by such treatments in order to recover the original amber. The use of concentrated acids, heat and enzyme treatments has been studied in the past and is currently being investigated by members of the Organic Materials Conservation Section at the National Museum (Jespersen and Meyer, 1984).

Figure 2.2 Gelatine was an early consolidation treatment for friable amber surfaces. With time it has darkened and shrunk, pulling the original amber surface away from the body of the object.

Based on the undesirable results of early active conservation treatments, it seems sensible to adopt an alternative preservation strategy. Inhibitive conservation techniques involve controlling the environments in which objects are placed during storage, display and transport, with the aim of slowing those chemical reactions which cause or accelerate deterioration. This may involve limiting the exposure of objects to sources of energy for degradation reactions such as heat, light. The levels of moisture and airbourne pollutants may also be controlled. If applied successfully, such an approach can help to prolong the useful lifetime of many objects at the same time. The majority of plastics objects in museums spend their useful lifetimes in storage areas. In addition, inhibitive conservation techniques, unlike active ones, are more likely to comply with the ethical practices of professional conservators, the major one of which is summarized in the code of practice (American Institute for Conservation, 1994):

'The conservation professional must strive to select methods and materials that, to the best of current knowledge, do not adversely affect cultural property or its future examination, scientific investigation, treatment or function.'

At the time of writing, little basic research has been conducted to establish the mechanisms by which amber degrades. International research projects have, instead, concentrated on elucidating the chemical constituents of amber, its botanical sources, provenance and inclusions. However, in order to slow the rate of degradation of amber, it is essential to have a deeper understanding of those factors which initiate and catalyse the degradation process. This was the main purpose of the research project described in this report.

The main objective of this study was to define the major factors which initiate or catalyse degradation of Baltic amber. This information was used in the development of an inhibitive conservation technique which would prolong the useful lifetime of Baltic amber for a longer period than was currently possible.

This was achieved via 4 minor objectives:

- literature search to define the status of research in this field.

- evaluation of the analytical techniques most likely to provide information concerning the chemical and physical properties of Baltic amber in good and degraded condition. These techniques were applied to the forms of Baltic amber most frequently encountered in the National Museum's collections.

- based on the data obtained, major changes to Baltic amber on ageing were determined using qualitative and quantitative techniques.

- factors most likely to initiate or catalyse deterioration were evaluated by examining their effect on undeteriorated amber under accelerated thermal ageing conditions, known to promote degradation.

3. Baltic amber; structure and deterioration

Origin and chemical structure

Amber originates as a liquid resin produced by a conifer tree, *Pinus succinfera,* not related to the modern Pinus species. Fossilization of amber (a process in which liquid resin is transformed to solid amber) occurs in two apparent stages. Partial polymerization occurs first; cross-linking and organization of terpeniods in the tree resin take place over thousands of years. The process follows a free-radical reaction mechanism in the presence of heat and pressure. Copal is the product of this stage, a hard material, although volatile terpene oils are still present. The oils evaporate over a period of millions of years to form amber.

Baltic amber is a high molecular weight cross-linked polymer, the product of esterification of a polyvalent alcohol with a dibasic acid. The polyvalent alcohol is the co-polymer of communal and communic acid as found in kauri resin while the dibasic acid is succinic acid. The esterification process introduces cross-links either between different polymer molecules or different parts of the same molecule, thereby increasing average molecular weight and structure rigidity, while reducing solubility. Sea water has been cited as a catalyst for the fossilization process (Moreno, 1999), however this idea has not been further discussed by other researchers in the field. Baltic amber is also known mineralogically as succinite, due to the high content of succinic acid $HOOCCH_2CH_2COOH$ (up to 8%) (Moreno, 1999). However, it has been suggested that succinic acid is not an original component of amber, but a degradation product of abietic acid (Rottlaender, 1970).

Amber also has some properties of ion-exchange resins due to the presence of free carboxylic acid groups on the polymer. When extracted with tetrahydrofuran, the polymer contains soluble (20-25%), and insoluble (65-75%) fractions. The insoluble fraction has been identified as crosslinked polyabietic acid (Urbanski, 1984). The empirical formula of Baltic amber has been stated both as $C_{10}H_{16}O$ (Brydson, 1999) and $C_{79}H_{10.5}O_{10.5}$ (Frondel, 1968). Sulphur is present in small quantities (0.26-0.34%) and is used to distinguish Baltic amber from other natural resins. A small amount of inorganic matter is also present.

In addition to the polymeric material, Baltic amber is also composed of lower molecular weight volatile compounds (2-5%), including aromatic hydrocarbons (cymenes) and monoterpenes, including borneol, camphor, fenchyl alcohol and fenchone. Terpenoids, found in all natural resins, are based on linking isoprene or 2-methyl-1,3-butadiene (C_5H_8) units.

C
|
tail   C=C- C=C   *head*

One isoprene unit

monoterpenes, C10 : head to tail linkage of two isoprene units
sesquiterpenes, C15: head to tail linkage of three isoprene units
diterpenes, C20: head to tail linkage of four isoprene units

triterpenes, C30: tail to tail linkage of two sesquiterpene units; 6 isoprene units in total
tetraterpenes, C40: tail to tail linkage of two diterpenes ; 8 isoprene units in total

Source: (Moreno,1999)

The fact that diterpenes can be detected in amber suggests that at no time can it have
been subjected to severe geological conditions which would have lead to loss of
functional groups and the subsequent formation of hydrocarbons.

Physical properties
The colour of Baltic amber is most frequently golden-yellow, but ranges from
colourless to deep red-brown. Amber may appear cloudy, due to the presence of
bubbles of gas which accumulate during the escape of volatile components during its
formation. The size of the gas bubbles and their spatial position control the colour and
clarity; amber possessing a large number of bubbles in the greatest concentration
appears white.

Amber does not have any crystalline areas, so has no cleavage planes. It fractures
conchoidaly. The hardness of Baltic amber increases from bony amber ($20kg/mm^2$) to
bastard ($25kg/mm^2$) and ordinary clear transparent amber ($26.2kg/mm^2$).
Measurements vary within individual pieces of amber because of its heterogeneous
structure (Savkevich, 1967). It is slightly harder than a fingernail.

Density of amber is between $1.05-1.095g\ cm^{-3}$ but such values are influenced by
inclusions of air bubbles (known as foamy amber) or minerals. Amber does not float
in sea water, only in heavily saturated salt water. Baltic amber decomposes on
melting, depending on the rate of heating, temperatures range from 290-420ºC. Such a
range indicates that Baltic amber comprises a high level of polymerization and,
perhaps, crosslinking. Amber becomes thermoplastic above 150ºC and produces 'oil
of amber' plus a residue of amber colophony or amber pitch. When burnt, amber
produces a steady flame with black smoke.

There are no solvents which completely dissolve amber-it is insoluble in ketones, up
to 10% soluble in hydrocarbons, up to 20% in chloroform and ethers, and up to 25%
in alcohols. Atmospheric oxidation or weathering increases solubility, particularly in
polar solvents. Nitric acid also causes decomposition (Brydson, 1999).

Analytical techniques applied to amber

Infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy has been applied to amber mainly to establish whether a resin is fossil or recent and to obtain provenance information. It is an effective technique for the examination of amber because polymerization preserves all the original functional groups with the exception of C=C, though the absorbances may be weaker in the fossilized material. Assignments of chemical groups to FTIR bands are summarized in Table 3.1. A typical FTIR spectrum is presented in Figure 3.1.

Baltic amber shows a highly characteristic broad and perfectly horizontal shoulder between 1250 and 1175 cm^{-1}, followed by a sharp absorption peak which reaches maximum intensity just below 1150cm-1, attributed to C-O stretch. Oxidized amber shows a change in the slope of the shoulder between 1250 and 1150cm^{-1} (Beck, 1965). A shift in the infrared bands attributed to C-C bend from 1600cm^{-1} to higher wavenumbers was also observed during oxidation. This suggested a transition from conjugated to isolated double bonds (Alekseeva, 1966).
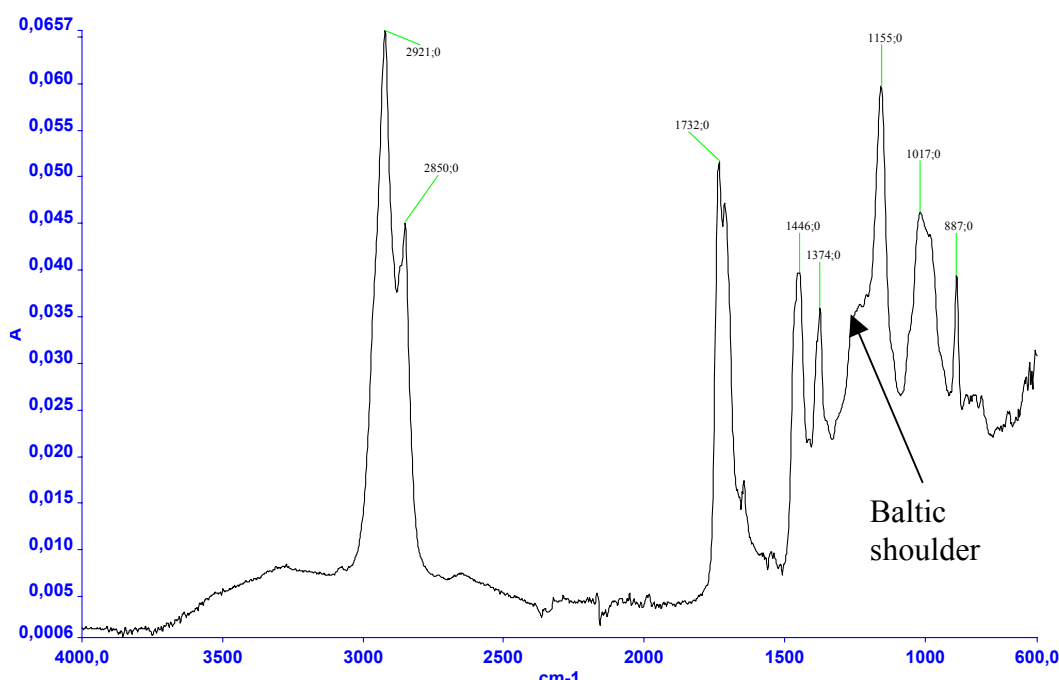

Figure 3.1 Typical FTIR spectrum of Baltic amber, showing the definitive Baltic shoulder area. The shoulder is not horizontal, suggesting that the sample is partially oxidized.

wavenumber (cm^{-1})	assignment to chemical group
3500	O-H stretching, due to atmospheric water vapour absorbed during formation of amber
3095	exocyclic methylene
2950	C-H stretching
1700	C=O
1650	O-H bending or C=C stretch , non-conjugate
1625	exocyclic methylene group
1470	C-H bending
1380	C-H bending
1250-1000	C-O bonds, characteristic of succinite
1250-1175	perfectly horizontal 'Baltic shoulder', becomes negative slope in oxidised amber
885	CH$_2$ out of plane bending of H atoms

Table 3.1 Assignment of infrared bands for Baltic amber
Source: Moenke,1961 and Beck, 1986

Near Infrared-Fourier Transform (NIR-FT)-Raman spectroscopy
NIR-FT-Raman spectroscopy has chiefly been used to distinguish between genuine and false, or synthetic, amber (Edwards, 1996). It has also been used to establish the structure of amber from various sources and, thereby, to identify its origin. The advantage of FT-Raman spectroscopy over many other techniques is that samples need no preparation. However, practical difficulties such as strong fluorescence when the source laser is applied to the sample in the visible region, first have to be overcome. The intensity of bands at 1646 cm^{-1} (attributed to C=C) and at 1450 cm^{-1} (attributed to CH$_2$) were ratioed and found to be lower for Baltic amber (0.35) than for amber from other origins which gave values up to 0.68 (Moreno, 2000). Such low values indicate a higher maturation of Baltic ambers compared to, for example, those from South America.

Gas chromatography-mass spectrometry (GC-MS)
The ether-soluble fraction of Baltic amber was found to contain many diterpenoids of the abietane, primarane and labdane series using GC-MS. The tetrahydrofuran-soluble fraction comprised p-cymene (49% by weight), fenechol (10% by weight), 1,8-cineol (8% by weight), borneol (6% by weight) and camphor (3% by weight) (Urbanski, 1976). Pyrolysis GC-MS has also been used to identify amber objects (Bocchini, 1988), and results indicate that fossilized amber has a primary chemical network consisting mainly of monoterpenes and sequiterpenes (Heck, 1999).

Thin-layer chromatography (TLC)
TLC has been used to identify chemical compounds in Baltic amber and to compare its structure with those of other resins (Labez, 1968). TLC of ethanolic extracts of amber have been shown to contain carboxylic acids, esters, α-keto acids, α-hydroxy acids, aldehydes, ketones, aliphatic, aromatic and unsaturated hydrocarbons, terpenes and steriods (Matuszewska, 2000).

Deterioration of Baltic amber

Despite the fact that amber is many millions of years old and might be thought to have achieved chemical stability, this is not the case.

Oxidation or weathering of the surface of amber is widely accepted to be the major cause of deterioration, although the detailed mechanism remains unpublished. Degradation is manifested as darkening of the material as a result of oxidation of C=C bonds to form acid and ester groups. The formation of a weathering crust at the surface is also observed. The hardness of an oxidized layer in amber is 15-40% higher than that measured before deterioration (Savkevich, 1967). Either pits form in the surface of the amber due to increased sensitivity to water, or the surface becomes raised (Srebrodoloskii, 1979). As degradation progresses, the surface fragments. An investigation into the effect of indoor climate on Dominican amber in a museum collection, suggested that amber was more humidity sensitive than has generally been appreciated (Williams, 1990). The study concluded that exposure to both high and low levels may promote deterioration.

Carbon, hydrogen and sulphur contents of amber reportedly decreases as a result of deterioration, while oxygen content increases. Weight also increases during oxidation, as does peroxide number and acid number. Oxidized amber can be used to initiate the polymerization of styrene and methyl methacrylate following a free radical reaction (Serganova, 1964).

4. Research project – experimental methods

Overview of experimental design
The first objective of the experimental study was to define which environmental factors, if any, initiated or catalysed the degradation of fresh Baltic amber in good condition.

Samples of recently mined, undeteriorated, amber were exposed to various environments, all of which are frequently used to store and display organic materials in museums. Due to lack of time and the opportunity to compare the results obtained from this project with those of other researchers, accelerated thermal ageing was used to initiate degradation instead of natural ageing. Non-destructive examination techniques or those causng minimal damage were used to identify and quantify changes in visual, chemical and structural properties of samples during thermal ageing (Table 4.1).

technique	frequency of measurement during thermal ageing	depth of analysis	information available
visual examination/ photography	every 7 days	whole sample	-change in colour, surface appearance and tackiness on ageing
weight loss	every 7 days	whole sample	-quantitative loss of volatiles
Attenuated Total Reflection-Fourier transform infrared (ATR-FTIR) spectroscopy	every 7 days	approximately 2μm, depending on wavelength	-definitive chemical groups -changes in chemical groups due to degradation
Low-vacuum scanning electron microscopy (LV-SEM)	as required	2-3μm	-morphology and physical microstructure - elemental composition of surface and cross-sections
colour measurement using Natural Colour System	every 7 days	surfaces of sample	-change in colour of surfaces caused by deterioration

Table 4.1 Examination techniques applied to samples of amber

Preparation and characterization of amber samples

Large (approximately 80 x 60 x 30mm) raw pieces of Baltic amber originating from a mine in Kaliningrad were bought from Ravfehrn A/S, a company based in Vangede, Denmark. Pieces were selected for their visible homogeneity and pale colour. Samples were cut to size with a hack saw and polished to remove the original surface crust and roughness using a Struers water- cooled rotating, polishing machine fitted with silicon carbide papers grades between P#200 and P#2400. Attempts were made to minimize heating of the surfaces of samples during preparation. Large (approximately 20 x 20 x 20 mm) and small samples (approximately 5 x 5 x 5mm) were prepared in order to investigate whether the influence of bulk was a factor in the rate and extent of deterioration.

Unaged amber was characterized using Fourier Transform Infrared (FTIR) spectroscopy, thermal analysis and water content.

Examination by FTIR spectroscopy
Attenuated Total Reflection Fourier transform infrared (ATR-FTIR) spectroscopy was used to characterize the chemical groups present at surfaces of prepared sample material, non-destructively.

Spectra were collected over 30 scans at a resolution of $4cm^{-1}$ between $4000cm^{-1}$ and $600cm^{-1}$ (the lower limit of sensitivity for ATR), using an ASI DurasamplIR single reflection accessory with an angle of incidence of 45° and fitted with a diamond internal reflection element in a Perkin-Elmer Spectrum 1000 FTIR spectrometer. Initial trials showed that 30 scans were the minimum number required to obtain well-resolved spectra for the samples. The high refractive index of diamond compared with that of amber (2.4 and 1.5 respectively) allowed absorbance data to be collected from a depth approximately equal to that of the wavelength of the infrared radiation, a maximum depth of approximately 2 microns (Coombs,1999). Background spectra were collected from 30 scans of the empty, clean accessory open to air.

The quality of spectra depended on intimate contact between the DurasamplIR reflection element (the diamond crystal had an active area of 1mm diameter) and the surface of interest. Identical pressure distribution was achieved for all samples using the flat, circular tip of the pressure device (3mm in diameter) supplied with the accessory in combination with the torque limiter which allowed the press to be tightened to the same, repeatable level.

A representative spectrum is shown in Figure 4.1. It is typical of that obtained from Baltic amber. In particular, the presence of the definitive 'Baltic shoulder' between 1250 and 1175 cm^{-1} confirms that the amber cannot be from another geographical source. In addition, the negative slope of the shoulder suggests that, although there is likely to be some oxidized material present, the condition of the amber is largely undeteriorated.

Figure 4.1 ATR-FTIR spectrum of prepared amber samples from Kaliningrad with the major molecular bonds attributed to bands in the spectrum
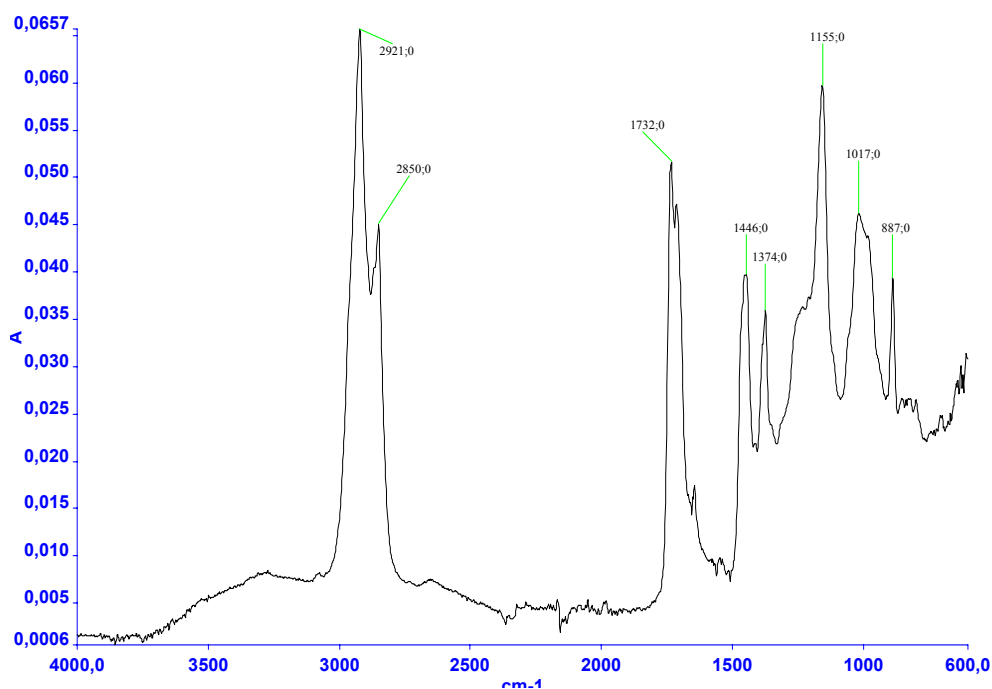
wavenumber (cm^{-1})	molecular bond
3800-3200	O-H stretching due to water from atmosphere or contained in amber
2920	C-H stretching
1730	C=O
1650	O-H bend and C=C stretch, non-conjugated
1450	C-H bend
1380	C-H bend
1250- 1175	definitive 'Baltic shoulder' –horizontal in unoxidised amber, slopes negatively in oxidized amber
1155	C-O deformation
887	CH$_2$ out of plane bending of H atoms

Thermal analysis

Thermal analysis was used to examine the weight lost by sample material on heating between room temperature and 800°C in the absence of oxygen. Weight loss corresponds to water, volatile material and degradation products produced on heating in the absence of oxygen. Products may be identified both by their molecular weight and by the temperature at which they are produced.

In order to relate the composition and behaviour of prepared amber samples from Kaliningrad to that of 'real' amber objects from the National Museum's collections, a microsample of Baltic amber which had been excavated from a waterlogged moor in Denmark and another which had been excavated from a dry archæological site, were

thermally analyzed at the same time and under identical conditions. Thermal analyses were carried out by Dr. Marianne Odlyha at Birkbeck College, University of London, England, using a Shimadzu TGA instrument.

The traces obtained for the new amber from Kaliningrad, the moor and that from the dry ground were similar (Figure 4.2) suggesting that their chemical structures and response to heating were similar. New amber and that excavated from dry ground exhibited a distinct stage in which physically adsorbed water was lost, early in the heating process. In contrast, amber from the moor, did not have a discrete stage at which loss of water took place; it was, instead, associated with the onset of decomposition. The onset of decomposition occurred at around 380°C for new amber compared with 320 and 350°C for dry earth and moor-buried amber respectively. These results indicated that changes in chemical composition took place during ageing which caused a reduction in thermal stability.
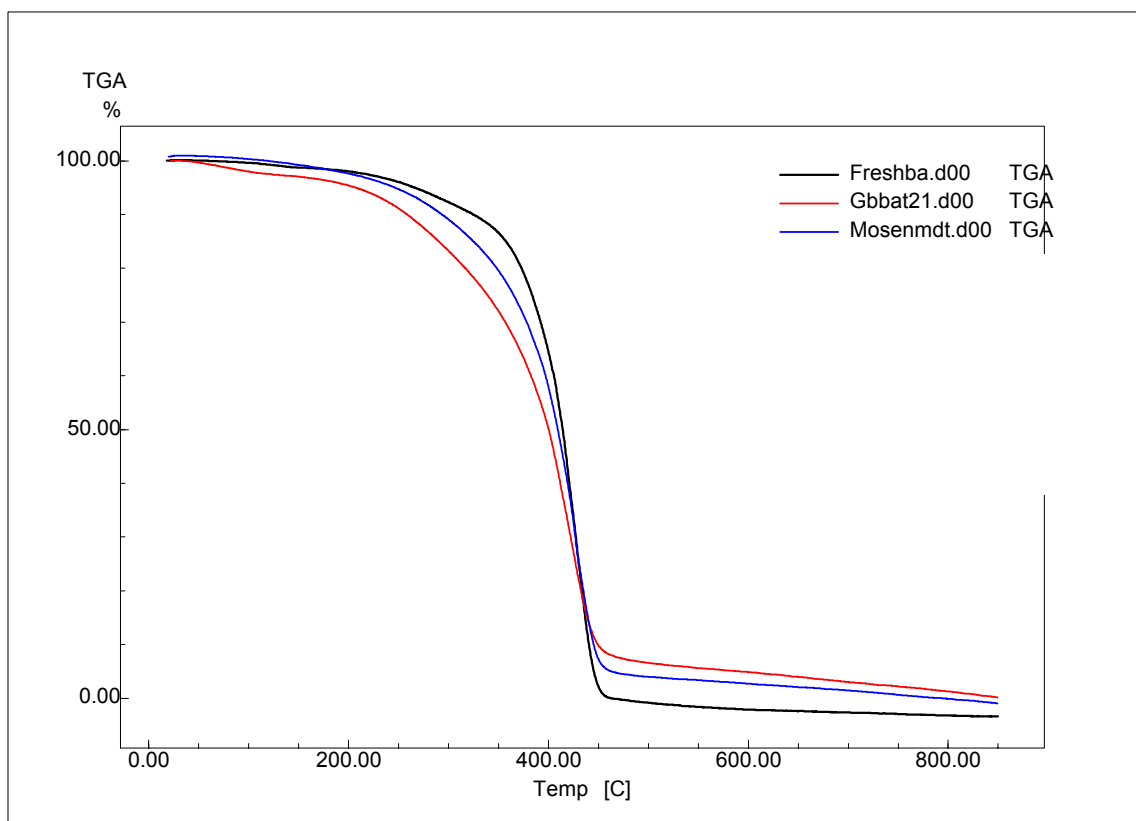

Figure 4.2 Results of thermogravimetric analysis for new amber from Kaliningrad (black trace), dry-earth buried amber (blue trace) and wet moor-buried amber (red trace)

Water content
Water content of new amber was determined by drying three pre-weighed samples (2g) at 110 ± 1°C in a convection oven until they achieved constant weight (± 0.001g). Samples exhibited no discolouration and the measured in weight was attributed to water. Water content was determined as between 0.6 and 0.7%.

Preparation of storage environments

Large and small samples were exposed to various environments, all of which were frequently used to store and display organic materials in museums (Table 4.2). Accelerated thermal ageing in the absence of light was used because it was thought to represent the natural ageing environment in a museum store more accurately than accelerated exposure to light.

Since a previous experimental study into the deterioration of amber at the National Museum had successfully used a thermal ageing temperature of 100°C for a period of one month, a regime which neither softened nor melted samples, the same ageing procedure was adopted for the present work.

All storage environments were maintained at 100±1 °C and achieved using a convection oven. Enclosed environments were created in wide-neck Pyrex glass flasks (100mL) fitted with heavy duty melamine resin screw caps lined with polytetrafluoroethylene (PTFE) as shown in Figure 4.3. All materials used were selected for their very low absorption of volatiles or water vapour, high chemical stability and ability to isolate the ageing environment from the exterior conditions. Samples of polished amber were contained in position in the centre of the flask in a fine nylon net caught between the cap and screw thread. The purpose was to provide equal opportunity for movement of gases and vapours around all surfaces of the sample. Adsorbent materials were used either to modify the properties of the air inside flasks prior to ageing or to remove degradation products formed during the ageing process.

Open environment was achieved by placing samples in an open glass petri dish (Figure 4.4).

All environments were created under ambient conditions before being placed in a convection oven and heated, over a period of 8 hours, to the 100± 1°C ageing temperature.

Table 4.2 Experimental storage environments used to thermally age new Baltic amber

environment *	equivalent museum storage	function	how achieved
open oven	naturally ventilated storage area or display case	avoid build-up of pollutants	samples placed on glass petri dish in convection oven
closed	box or other container	exclude dust, buffer climate variations	samples suspended in closed screw-cap flask
high relative humidity	high RH	moisten air	water (20mL) in base of closed flask
low relative humidity	low relative humidity (RH)	dry air	silica gel placed in base of closed flask
oxygen-free	oxygen-free environment	inhibit oxidation pest control	Ageless oxygen absorber sachets placed in base of each flask, before flushing with N_2

*** all environments were maintained at 100 ±1°C*

Figure 4.3 Experimental storage environments used to thermally age amber. From left to right: open ageing, closed, high RH, low RH, oxygen-free
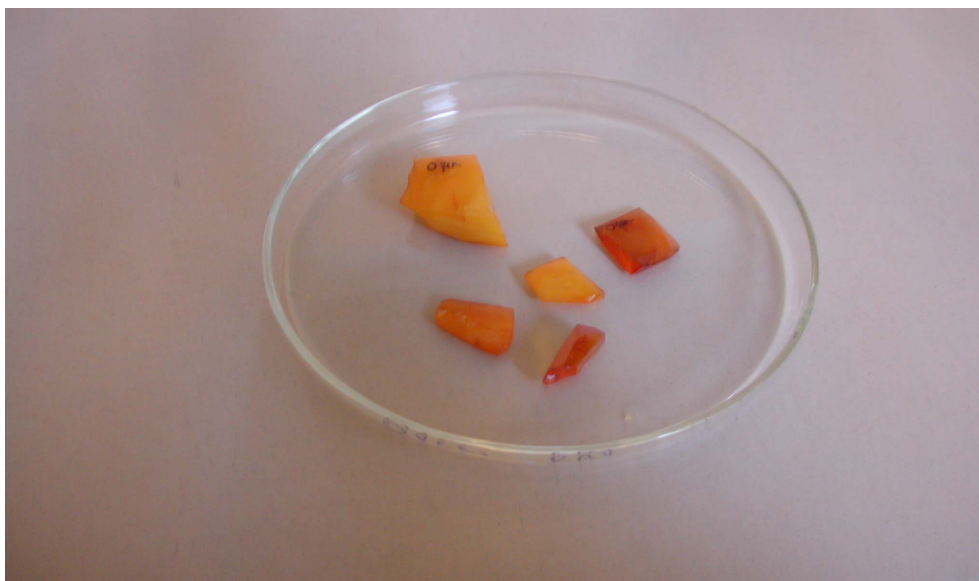
Figure 4.4 Detail of set up for open ageing of amber. Samples were placed on a petri dish before being placed in a convection oven at 100°C

Ageless® oxygen absorber

Ageless® oxygen absorber is a commercial product originally designed to inhibit the oxidation of foods during transport. It is available as gas-permeable plastic sachets containing finely-divided iron which oxidizes to form iron oxides in the presence of oxygen and water, taking the oxygen from the surrounding environment. The moisture is provided by the presence of potassium chloride in the sachet and is also a by-product of the oxidation reaction (Grattan and Gilberg, 1994*)*. Different grades of Ageless® are available; Ageless® Z is recommended for the preservation of materials with a water content of between 0 and 85%, so was considered suitable for use with amber. Ageless® Z has been used as a low-cost, convenient alternative to flushing with nitrogen for long-term oxygen-free storage of natural rubber in the British Museum (Shashoua, 1999).   It is claimed that Ageless® oxygen absorber reduces the oxygen concentration of an air-tight container down to 0.01% (100ppm) or less (Mitsubishi Gas Chemical Company, 1987).

To prolong the active lifetime of Ageless® during use, containers were flushed with oxygen-free nitrogen immediately prior to closing. Ageless® Eye is the oxygen indicator supplied with Ageless®; it is in the form of a pressed tablet which changes colour from pale pink (less than 0.1% oxygen) to dark blue (greater than 0.5% oxygen). Previous experience by the author suggested that Ageless® Eye tended to lose its sensitivity to oxygen after approximately six months usage, manifested by unreliable colour changes. Since the ageing period in this project was shorter than the stability period for Ageless® Eye, it was used and added to each container together with one sachet of Ageless® Z. Sachets were renewed weekly after flasks were opened to examine samples.

Silica gel

Silica gel is frequently used in museum showcases and storage containers to adsorb water vapour and achieve a specific RH in the surrounding airspace. The empirically determined quantity of silica gel required to buffer ambient RH is 20 kilograms per cubic metre of display case volume (Cassar, 1995). On the basis of this general rule, 100mL flasks would require 2g of silica gel at 20°C. Since the performance of silica gel at 70°C is not known accurately, an excess (5g) was used. Self-indicating silica gel, supplied by Merck Ltd., was conditioned at 150°C for 12 hours and cooled in a desiccator to 20°C prior to adding to the Pyrex flasks.

Accelerated thermal ageing procedure

Accelerated thermal ageing of all amber samples was carried out at the same time to minimise the effect on samples of variation in temperature and RH in laboratory and oven. All ageing was continued for a period of 35 days. An earlier study by Jespersen and Meyer suggested that this period was sufficient to initiate visible deterioration in Baltic amber.

Samples were removed weekly from their ageing environments for visual examination and photography, measurement of weight loss, discolouration and FTIR spectroscopy. On removing from the oven, samples were allowed to attain ambient temperature gradually over a period of 2 hours prior to examination. Low-vacuum scanning electron microscopy (LV-SEM) was carried out at the start and completion of the ageing period.

Weight loss

Weight loss is a simple technique used to identify whether chemical changes, loss of volatile material or water vapour had taken place during ageing. Prior to placing in their ageing environments, large and small amber samples were weighed to four decimal place accuracy using an electronic analytical balance. Throughout the thermal ageing process, samples were re-weighed once per week. Samples were removed from their ageing environment, whether it was flask or watchglass, and conditioned to ambient temperature (20-23°C) after patting their surfaces dry. Weight loss was determined immediately prior to examination by FTIR spectroscopy.

Change in appearance and colour of amber samples

The appearance of amber samples throughout the ageing process was recorded using a digital camera, Canon Coolpix 990. Samples were too optically dense to use a densitometer to measure the degree of darkening or colour saturation as has been used for similar research projects. Instead, a measuring system involving the visual comparison of amber samples with a printed colour card was used. The Swedish Natural Colour System divides colour cards into groups, attributing a code to each. The darkest area on each sample of amber, where colouration was uneven, was compared with cards using a fluorescent tube fitted with a diffuser as a source of light.

Natural daylight, was not used as a source because it's intensity varied greatly during the period of the study.

FTIR spectroscopy of amber samples

In this study, a method using Attenuated Total Reflection Fourier transform infrared (ATR-FTIR) spectroscopy was developed to quantify levels of degradation present at surfaces of all samples during accelerated thermal ageing.

Spectra were collected over 30 scans at a resolution of $4cm^{-1}$ between $4000cm^{-1}$ and $600cm^{-1}$ (the lower limit of sensitivity for ATR), using an ASI DurasamplIR single reflection accessory with an angle of incidence of 45° and fitted with a diamond internal reflection element in a Perkin-Elmer Spectrum 1000 FTIR spectrometer. Initial trials showed that 30 scans were the minimum number required to obtain well-resolved spectra for all samples. The high refractive index of diamond compared with that of amber (2.4 and 1.5 respectively) allowed absorbance data to be collected from a depth approximately equal to that of the wavelength of the infrared radiation, a maximum depth of approximately 2 microns (Coombs,1999).

The quality of spectra depended on intimate contact between the DurasamplIR reflection element (the diamond crystal had an active area of 1mm diameter) and the surface of interest. Identical pressure distribution was achieved for all samples using the flat, circular tip of the pressure device (3mm in diameter) supplied with the accessory in combination with the torque limiter which allowed the press to be tightened to the same, repeatable level. During thermal ageing, some samples, notably those undergoing open ageing, became embrittled and were damaged during examination by FTIR. Background spectra were collected from 30 scans of the empty, clean accessory open to air, at hourly intervals during examination of samples.

The method developed to quantify levels of degradation present at surfaces of all samples during accelerated thermal ageing was based on one used by Moreno et al for near infrared-Fourier Transform Raman spectroscopy to determine the extent of maturation in amber from various origins. This was based on the principle that, irrespective of the geographical or botanical origin of amber and the resins from which it is derived, several common age-dependent molecular transformation trends can be recognized. These included the progressive loss of olefinic bonds (particularly those located in exocyclic positions, decrease of functionalized products and an increasing proportion of aromatized components.

Moreno et al used the relation of Raman intensity of the band at $1646cm^{-1}$ (assigned to the simple aliphatic unsaturation of the olefin group C=C) compared with the intensity of the band at $1450cm^{-1}$ (assigned to the deformation of CH_2 bonds) to quantify the process of breakdown of C=C bonds (Moreno, 2000). In that study, the breakdown of C=C bonds was related to the extent of maturation of amber from the liquid resin stage. The intensity of the two relevant bands were ratioed and found to be lower for Baltic amber (0.35) than for amber from other origins. Such low values indicated a higher maturation of Baltic ambers compared to, for example, those from South America.

In the study described by this report, the same two bands were identified in the ATR-FTIR absorbance spectra of new Baltic amber from Kaliningrad, of Baltic amber which had been excavated from a waterlogged moor in Denmark and Baltic amber which had been excavated from a dry archæological site. Beer's Law, which specifies that spectral absorbance is proportional to the concentrations of two components in a mixture, was applied to the spectra.   The application of Beer's Law requires the use of two independent absorbance bands. Initial trials showed that the heights of bands at 1646 cm^{-1} (C=C), changed with deterioration, while the height of those at 1447cm^{-1} (CH$_2$) were unaffected.   Intensity may be related either to the height or area under the bands. In this study, heights of bands were used since the band at 1646 was overlapped which hindered independent area measurements (Figure 4.5). Heights of the two bands of interest were determined on raw absorbance spectra without manipulations or baseline corrections.

The quantitative technique was evaluated by applying it to spectra obtained from new Baltic amber from Kaliningrad, Baltic amber which had been excavated from a waterlogged moor in Denmark and Baltic amber which had been excavated from a dry archæological site. Ten spectra were run at random locations at the surfaces for each sample. The mean ratios of bands at 1646:1447cm^{-1} were:

origin of sample	mean ratio heights (1646:1447cm^{-1})
new Baltic amber from Kaliningrad	0.3 –0.4
Baltic amber from dry archæological site	0.4-1.0
Baltic amber from moor	0.7-0.8

The ratios obtained indicated that material with a more homogeneous material, namely new and moor-found amber, produced a narrower range of values than that with a friable surface and brittle body. The range of values obtained were similar to that measured by Moreno et al suggesting that the technique was appropriate for use in the present study. As physical changes in structure of amber, became more visible, the FTIR band attributed to C=C became less well resolved.
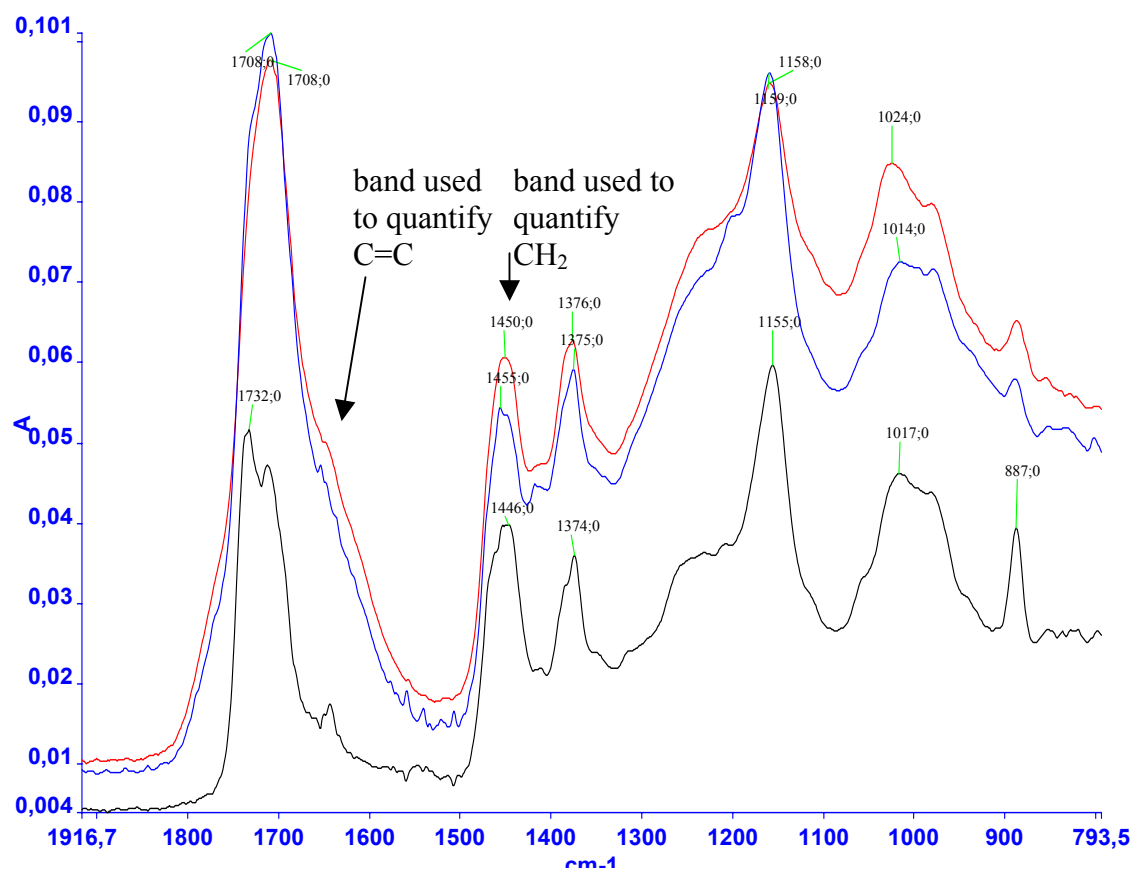
Figure 4.5 ATR-FTIR spectra of new Baltic amber from Kaliningrad (black line), Baltic amber from moor (blue line),   Baltic amber from dry archæological site (red line)

LV-SEM of amber samples

Scanning electron microscopy has not been widely used to examine amber surfaces because high vacuum instruments, almost exclusively used until 5 years ago, require coating with carbon or gold to obtain a good image and analysis. Such treatments generate heat, which is likely to vaporize volatile products such as terpenes and subsequently damage surfaces.

A Jeol SM LV-5310 scanning electron microscope was used to examine the surface morphology and elemental composition of selected samples before and after accelerated thermal ageing.   The principles and techniques of scanning electron microscopy and elemental analysis are described by Goldstein (1981). Samples (5x5mm) were adhered to aluminium stubs to examine their surface morphology. No mounting of sections was made to examine cross-sections.

Samples were examined at magnifications of either x 35, x500 and x1000. Cross-sections, lightly polished by water-cooled polishing wheel using silicon carbide grade P#2500 were also mapped for distribution of elemental carbon, oxygen, iron, sulphur, calcium and chlorine.

A beam current was maintained at 10KV and a spot size of 19 was used. Such low energy minimised damage to the samples which may have confused images and analyses.

5. Results and Discussion

Weight loss

Mean weight loss during the ageing period of 35 days at 100°C in various environments for new amber samples (initial mass around 4g) was low with an average loss of 0.05% . The rate of loss for all samples was highest during the first 14 days, before settling to equilibrium. Losses were likely to be due to water vapour and low molecular volatile components of amber. Since the water content of new amber samples had been measured at between 0.6 and 0.7% before ageing, it is unlikely that samples became completely dehydrated during the ageing process. A sweet, pine-like odour was detected when opening flasks to remove samples, suggesting that terpenoid products were present in the volatile materials. After opening flasks in which samples had been thermally aged, a yellow deposit was observed forming a ring around the outer edge of the lid's lining (Figure 5.1). It is likely that the deposit was formed by a volatile organic material produced by the amber.
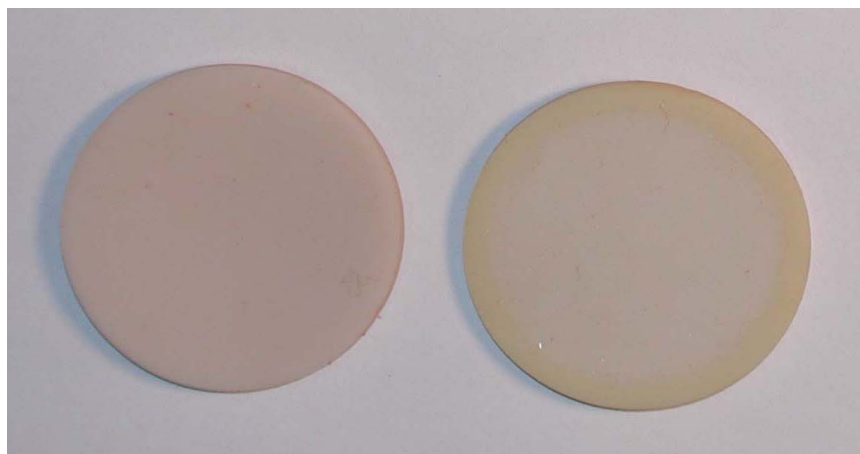
Figure 5.1 Left: new, unused cap lining for ageing flask.
Right: Cap lining has a ring of organic, yellow material
after 35 days thermal ageing of amber.

The environment in which amber samples were aged, clearly influenced the extent and rate of weight loss during the ageing period (Figure 5.2). Weight loss was greatest and most rapid for amber aged in open and oxygen-free environments. Since the temperature in the oven fluctuated by 1°C, samples aged on open dishes were exposed to localized air currents. This was not the case for samples in other, enclosed, environments. Overall, weight loss was lowest for samples aged in an environment with high relative humidity, probably due to the fact that the possibility of losing water vapour by diffusion or evaporation was small. Samples aged in a closed environment lost weight for the first 15 days of the ageing process, after which equilibrium was achieved and no further loss was measured.
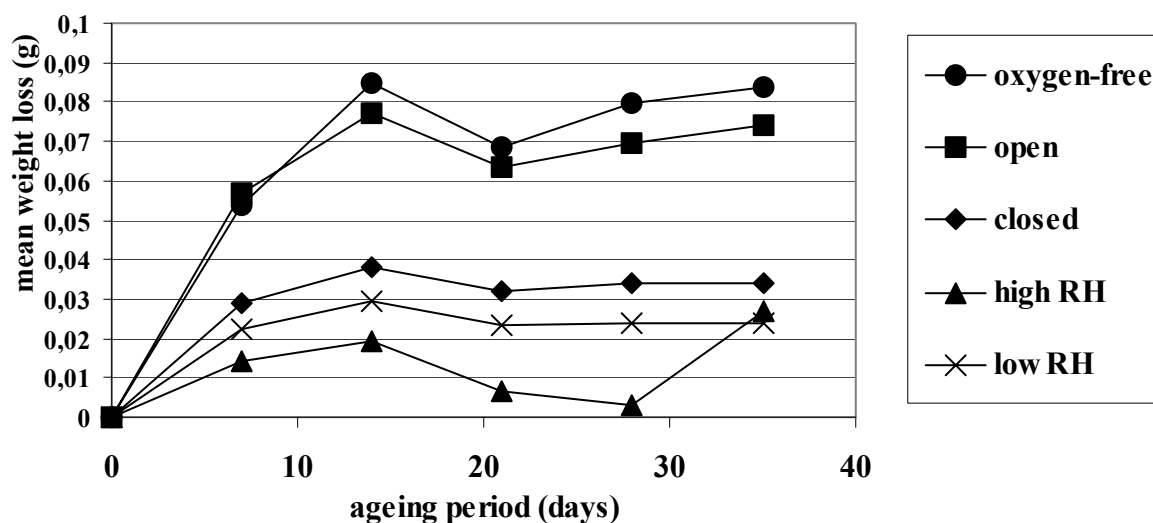
Figure 5.2 Weight loss from new amber samples during thermal ageing at 100 °C in various environments.

Change in appearance and colour of amber samples

New Baltic amber from Kaliningrad, used as experimental material in this study, was transparent, pale yellow and evenly coloured after preparation by cutting to size and polishing. The process used is further described in chapter 4, 'Research project-experimental details'. Thermal ageing caused a change in appearance and colour of all samples. The extent to which appearance was changed was dependent on both the ageing period and the environment in which samples were aged. In order to readily examine and compare progressive changes in colour and appearance, digital photographs of the same samples after ageing for 7, 14, 21, 28 and 35 days in open, closed, high RH, low RH and oxygen-free environments are shown in Figures 5.3-5.7.

Samples shown were selected because of their similar dimensions (approximately 25 x 25mm). The same piece of prepared, unaged amber was included in all photographs (visible on the right hand side of each) to facilitate comparison of colour and to reduce the affects of varying light intensities and the strength of printer toner on appearance of the images.

Samples generally became darker on ageing, but the ageing environment determined the rate and extent of discolouration. After only 7 days, samples aged in open, closed and low RH environments had visibly discoloured. Amber aged in those environments became progressively darker until completion of the ageing period (35 days). Samples aged in oxygen-free environment retained their original pale yellow colouration until the 21 day-stage; thereafter, they darkened progressively until

completion of the ageing period.   Amber aged at high RH also retained its original colour until it had been aged for 21 days, but thereafter discoloured slowly until completion of the ageing period and was the least discoloured sample after 35 days. Samples aged in an open environment were the most discoloured after ageing.

The findings and Natural Colour Measurement System numbers relating the colour of the darkest areas of samples, where discolouration was uneven, to the cards representing various colours are summarized in Table 5.1.

Table 5.1 Appearance and colour of experimental samples of Baltic amber before and after thermal ageing

| ageing environment of amber	colour description	Natural Colour Measurement System number
unaged **(least discoloured)**	pale yellow -even	1050-Y10R
high RH *	dark yellow –uneven-few red veins	1080-Y60R
oxygen-free *	dark yellow –even- red veins	1050-Y20R
low RH *	golden – even-red veins	2070-Y60R
closed *	reddish yellow-uneven-veins	1080-Y20R
open * **(most discoloured)**	reddish yellow-even-veins	2070-Y20R

* after thermal ageing at 100° C for 35 days
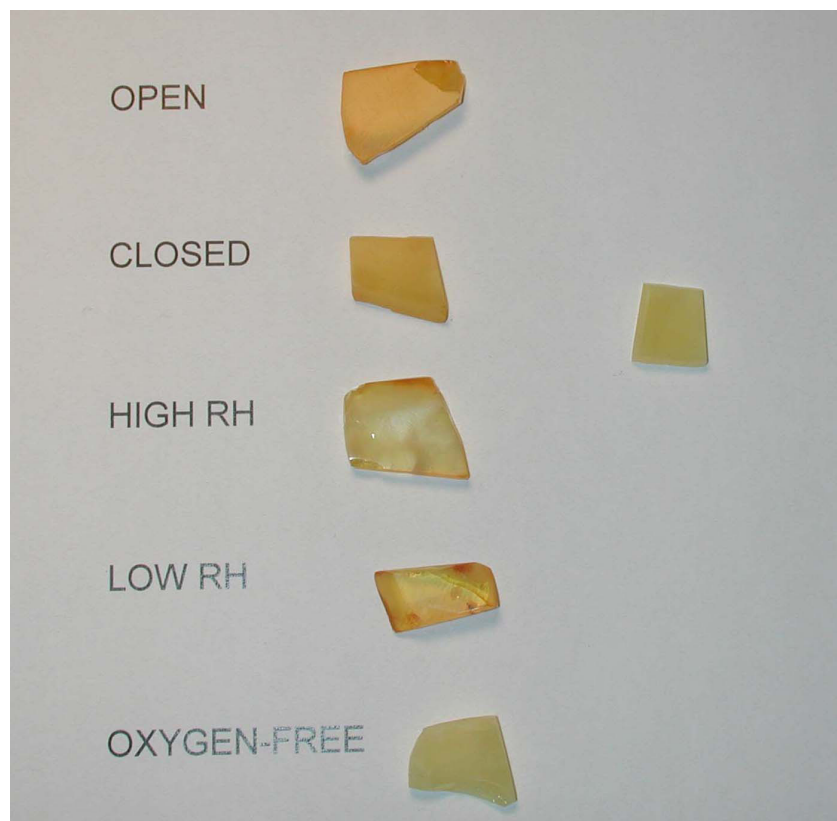
Figure 5.3 Amber samples (approximately 25 x 25mm) after 7 days thermal ageing in various environments. An unaged sample lies to the right of the picture for comparison.
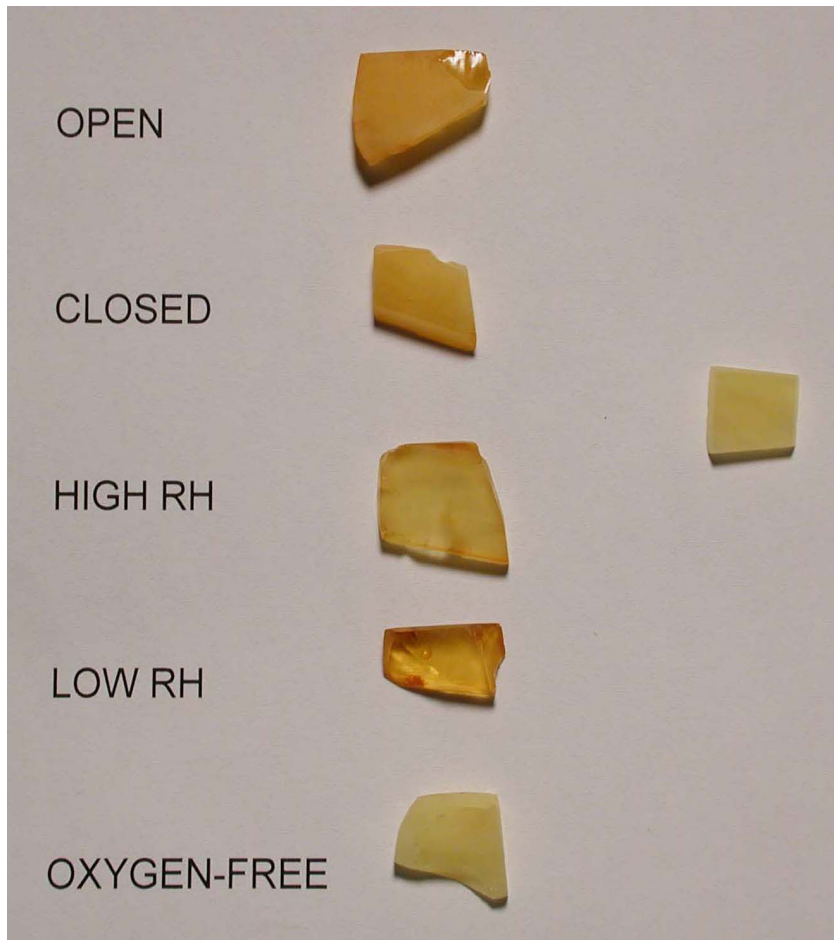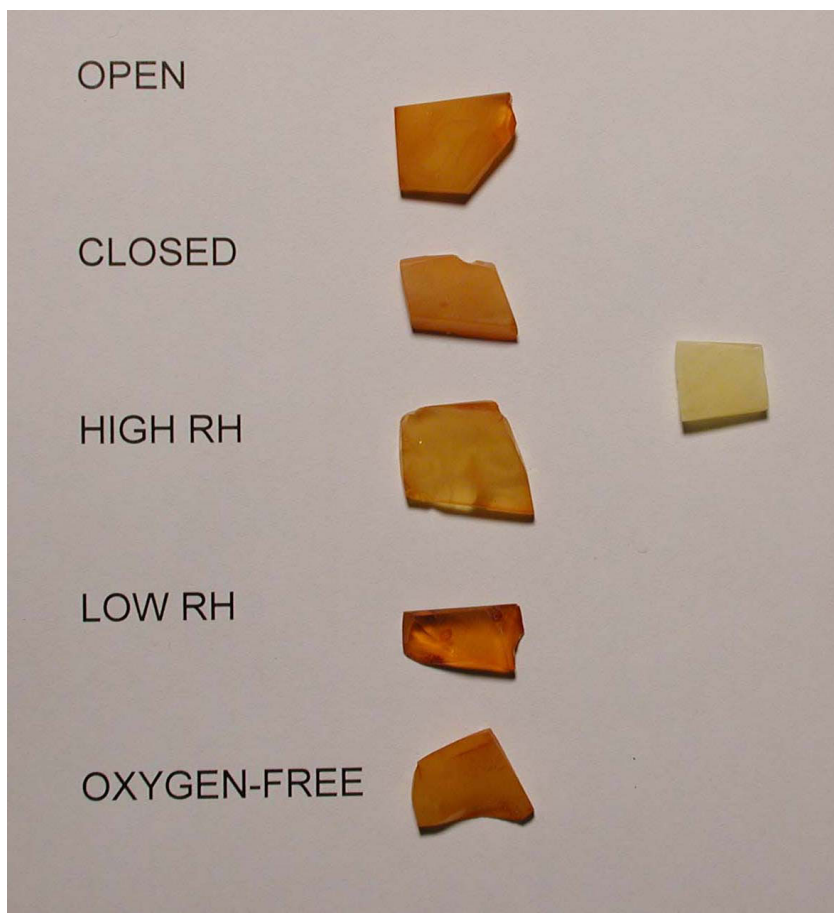
*Figure 5.4
Amber samples
(approximately 25 x
25mm) after 14 days
thermal ageing in
various
environments. An
unaged sample lies to
the right of the
picture for
comparison.*
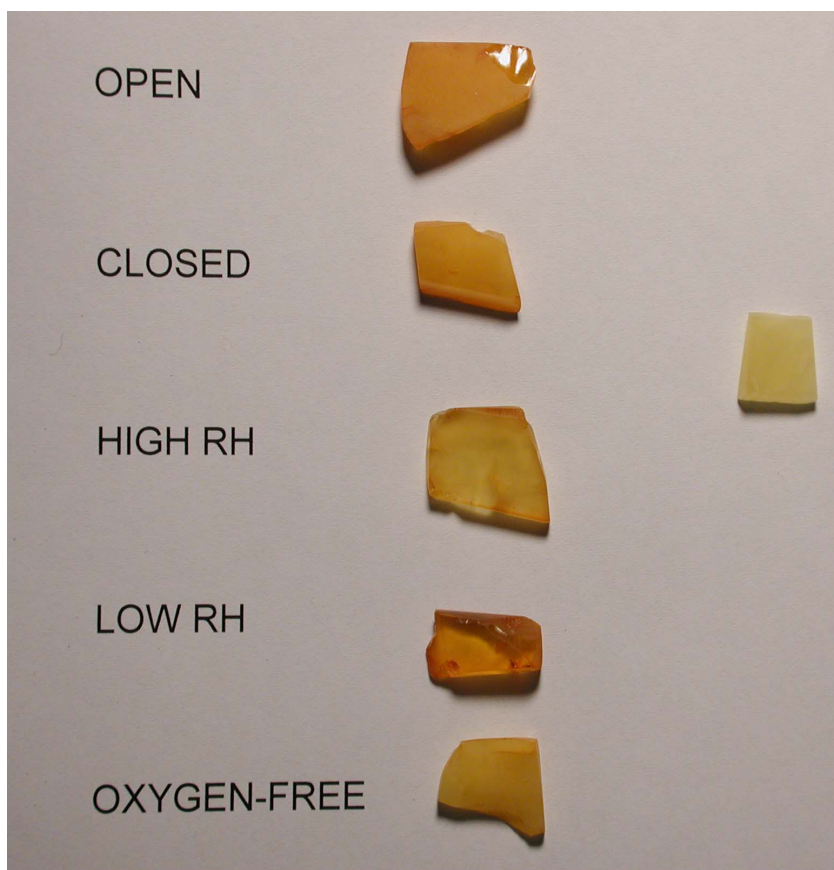
*Figure 5.5
Amber samples
(approximately 25 x
25mm) after 21 days
thermal ageing in
various
environments. An
unaged sample lies to
the right of the
picture for
comparison.*
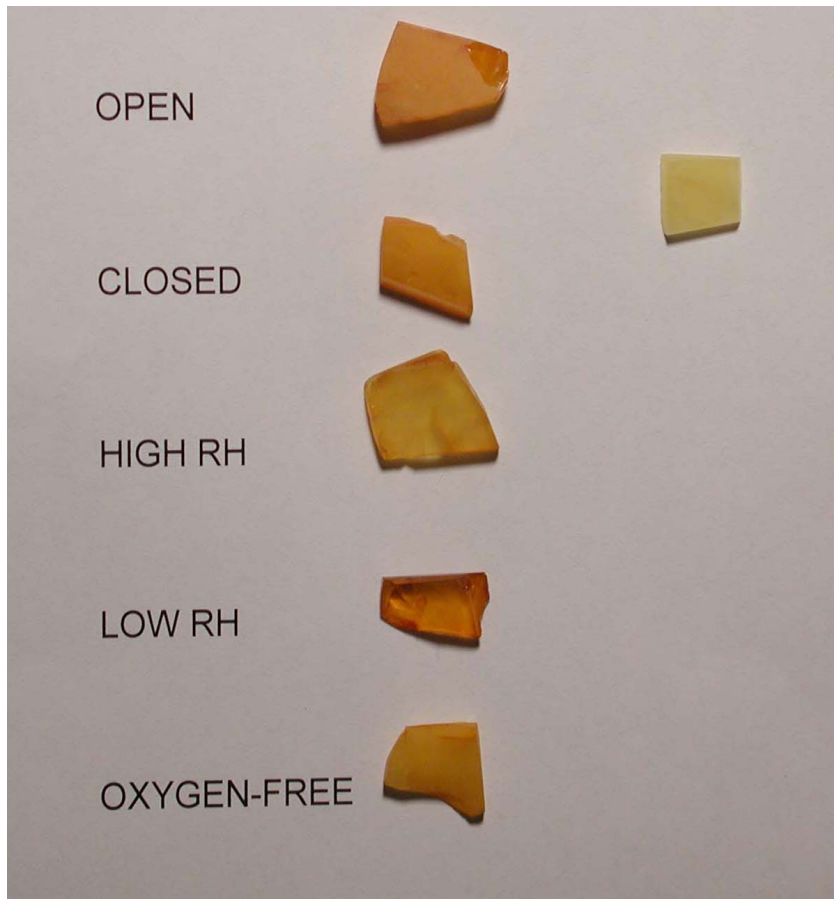
*Figure 5.6
Amber samples
(approximately 25 x
25mm) after 28 days
thermal ageing in
various
environments. An
unaged sample lies to
the right of the
picture for
comparison.*

*Figure 5.7
Amber samples
(approximately 25 x
25mm) after 35 days
thermal ageing in
various
environments. An
unaged sample lies to
the right of the
picture for
comparison.*

All samples developed red veins at the surfaces during thermal ageing, irrespective of the environment (Figure 5.8 and 5.9). Since the veins appeared to form in parallel lines, they may have been centres from which deterioration was initiated formed during the polishing process. However, since they were not confined to the surface, but penetrated into the body, they may also have been the result of localized deterioration reactions and unrelated to polishing or other treatment.

Figure 5.8 Baltic amber after ageing at high RH at 100°C for 35 days. Pale red veins have formed at surfaces and penetrate into the body of the material. Sample is approximately 30 x 30mm.

Figure 5.9 Baltic amber aged on an open dish at 100°C for 35 days has a high concentration of red veins, particularly around edges. Sample is approximately 30 x 30mm.

FTIR spectroscopy of amber samples

ATR-FTIR spectroscopy was carried out immediately after weight loss measurements for all samples at weekly intervals during the thermal ageing process. The extent of surface deterioration was determined by ratioing the absorbance intensities of bands at 1646 cm^{-1} (due to the concentration of C=C, which reduced with deterioration), against those at 1447cm^{-1} (attributed to CH_2, unaffected by deterioration of amber). Intensity may be related either to the height or area under the bands. In this study, heights of bands were used, since the band at 1646 cm^{-1} was overlapped. This hindered independent area measurements (Figure 5.10). Heights of the two bands of interest were determined on raw absorbance spectra without manipulations or baseline corrections. Spectra were run at 5 random positions on the surfaces of aged and unaged amber samples, the ratio A_{1646}/A_{1447} calculated for each spectrum and the mean value calculated.
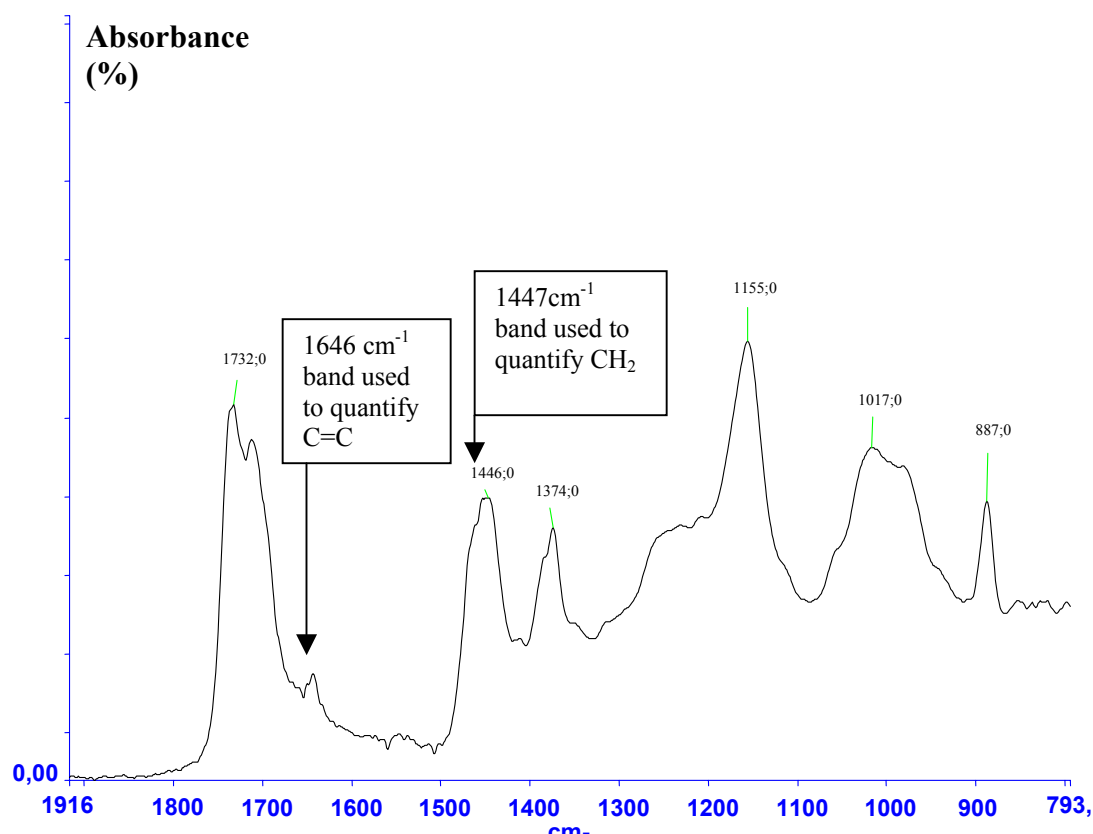
Figure 5.10 The extent of deterioration of amber samples was determined by ratioing the absorbance intensities of bands at   1646 cm^{-1} (due to C=C, which reduced with deterioration), against those at 1447cm^{-1} (attributed to CH$_2$, unaffected by deterioration) on raw absorbance spectra without manipulations   or baseline corrections

The reduction in C=C bonds (determined by calculating the mean ratio A_{1646}/A_{1447} taken at 5 places on the surface of amber samples, each of which comprised 30 scans) during the accelerated thermal ageing process, was plotted against the ageing period (Figure 5.11). As the number of C=C bonds are reduced by deterioration, the value of A_{1646} becomes lower.   However, since the value of A_{1447} is unaffected by deterioration, the ratio A_{1646}/A_{1447} reduces with deterioration. In short, using these bands to determine extent of deterioration, higher values signify a lower extent of deterioration while low values, signify greater deterioration. An error of ±0.05 should be taken into account when examining the results.

The environment in which amber samples were aged, clearly influenced the extent and rate of deterioration during the ageing period. By the end of the ageing period, samples stored at high RH showed least surface deterioration while those stored at low RH for the same period, exhibited most surface deterioration. Based on their effect at the end of the ageing period, the environments evaluated may be ranked from that causing the least to the greatest deterioration:

high RH   (**least surface deterioration**)
oxygen-free
closed
open
low RH   (**greatest surface deterioration**)

Samples aged in open and closed environments exhibited a more gradual rate of degradation than samples in other environments. Amber aged in both high RH and oxygen-free environments, degraded in discrete stages rather than at a steady rate. Since all the flasks in which all thermal ageing was conducted were opened for sampling once every 7 days, the change in rate of degradation may have been affected by that process. However, disturbance was minimal and, in the case of the oxygen-free environment, fresh oxygen absorber was introduced after opening to examine samples.
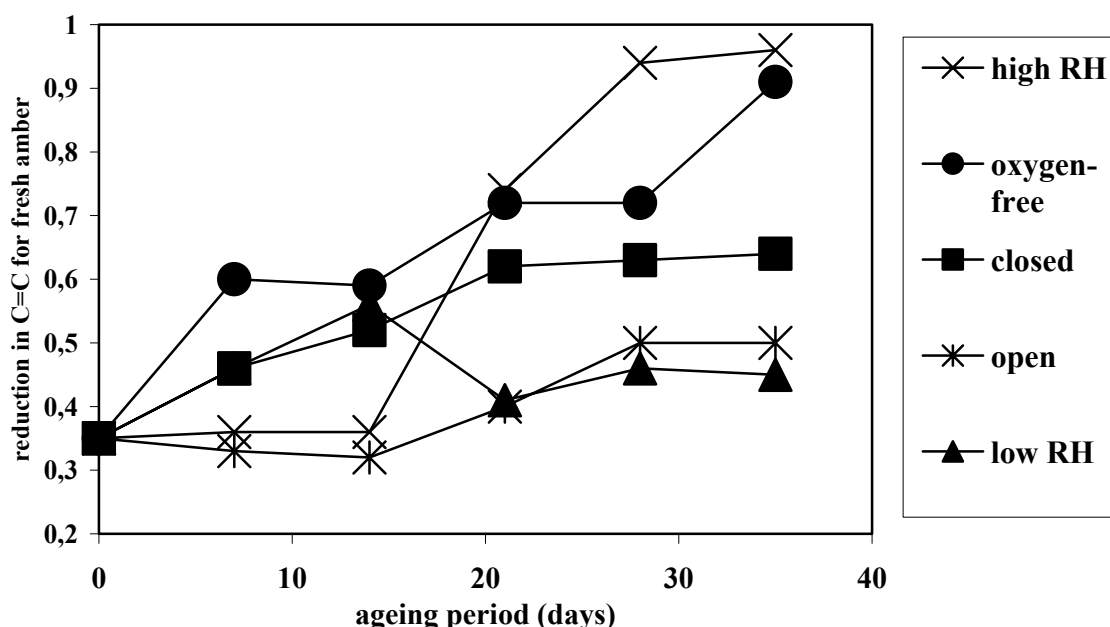

Figure 5.11 Reduction in C=C bonds, resulting from deterioration, for new Baltic amber during thermal ageing in various environments. Higher values are an indication of less deterioration-high RH environment caused least breakdown of C=C bonds, while low RH caused greatest.

LV-SEM of amber samples

A Jeol SM LV-5310 scanning electron microscope was used to examine the surface morphology and elemental composition of samples during preparation by polishing and again after accelerated thermal ageing. Samples (5x5mm) were adhered to aluminium stubs to examine their surface morphology. Amber samples were examined at magnifications between x 35 and x1000. Cross-sections, lightly polished by water-cooled polishing wheel using silicon carbide grade P#2500 were also mapped for distribution of elemental carbon, oxygen, iron, sulphur, calcium and chlorine. The areas with the brightest or lightest appearance on maps were those containing the highest concentration of that element being analysed .

Unaged amber

Prior to preparation, the raw amber used as experimental material had an inhomogeneous, uneven surface with superficial inclusions of rock and stone from its original surroundings in Kaliningrad (Figure 5.12). After cutting to size and water-cooled polishing, surfaces became more homogeneous and even (Figure 5.12). However, light parallel indentations resulting from the polishing process, were visible.
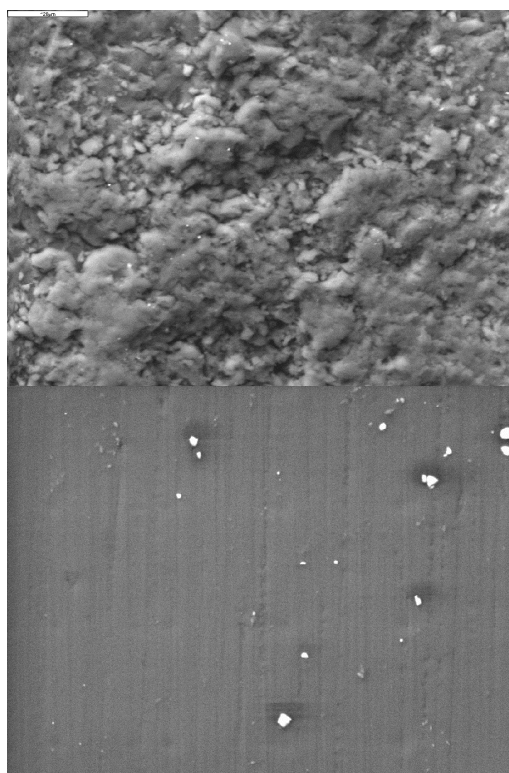
Figure 5.12 Scanning electron micrograph of surface of unprepared, Baltic amber from a mine in Kaliningrad, showing the original surface crust. Surface contained particles of rock and earth associated with its uneven texture. Small white bar in top left hand corner represents 20 µm.

Figure 5.13 Surface of Baltic amber from Kaliningrad after cutting and water-cooled polishing. Bright white spots are pieces of silicon carbide paper which adhered to the surface.

Examination of the surface of raw unpolished material from Kaliningrad by LV-SEM at a magnification of x 500, showed the presence of a regular hexagonal pattern. Elemental analysis using LV-SEM of the same surface, showed the presence of carbon, oxygen, sodium, magnesium, aluminium, silicon, sulphur, chlorine, potassium, calcium, titanium and iron (Figure 5.14). It was likely that sodium,

magnesium, aluminium, silicon, chlorine, potassium and titanium were not components of amber itself, but were deposited on the surface from the orginal surrounding clay and rock. The presence of sulphur was one of the defining characteristics of Baltic amber. Comparison of the surface morphology of a new sample with that of a piece of amber representative of that excavated from a waterlogged moor in Denmark showed a similar, though less well-defined hexagonal design, with cracks also present (Figure 5.15). Elemental analysis of the surface, identified the presence of the same elements found in the material from Kaliningrad, with the exception of magnesium and titanium.

The similarities both of surface morphology and elemental composition, supported the data from ATR-FTIR spectroscopy that the Kaliningrad material was a suitable model on which to examine the effects of various environment on the rate and extent of degradation, and extrapolate the results to Baltic amber in the collections of the Museum.
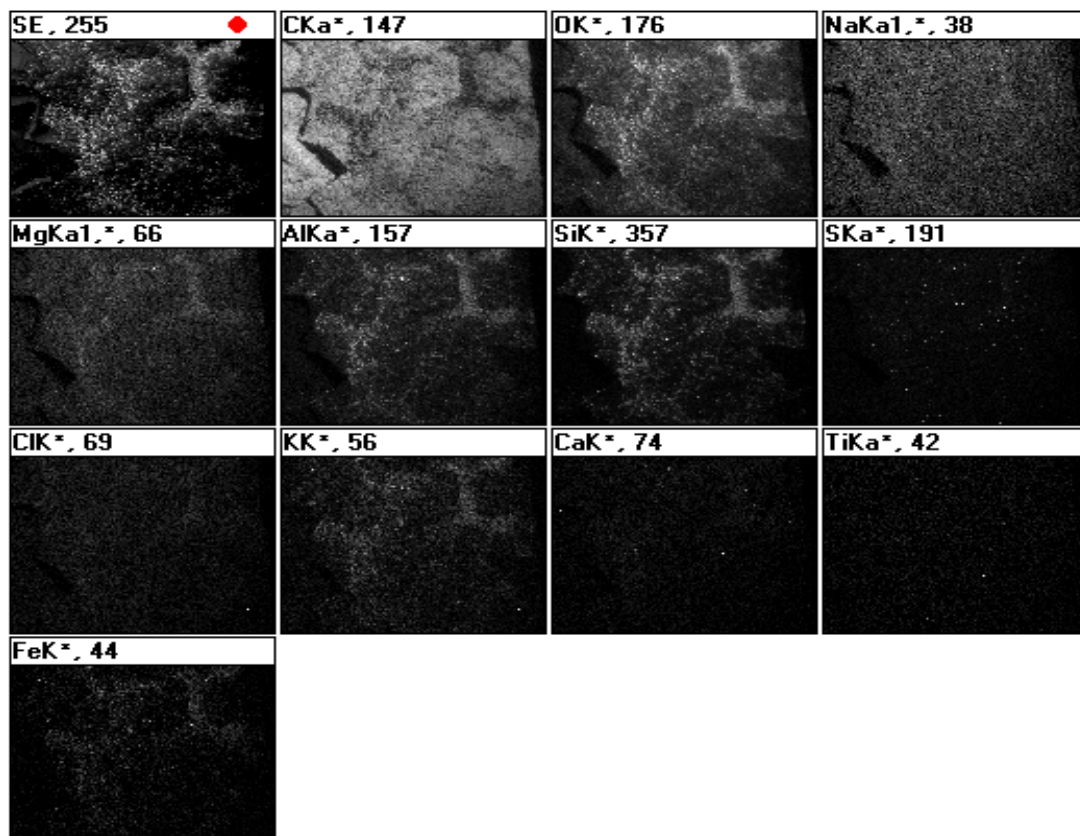

Figure 5.14   LV-SEM secondary image of raw, unpolished amber from Kaliningrad showing surface morphology (top left). Elemental mapping shows the presence of:
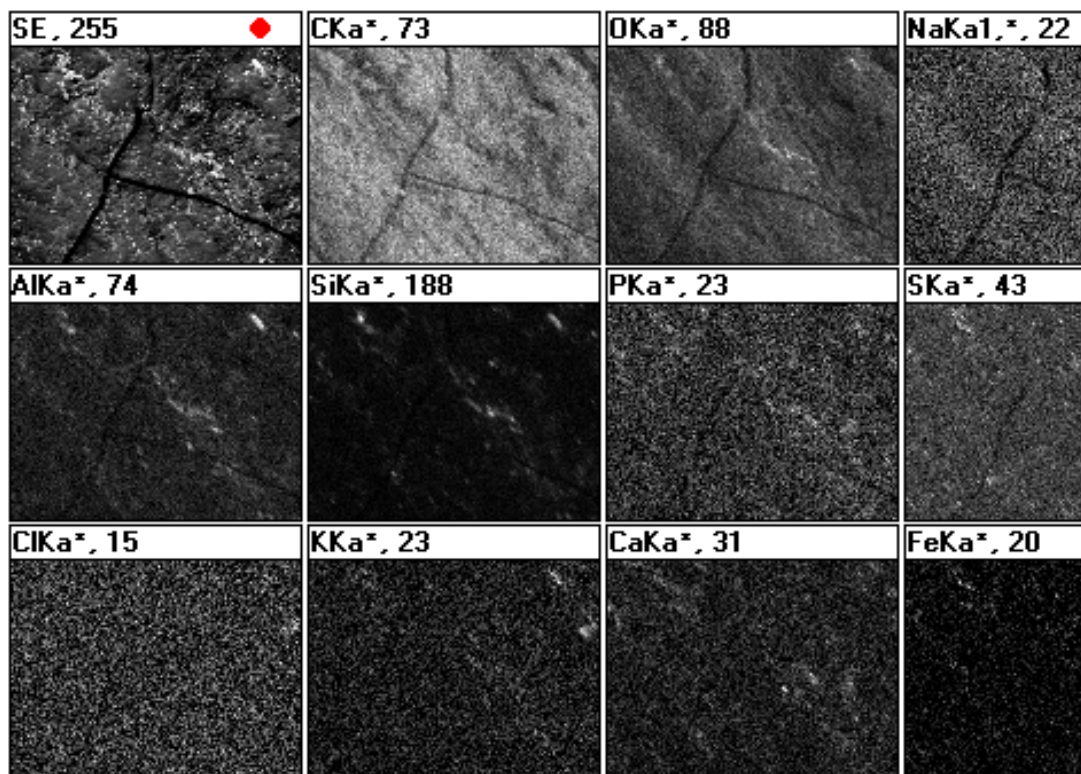*Top row left to right Carbon (C), Oxygen (O), Sodium (Na)*
Second row left to right, Magnesium (Mg) ,Aluminium (Al), Silicon (Si),Sulphur (S)
Third row, left to right, Chlorine (Cl), Potassium (K), Calcium (Ca), Titanium (Ti)
Lower row , Iron (Fe)
Areas with the brightest appearance on maps are those containing the highest concentration of that element being analysed

Figure 5.15 LV-SEM secondary image of Baltic amber from a waterlogged moor in Denmark showing surface morphology (top left). Elemental mapping shows the presence of :
Top row *left to right Carbon (C), Oxygen (O), Sodium (Na)*
Second row *left to right, Aluminium (Al), Silicon (Si),Phosphorous (P), Sulphur (S)*
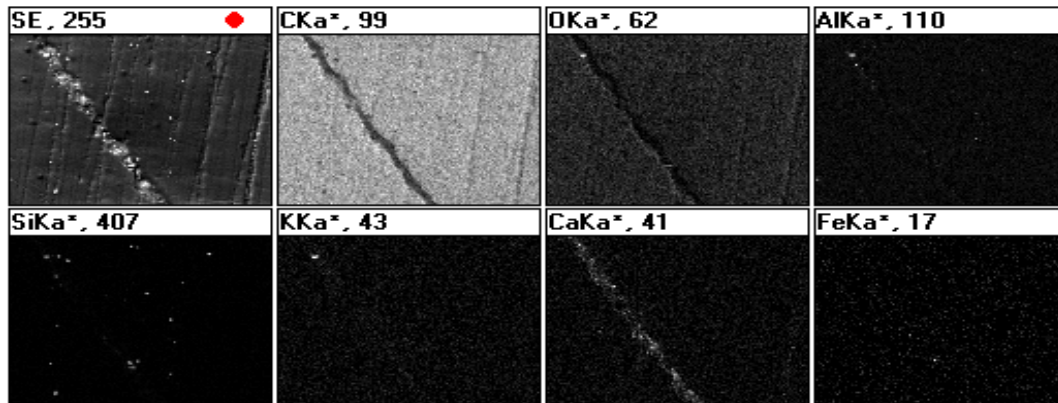**Lower row***, left to right, Chlorine (Cl), Potassium (K), Calcium (Ca), Iron (Fe)*

Areas with the brightest appearance on maps are those containing the highest concentration of that element being analysed

Thermally aged amber
Examination of the surface morphologies and elemental composition of samples of Baltic amber after 35 days thermal ageing in various environments, suggested that ageing environment had an influence on both properties.

Amber thermally aged in an open environment, that is one where volatile materials could readily leave the surface of the sample, developed small, but deep cracks at the most exposed surfaces (Figure 5.16). Elemental analysis suggested the cracks to be richer in calcium than the surrounding, polished areas, although the reason for this is unclear. It may be attributed to the presence of hard water used in the polishing process, drying within the crack. The cracks also appeared to be slightly depleted in oxygen compared with amber flanking the cracked areas, but this may be due to the exposure of fresh, less oxidized material inside the crack. All other elements were evenly distributed over the surface, in a similar way to the unaged material.

The surface morphology of amber after ageing in an open environment was typical of that shown by Baltic amber excavated from a dry earth burial site, now part of the National Museum's collections, though the archæological material exhibited a higher concentration of cracks (Figure 5.17).


Figure 5.16 Ageing experimental Baltic amber samples for 35 days in an open environment at 100°C produced a diagonal crack similar to that found in amber from a dry burial site (LV-SEM secondary image top left corner). The crack was found to contain high levels of calcium, perhaps from the hard water used to polish the sample.
LV-SEM showed the presence of:
Top row *left to right Carbon (C), Oxygen (O), Aluminium (Al)*
Second row *left to right Silicon (Si), Potassium (K), Calcium (Ca), Iron (Fe)*

Areas with the brightest appearance on maps are those containing the highest concentration of that element being analysed
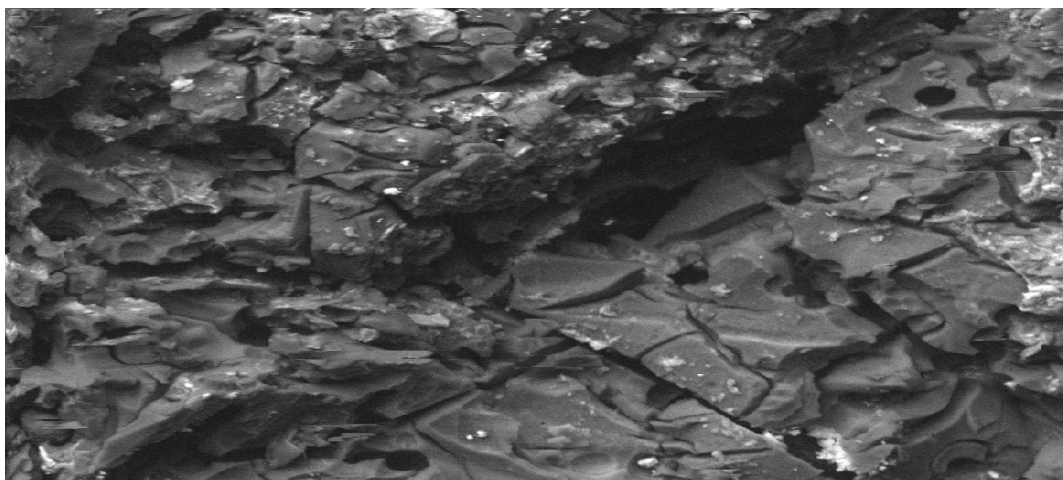
Figure 5.17 Baltic amber excavated from a dry burial site typically shows a diagonal crack and friable, cracked upper surface.

Comparing samples aged in high RH with those aged at low RH conditions, shows minimal differences in surface morphology between the two (Figures 5.18 and 5.19). However, elemental compositions between the two aged materials, suggest that those aged at low RH had higher concentrations of oxygen, particularly at the sides and corners, than those aged at high RH. All elements, oxygen included, were evenly distributed over the surfaces. This indicated that oxidation products, resulting from degradation, were present in higher concentrations when amber was stored at low RH than at high RH.

Surface morphologies of amber aged in oxygen-free environment was appeared similar to that of amber aged at high RH, although a few small cracks were present at the surfaces. The elemental analyses of both were identical.

Figure 5.18 LV-SEM secondary image of Baltic amber thermally aged at high RH, showing surface morphology (top left corner). Elemental mapping shows the presence of :

Top row *left to right Carbon (C), Nitrogen(N)*
Second row *left to right, Oxygen (O), Aluminium (Al),Chlorine (Cl)*
Lower row *left to right, Potassium (K), Calcium (Ca), Iron (Fe)*

Areas with the brightest appearance on maps are those containing the highest concentration of that element being analysed
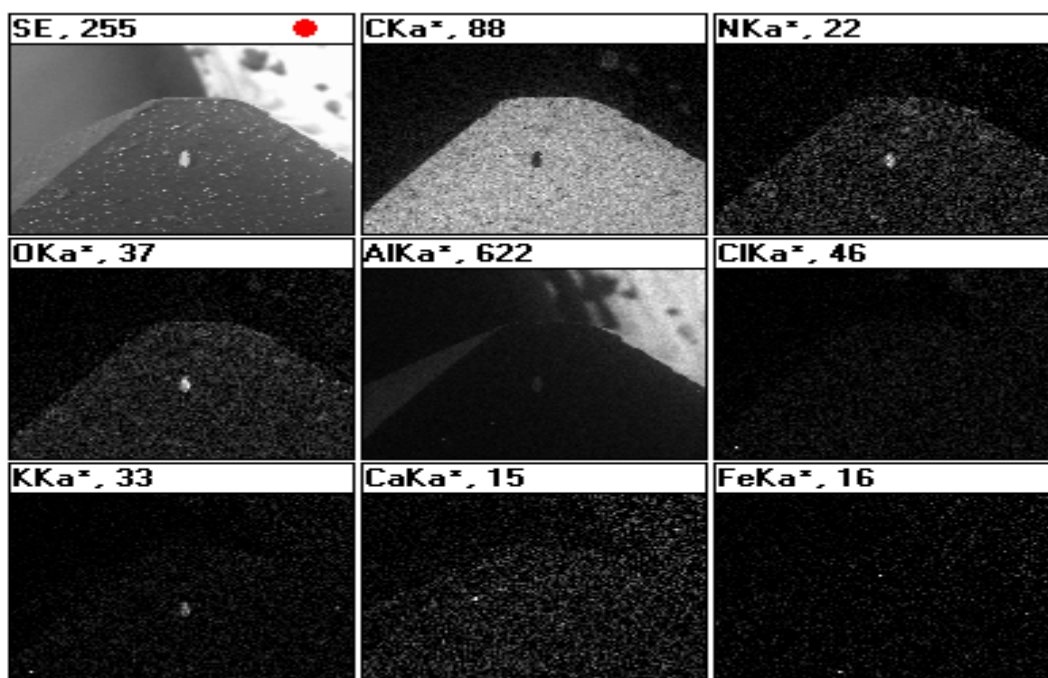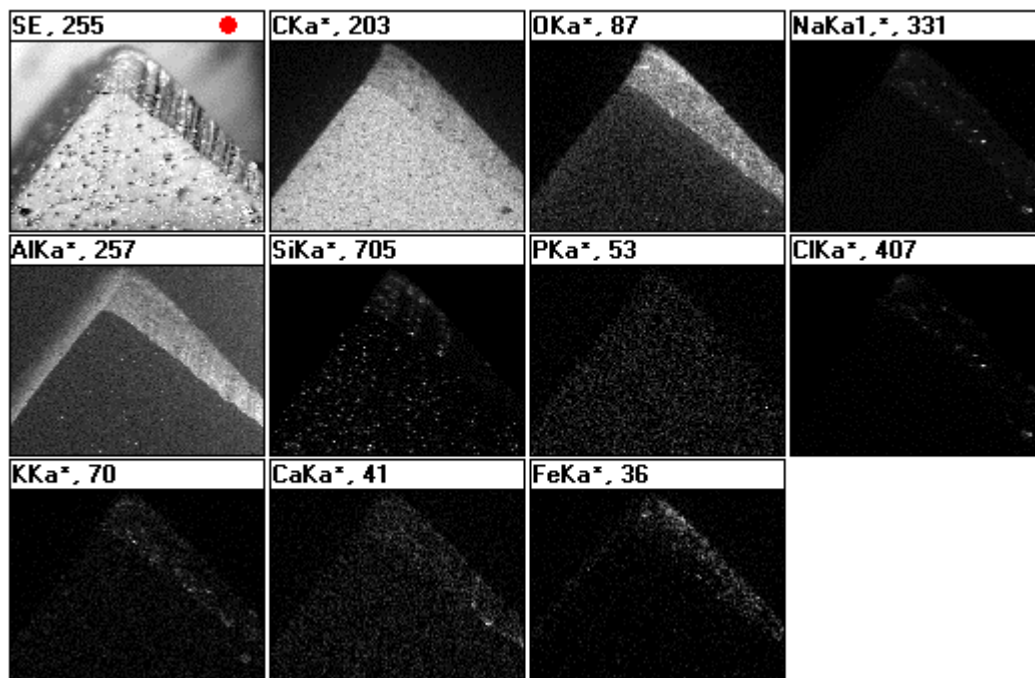
Figure 5.19 LV-SEM secondary image of Baltic amber after thermal ageing at low RH showing surface morphology (top left corner). Elemental mapping shows the presence of :
Top row *left to right, Carbon (C), Oxygen (O), Sodium (Na)*
Second row *left to right, Aluminium (Al), Silicon (Si),Phosphorous(P),Chlorine (Cl)*
Lower row *left to right, Potassium (K), Calcium (Ca), Iron (Fe)*

Areas with the brightest appearance on maps are those containing the highest concentration of that element being analysed

Summary of results of all analytical techniques

Findings from all analytical and examination techniques indicated that the environment in which samples of new Baltic amber were aged, influenced the rate and extent of deterioration. In general, the ageing environments which involved enclosing amber in a container, thereby creating a controlled microclimate, were measurably more effective at inhibiting discolouration, weight loss, degradation of chemical and physical properties than exposing samples to the variations of an open environment.

All analytical techniques used also suggested that the presence of oxygen, generally thought to be the cause of deterioration of amber, was not the only factor in

deterioration process. The presence of water vapour was important to the rate and extent of deterioration. This finding was unexpected since the influence of water on the degradation mechanism of Baltic amber has not been discussed in the literature. Using the analytical techniques employed in this project, it was not possible to establish whether the water molecules were bound to amber's polymeric structure or association was purely physical. Such information is necessary to define the role played by water in the degradation mechanism.

Weight loss, although low under all thermal ageing conditions examined here, was greatest when amber was aged on an open petri dish compared to when samples were enclosed. This was expected since, in open conditions, surfaces were exposed to weak air currents caused by the small variations in temperature within the oven air space and, therefore, the opportunity for evaporation of volatile materials from surfaces was greater. Ageing in an environment with high RH, resulted in the lowest weight loss, since the saturated atmosphere discouraged further loss of water from amber samples. Loss was therefore more likely to have originated from volatile terpenoids.

The extent of discolouration, the most recorded and obvious result of deterioration of Baltic amber, was also dependent on the environment in which samples were aged. Samples aged in an open environment darkened most, while those aged at high RH showed visible but minimal change in colour by comparison. Storage in an oxygen-free environment inhibited discolouration initially, but its effectiveness was lessened in the longer term and superseded by that of high RH.   These findings correlated well with weight loss results, and indicated that oxygen was not the only factor in the deterioration process, but that water must also participate.

ATR-FTIR spectroscopy was used to quantify breaking of C=C bonds, those most vulnerable during degradation, at the surface of amber samples. The environment in which amber samples were aged, clearly influenced the extent and rate of deterioration during the ageing period. By the end of the ageing period, samples stored at high RH showed least surface deterioration while those stored at low RH and under open conditions for the same period, exhibited most surface deterioration. Considering these results together with those for discolouration, indicates that the presence of moisture inhibits chemical degradation of amber. At low concentrations of water vapour, breaking of C= C bonds   occurred more rapidly and to a greater extent than when it was present at higher concentrations.

Elemental analysis using LV-SEM showed that the concentration of elemental oxygen, a component of degradation, was lower at the surfaces of amber aged in high RH and in oxygen-free environments than in others. These results suggested that both oxygen and water were significant factors in the degradation of Baltic amber.

6. Conclusions

Findings from all analytical and examination techniques employed in this research project, indicated that the environment in which new Baltic amber is stored, influenced the rate and extent of deterioration. In general, the ageing environments which involved enclosing amber in a container, thereby creating a controlled microclimate, were measurably more effective at inhibiting discolouration, weight loss, degradation of chemical and physical properties than those which exposed samples to the variations of an open environment. Findings from weight loss and discolouration measurements, ATR-FTIR spectroscopy and LV-SEM also suggested that the presence of oxygen, generally thought to be the cause of deterioration of amber, was not the only factor in the deterioration mechanism.

The presence of water vapour was also important to the rate and extent of deterioration. Using the analytical techniques employed in this project, it was not possible to establish whether the water molecules were bound to amber's polymeric structure or association was purely physical. Such information is necessary to define the role played by water in the degradation mechanism. Analysis of amber samples using FT-Raman spectroscopy, a technique not available to the National Museum at the time of writing, is likely to provide such information.

Although model samples of Baltic amber were used in this investigation, analysis by infrared spectroscopy and scanning electron microscopy suggested that they had similar chemical and physical structures to naturally aged material from the National Museum's collections. Based on this information, the effectiveness of the storage environments evaluated could be extrapolated to museum objects containing deteriorated amber.

The main objective stated at the beginning of this research project has been achieved. The major environmental factors which initiate or catalyse degradation of Baltic amber, have been identified as both oxygen and water. Prior to this study, oxygen alone had been identified as the sole cause of deterioration in publications concerning Baltic amber.

The results from this project can be used in the development of an inhibitive conservation technique which will prolong the useful lifetime of Baltic amber in museum stores for a longer period than is currently possible. Since it is important to define environmental conditions for a museum store as accurately as possible, further research to refine the most effective levels of RH and oxygen should be carried out.

7. References

Note: All references to Web sites are as found March 2002

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8. Suppliers of chemicals used in the research project

Baltic amber
Ravfehrn A/S, Søborg, Copenhagen, Denmark

Silica gel-self indicating
Merck KGaA, 64271 Darmstadt, Germany

Ageless ® oxygen absorber
Mitsubishi Gas Chemical Company Inc., Mitsubishi Building, 5-2 Marunochi 2-chome, Chiyoda-ku, Tokyo 110, Japan