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AMBER-LIKE FOSSIL RESIN FROM NORTH QUEENSLAND, AUSTRALIA

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ABSTRACT

Australia has appeared devoid of fossil resin occurrences except for several very small deposits in Victoria. Recently, however, pieces of amber-like fossil resin have been discovered on remote beaches near Cape Weymouth on the east coast of Cape York Peninsula in north Queensland. They appear to derive from Quaternary deposits bordering the coast. The material ranges in colour from clear pale yellow through to dark brown and almost opaque. Numerous inclusions are present, including fossilised insects. Tests show specimens include both copal and amber, making them of interest to gemmologists. FTIR spectra show the fossil resins to be broadly similar to Baltic amber and Kauri gum (copal) but markedly different in their finer detail.

INTRODUCTION

In 2003 two north Queensland residents, Dale Wilkes and Beth Norris sent specimens of amber-like material to the Australian Museum for identification and testing. They had collected the specimens along the high tide strandline on some remote beaches near Cape Weymouth, on the east coast of Cape York Peninsula. Initial testing confirmed that the material was, indeed, an amber-like fossil resin. This immediately raised the following questions. Where does the material come from and what is its botanical origin? Subsequently, pieces were found several kilometres inland and several kilometres apart on lowlands flanking the beaches. The area is covered by Quaternary sediments overlying metamorphic rocks and supporting dense rainforest (Willmot & Powell 1977). This distribution suggests that the amber-like resin comes from the Australian mainland rather than any overseas source. It seems likely that the lumps are washed out to sea during the wet season to be subsequently re-deposited along the high tide mark by local coastal currents and waves.

Although deposits of fossil resins have an extensive world wide distribution (see the map in Langenheim 2004 p.148), their occurrence in Australia was previously confined to a few very small deposits at Yallourn, Allendale and Lal Lal in Victoria (Watson 1925, Poinar 1991). For this reason, the Cape Weymouth finds are significant.

Amber has a long historical record. Since prehistoric times, Baltic amber has been used for adornment. Pliny The Elder (AD 23-79) in his book *Historia Naturalis* describes Baltic amber as a luxury item and also correctly identifies it as the resinous product of a type of pine tree (Healy 1991, p. 369-370). Baltic amber is also known as succinite, since succinic acid can be distilled from it. Because of its abundance and stability, some regard Baltic amber, or succinite, as the only true amber. However, stable fossil resins are also found elsewhere around the world and the term 'amber' is now often used in a loose, generic sense to refer to all fossil resins. Fossil resins have many varietal names reflecting particular characteristics such as locality, mode of occurrence and appearance. A classified list of names is given in BOX 1.

Besides being ornamental, amber has great scientific interest because of the many small (terrestrial) animals and plants that were embedded in it and subsequently preserved. Ancient air and water has also been preserved in tiny bubbles within the fossil resin.

CHARACTERISATION OF FOSSIL RESINS

During fossilization plant resins undergo physical and chemical changes termed taphonomic changes. The factors controlling

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these changes are time, heat and pressure. The depositional environment in which the resin is preserved is also important and needs to be deficient in oxygen. The relative effects of these variables differ from locality to locality.

Resins are a water-insoluble mixture of complex, aromatic hydrocarbons secreted by some plants. They are mostly terpenoid and/or phenolic secondary compounds that harden on contact with air. They are distinct from gums, another plant product often confused with resins, which are polysaccarides and water-soluble. The composition of the original resin and the degree and extent of maturation during fossilization determine the nature of the final product.

A sequence (resin → copal → amber) is apparent in which copal has physical and chemical properties intermediate between resin and 'true amber', the end product. The processes causing the maturation of resin to 'true' amber are complex but involve polymerisation (extensive cross-linking) of the terpenoid and phenolic components of the resins and expulsion of the more volatile components. The stage at which copal becomes amber is indeterminate but, generally, material that is several million or more years old is sufficiently polymerised to be classified as amber (Grimaldi, 1996, p.16).

Anderson & Crelling (1995) have compiled a chemical classification of fossil resins recognising eight main classes which gives an indication of their botanical origin. This classification is reproduced in BOX 2.

Instrumental techniques

The Cape Weymouth specimens were examined with a standard gemmological microscope for their appearance and inclusions. They were then subjected to standard gemmological tests at the Australian Museum, involving spot testing with ethanol (to discriminate between copal and amber), determination of refractive index, reaction to ultra violet light and application of a hot point (to determine odour). Because the specimens floated on water and therefore had a specific gravity less than 1, a standard specific gravity test was not possible. This property was determined by first weighing the specimen in air (to obtain the mass), then measuring the volume of water displaced (volume) and using the formula SG = mass ÷ volume. Specimens were held underwater by a pin inserted into the specimen.

Fossil resin samples from Australia (three samples from the Cape Weymouth area), New Zealand (Kauri gum), and the Baltic region were analysed by Fourier transform infrared spectroscopy (FTIR). Spectra were recorded at room temperature, from pellets comprised of 1.5 mg of sample and 220 mg of anhydrous KBr, in the 4000 - 400 cm^{-1} range using a Perkin Elmer 'Spectrum One' instrument operating at a resolution of 1 cm^{-1}. Typically, 32 interferograms were collected for each spectrum. This was done at the University of Western Sydney, North Parramatta campus.

Cape York fossil resins

Appearance

When recovered, the fossil resin specimens typically have a pitted surface covered with a thin, opaque, brown crust, mottled with cream coloured chalky patches and streaks (Fig. 1).

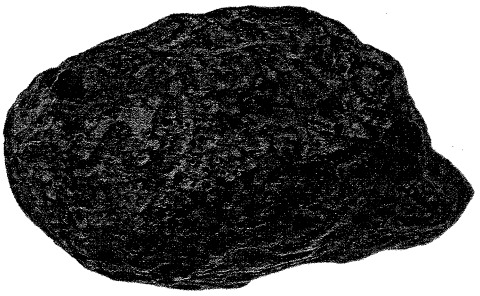

Fig. 1. Fossil resin with a weathered crust as found on the beach. Specimen 35 mm across. Photo S. Humphreys.

Specimens range in diameter from a few millimetres to approximately 190 mm. Shipworms *(Teredo sp.)* have tunnelled into some of the specimens leaving 4-6 mm diameter holes sometimes containing their still-intact shells (Figs. 2 & 3).

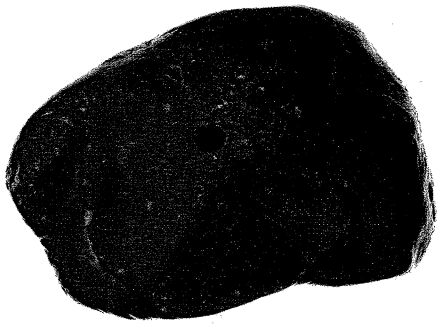

Fig. 2. Specimen with weathered surface, displaying the entrance of a shipworm *(Teredo sp.)* burrow. Photo S. Humphreys. Specimen Australian Museum (D53545).

BOX 1

CLASSIFICATION OF NAMES APPLIED TO FOSSIL RESINS

Many names have been used to label fossil resins. In this table these names have been classified according to some dominant property for which the name was coined. Most of the names were culled from a list compiled by R.V. Dietrich on his web site gemRocks.

LOCALITY (geographical region of occurrence)

Bacalite - white to yellowish amber from Baja California, Mexico.

Baltic amber (also termed Danish, Finnish, Norwegian, Swedish or even English/British amber) - named for its source along the shore of or beneath the Baltic Sea, with the country names sometimes applied to amber from or near their Baltic shore.

Burmite (sometimes spelled bermite = Burmese amber) - cherry red and redish brown amber from Myanmer (Burma).

Chemawinite (cedarite) - amber from Cedar Lake, Manitoba.

Delatynite (delatenite) - amber from the vicinity of Delyatyn in the Carpathian Mountains of the Ukraine.

Fushin amber - insect bearing ambers from the coal seams of the Fushin district, China.

Krantzite - soft fossil resin that occurs sporadically in the Saxony coal region.

Siegburburgite - fossil resin from Bonn, Germany. It has a range of colours and is partly soluble in alcohol.

Simetite (also called Sicillian amber and 'tears of Helaides') - brown, red, yellow-orange and yellowish green amber from the Mediterranean. Much of this amber exhibits a bluish fluorescence.

Telegdite - resin found in lignite at Szascsor, Transylvanian district.

MODE OF OCCURENCE (geological environment of occurrence)

Ajkaite (also spelled ajkite) - a fossil resin, typically sulphur-bearing, that ranges in colour from dark reddish brown to pale yellow and occurs in lignite, i.e. brown coal.

Ambrite (sometimes spelled amberite) - variously described as a yellowish and transparent or yellowish gray and subtransparent fossil resin or retinite found in the coalfields of New Zealand.

Ambrosine - a clove brown succinite found to occur as sporadic rounded masses in some phosphate beds.

Pit amber - name sometimes given to amber that is recovered, usually from unconsolidated sediments, by strip mining procedures.

Resinite - small particles of fossil resin in coal deposits. Also the name given by Anderson & Crelling to class 1 fossil resins.

Scoopstone - amber scooped, commonly along with seaweed, from the sea. This term is applied most frequently to Baltic amber recovered near Poland.

Schraufite - a reddish resin that occurs with jet in the Russian Carpathian mountains.

Seastone - amber found on the shore, especially along the southern coast of the Baltic Sea.

APPEARANCE AND PHYSIO-CHEMICAL PROPERTIES

Almaschite - see Rumanite.

Beckerite - soft, dark brown opaque amber-like fossil resin. This designation is applied most frequently to this kind of material from the Baltic Sea region.

Bone amber - see osseous amber.

Butter amber - a yellow subtranslucent amber.

Fatty amber - name sometimes given amber that resembles goose-fat.

Gedanite - fossil resin that closely resembles but which is much more brittle than typical amber. This name is sometimes referred to an unripe amber, especially from the Baltic Sea region.

Osseous amber (bone amber) - white to brown, opaque or nearly opaque amber, the texture of which resembles bone or ivory; the opacity of which is due to the presence of many tiny extremely small bubbles.

Retinite - (a) a general term for a large group of fossil resins of variable composition characterized by the absence of succinic acid and found in the younger brown coals or in peat. (b) any fossil resin of the retinite group such as glessite, krantzite, muckite and ambrite.

Rumanite (Romanian amber), sometimes referred to as Romanite) - an amber that appears nearly black but can be seen to be dark reddish yellow-brown or even bluish when viewed closely under direct high light. It characteristically exhibits many cracks. The name almashite has been given to some of this amber.

Stantienite (black amber) - a black or nearly black, virtually opaque fossil resin that roughly resembles coke.

Succinite - term applied to amber that yields succinic acid when dry distilled.

DEGREE OF MATURATION (extent of diagenetic change)

Unfossilized resins

Animé (also called *gum animé*) - Holocene copal-like fossil resin frequently mistaken for amber.
Dammar (dammar or gum dammar) - an amber-like resin from Southern India and Malaysia.
Resin - a lipid soluble mixture of volatile and non-volatile terpenoid and/or phenolic products produced by a number of plants.

Semi matured

Copal - an amber-like resin, typically softer than amber. It has been recorded from the West Indies, Central and South America, West Africa, Madagascar, the island of Zanzibar, eastern India, and the East Indies, including the Philippines. A similar resin from Highgate near London, England has been called copaline or copalite. At least some copal can be distinguished from amber by placing drops of ether, chloroform, or alcohol on the unknown - copal dissolves leaving a dull spot whereas typical amber is not so-affected. Like amber, copal commonly contains insects and other materials. Of particular interest are the inclusions of a fluid, possibly blood, within a midge found in copal from Madagascar.

Matured

Amber - "true amber" usually insoluble in alcohol.

BOTANICAL ORIGIN (plant source of fossil resin)

Elemi - a group name for a fragrant resin of several angiosperm trees especially of the genera Canarium and Protium.
Glessite - opaque reddish brown to brown fossil resin with some angiosperm as its source.
Kauri gum - It is not a gum but a copal. From New Zealand. A drop of alcohol will cause a polished surface to loose its transparency in a minute or two.
Mountenite - name sometimes used as overall term for fossilized tree resins.

TRADE NAMES AND TREATED FOSSIL RESINS

Braunschweiger clear amber - trade name used by Germans for a high quality transparent amber.
Persian amber - a trade name for copal.

BOX 2

ANDERSON & CRELLING'S FOSSIL RESIN CLASSIFICATION

This table has been taken from and modified from Argonne National Laboratory Chemistry Division web page written by K.B. Anderson.

Class I
Resinites derived from polymers of labdanoid diterpenes plus labatriene carboxylic acids, alcohols and hydrocarbons. (Ambers with a labdane skeleton and show an affinity with the *Araucariaceae* family.

Class IA ... polymers and copolymers of labdanoid diterpenes normally including but not limited to communic acid and communol plus significant amounts of succinic acid ... Succinite (Baltic amber).

Class IB ... polymers and copolymers of labdanoid diterpenes normally including but not limited to communic acid, communal and biformine. Succinic acid is not present ... Fossil kauri amber.

Class IC ... polymers and copolymers of labdanoid diterpenes normally including but not limited to ozic acid, ozol and enantio biformenes ... Mexican and Dominican ambers.

Class II
Based on polymers of bicyclic sesquiterpenoid hydrocarbons, especially cadinene and related polymers... Utah and Indonesian amber.

Class III
Natural fossil polystyrene... Siegburgite and some New Jersey amber.

Class IV
Non-polymeric, incorporating sesquiterpenoids based on cedranine... Moravian amber and retinites from European brown coals.

Class V
Non-polymeric diterpenoid carboxylic acid especially based on abietane, pimarane and iso-pimarane... Fossil resins from the genus *Pinus*.

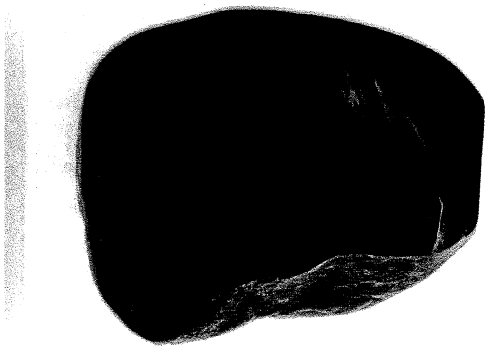

Fig. 3. Reversed polished side of amber specimen in Figure 2 (D53545). Photo S. Humphreys.

In these warm latitudes, Teredinids breed the year round so the presence of bore holes does not indicate a seasonal marine residence of the specimens (Ibrahim 1981). The internal appearance and colour revealed by smoothing the surface and polishing with a cloth show the specimens to range from a transparent, pale yellow to an opaque, deep brown to very dark red (Fig. 4).

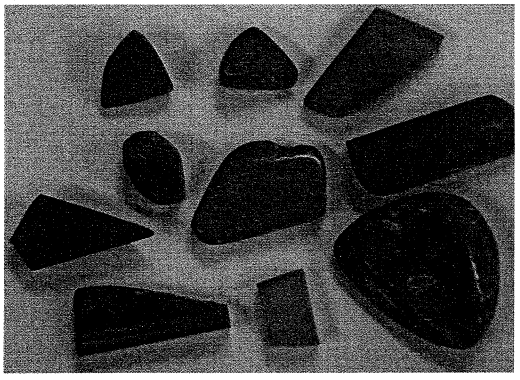

Fig. 4. A selection of polished Cape Weymouth specimens showing range of colours. Sizes 8-16 mm. Photo D. Colchester.

Gemmological properties

For gemmological purposes, the distinction between copal and 'true amber' depends on their reaction to solvents. A sticky patch indicates partial solubility and identifies the specimen as copal. Some Cape Weymouth specimens were inert to 98% ethanol while others were partially soluble. This indicates a range of maturation from semi-matured to matured fossil resin. Spot refractive index readings gave a single refractive index. of approximately 1.52 (slightly lower than Baltic amber). Five measurements of specific gravity were taken. These ranged from 0.96 - 0.98 (Baltic amber is 1.07). All specimens fluoresced more strongly under long-wave ultraviolet light than under short-wave, which was considerably weaker. Fluorescence ranged from chalky white through yellow to mustard brown. When a heated needle was applied to a specimen, a slight resinous odour was apparent.

Insect inclusions are common (Fig. 5). Other internal features include alternating clear and patterned bands (Fig. 6) and crowds of tiny round to ovoid bubbles (Fig. 7)

Fig. 5. A midge in Cape Weymouth amber. Specimen 65 mm across. Photomicrograph S. Lindsay. Magnification 25x.

Fig. 6. Alternating clear and patterned bands in amber from Cape Weymouth. Photomicrograph G. Webb. Magnification 20x.

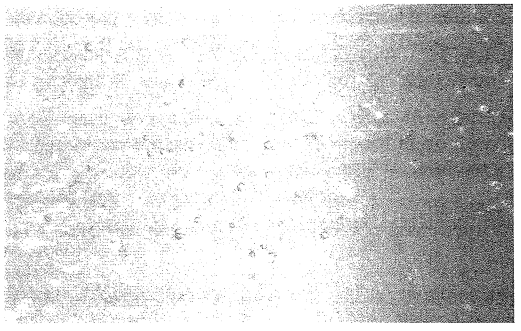

Fig. 7. Round and ovoid bubbles in Cape Weymouth amber. Photomicrograph G. Webb. Magnification 20x.

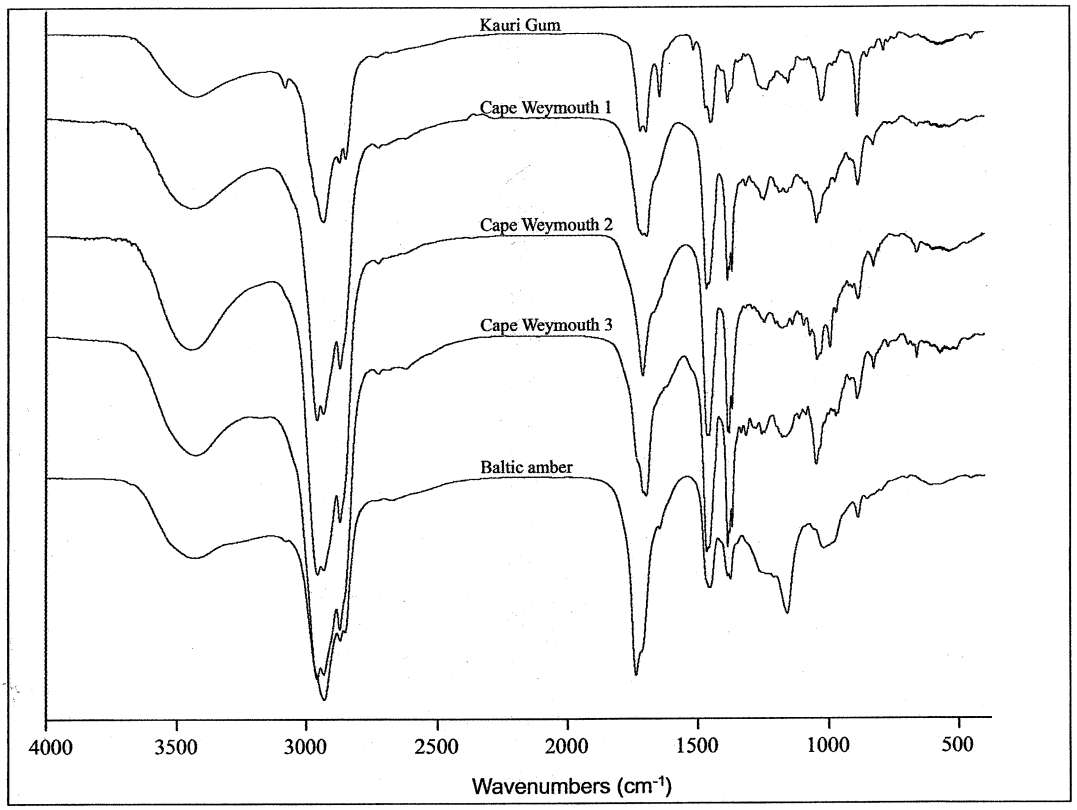

Fig. 8. FTIR spectra of 3 (three) Cape Weymouth specimens compared with the FTIR spectra of Kauri gum (a copal) and Baltic amber.

FTIR Spectroscopy

The chemical characterisation of the fossil resins was investigated by FTIR spectroscopy. A significant portion of fossil resin is an insoluble polymer, and this technique is suited to the analysis of these materials because it possesses both high sensitivity and the ability to analyse small quantities of solid samples. The resulting spectra provide a general qualitative-quantitative assessment of the presence of various kinds of bonds and functional groups by virtue of their vibrational energy patterns. It is an effective technique for resin analysis because the polymerisation process preserves all the original functional groups with the exception of C=C bonds, which diminish with maturation. Infrared spectroscopy has been used to characterise related fossil resins derived from different sources (Beck *et al.* 1964, Beck 1986, Czechowski *et al.* 1996). In this study, particular care has been taken to acquire the spectra at a high resolution of 1 cm-1 to aid in the assignment of the characteristic bands.

The infrared spectra of five fossil resins are shown in Fig. 8.

In general terms the spectra have similar features for all samples. Assignments of chemical groups to FTIR bands are summarised in Table 1.

Characteristic bands corresponding to functionalities present in the majority of reported fossil resins are also present in the three samples from the Cape Weymouth area. These include the presence of hydroxyl groups, olefinic functionalities, ketone and ester groups and saturated alkyl groups. As established by Beck *et al.* in 1965, Baltic amber shows a highly characteristic band at approximately 1160 cm^{-1} (symmetric stretching of the C-O bond in esterified succinic acid) that is preceded by a broad flat shoulder known as the "Baltic shoulder". This feature was later attributed to absorption of ester groups of polyester-like structures (Matuszewska & Karwowski 1999). Beck established that the slope of this shoulder is indicative of the degree of oxidative degradation of the succinate, with well preserved amber displaying a perfectly horizontal shoulder—this

Kauri Gum	Cape Weymouth	Cape Weymouth	Cape Weymouth	Assignment
3422 (s, broad)	3444 (s, broad)	3447 (s, broad)	3427 (s, broad)	ν_s(O–H)
3082 (m)	–	–	–	ν(C–H) exocyclic methylene
2931 (vs) 2871 (s) 2848 (s)	2957 (vs) 2933 (vs) 2870 (s)	2956 (vs) 2931 (vs) 2870 (s)	2958 (vs) 2931 (vs) 2871 (s)	ν_{as}(C–H) & ν_s(C–H) in methyl and methylene groups
1718 (s) 1696 (s)	1724 (s) 1711 (s) 1694 (s)	1710 (s)	1730 (s) 1707 (s) 1697 (s)	ν_s(C=O) in ester and ketone groups
1644 (s)	–[a]	1666 (m)	–	ν_s(C=C) or δ_s(O–H)
1468 (s) 1449 (s)	1465 (s) 1456 (s)	1463 (s) 1456 (s)	1466 (s) 1457 (s)	δ_{as}(CH_3) and δ_s(CH_s)
1384 (s) 1374 (s) 1367 (s)	1385 (s) 1378 (s) 1368 (s)	1385 (s) 1379 (s) 1368 (s)	1385 (s) 1378 (s) 1367 (s)	δ_s(CH_3)[b] and δ_s(C–O–H) in-plane bending
1262 (m) 1249 (m) 1232 (m)	1253 (m) 1243 (m)	1243 (m)[c]	1287 (m) 1278 (m) 1254 (m) 1243 (m)	Wagging and twisting of C–H bonds in methylene groups
1153 (m) 1025 (s)	1186 (m) 1159 (m) 1045 (s) 1031 (m)	1174 (m) 1138 (m) 1096 (m) 1071 (m) 1045 (s) 1030 (m)	1176 (m) 1164 (m) 1048 (m) 1034 (m)	ν_s(C–O) in esters and alcohols
985 (m) 973 (m)	1000 (m) 974 (m)	995 (m) 973 (m)	1015 (m) 973 (m)	δ_{as}(=C–H) out-of-plane deformation
888 (s)	886 (m)	887 (m)	892 (m)	ω(C=CH_2) out-of-plane wagging

[a] A shoulder is evident on the main band at 1694–1724 cm^{-1}

[b] Splitting of this band into three distinct weaker bands is strongly indicative of the presence of tertiary and quaternary methyl groups

[c] This band is asymmetric and is likely to contain a shoulder

Table 1. Assignments for FTIR bands (in cm-1) observed for fossil resin samples.

taking on an increasingly negative slope with advancing oxidation. The shoulder is not horizontal for the sample of Baltic amber examined in this study (Fig. 8), indicating that the sample is partially oxidized. This specific arrangement of bands between 1100-1300 cm^{-1} is not present in any of the other resins examined, though it has been noted for other non-European resins (Broughton 1974, Beck 1986). Additional differences in the spectra are also apparent. Of particular significance is the occurrence of three bands near 890, 1660 and 3080 cm^{-1} which correspond to exocyclic double bonds (Streibl *et al.* 1976). These are easily recognisable in samples of lower age such as Kauri gum and are notably absent in older resins such as Baltic amber. The resinites from the Cape Weymouth area represent an intermediate case where only the 890 cm^{-1} (out-of-plane wagging) and 1660 cm^{-1} (symmetric C=C stretching) bands are found. Notably, the latter band is present as a shoulder on the main band ca 1700 cm^{-1} in samples 1 and 2 from the Cape Weymouth area. This distinct feature enables the samples to be classified into three distinct age groups, regardless of occurrence. Kauri gum is a copal, Baltic amber is a fully matured fossil resin, and the three samples of fossil resin found near Cape Weymouth in North Queensland are intermediate in the copal-amber transitional

series. Our conclusion is supported by the results of the gemmological characterisation and the high degree of skeletal information derived from small sharp peaks in the "amber fingerprint region" between 880-1300 cm^{-1}. It has been established that older resins display a considerably smoother profile in this region (Grimalt *et al.* 1987). Differences in the chemical composition of the fossil resins from Cape Weymouth, as indicated by the infrared spectrum, are likely to be a consequence of several taphonomic variables. However their overall similarity is consistent with a similar paleobotanical origin.

Discussion & Conclusions

A significant Australian occurrence of amber-like fossil resin is to be found on the east coast of the Cape York Peninsula near Cape Weymouth. Gemmological testing has shown the fossil resin to be stable to semi-stable and hence suitable for gemmological purposes, while the insect inclusions are of scientific importance. FTIR spectra of the fossil resins have a broad similarity with FTIR spectra of kauri gum (a copal) and Baltic amber (a fully matured fossil resin), but are sufficiently different in the finer detail to have their own distinctive signature. Data obtained from pyrolysis gas-chromatography mass-spectrometry (GC-MS) and solid- and liquid-state nuclear magnetic resonance spectroscopy (NMR) are currently being analysed to itemise and identify the organic chemical components in order to establish their botanical origin.

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