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THE RESINOUS CARGO OF THE *JAVA SEA WRECK**

J. B. LAMBERT[1]†, A. J. LEVY[1], L. C. NIZIOLEK[2], G. M. FEINMAN[2], P. J. GAYFORD[2], J. A. SANTIAGO-BLAY[3] and Y. WU[4]

[1]*Department of Chemistry, Trinity University, One Trinity Place, San Antonio, TX 78212, USA*
[2]*Integrative Research Center, The Field Museum, 1400 S. Lake Shore Drive, Chicago, IL 60605, USA*
[3]*Department of Paleobiology, National Museum of Natural History, Washington, DC 20560, USA*
[4]*Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 70208, USA*

A number of blocks of resinous materials were found in the cargo of a 12th- to 13th-century shipwreck, discovered in the late 1980s in the Java Sea near the Indonesian islands of Sumatra and Java and excavated in 1996. These well-preserved blocks presumably were trade materials used for religious, medicinal, cosmetic, decorative or practical purposes. Such materials, derived from plants and termed exudates, generally include frankincense, myrrh, 'gum benjamin', liquidambar, dragon's blood, dammar, copal and amber. The source of the cargo resin could not be determined from the site. Investigation by nuclear magnetic resonance (NMR) spectroscopy has revealed that the molecular structure corresponds to that of modern resin from the plant family Dipterocarpaceae, known in trade as dammar and closely resembling Group B copal and amber. Other molecular classes of exudates are excluded. Such materials are not present in the Middle East, which then cannot be their source. The NMR spectra differ from those of Group B samples from Australia, Papua New Guinea and Indonesia, but resemble those from India or Japan. The spectra indicate that the saline environment had a similar effect on the molecular structure to heating and aging.

KEYWORDS: DAMMAR, EXUDATES, *JAVA SEA WRECK*, MARITIME TRADE, MATURATION, NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY, RESIN

INTRODUCTION

The *Java Sea Wreck* was found in the late 1980s by fishermen working in the Java Sea close to the small islands of Bangka and Belitung, near Java and Sumatra in Indonesia (Fig. 1) (Mathers and Flecker 1997). In 1996, Pacific Sea Resources, a US-based salvage company, was granted a license to carry out recovery efforts, which were done under the supervision of underwater archaeologist Michael Flecker. After recovery, according to the agreement between Pacific Sea Resources and the Indonesian authorities, half of the material was given to the Indonesian government and half was donated to the Field Museum of Natural History in Chicago. There, researchers have been working to identify sources of the vessel's cargo, map ancient trade routes and reconstruct social relationships that linked communities from different corners of the globe. The project described in this paper represents the work of an interdisciplinary team of chemists and archaeologists from a number of research institutions, who have been investigating the characteristics and possible origin of one of the most highly valued trade commodities of Song-dynasty China – aromatic resin. Several publications by Flecker (2003, 2005–6, 2011)

*Received 26 March 2016; accepted 8 July 2016
†Corresponding authors: email jlambert@northwestern.edu, lniziolek@fieldmuseum.org

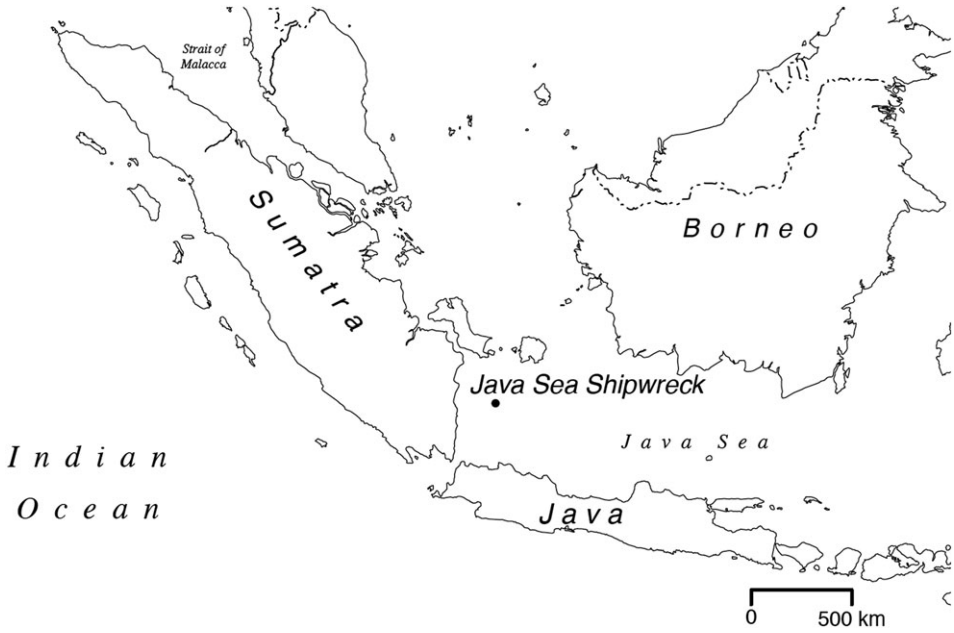

Figure 1 *A map showing the location of the Java Sea Wreck (illustrator David Quednau).*

and by Mathers and Flecker (1997) have described the recovery of the *Java Sea Wreck*, some basic points of which are reviewed here.

The wreck lay approximately 26 m below the water's surface. After 2 months of excavation, more than 12 000 relatively intact pieces of ceramics were recovered – just over 12% of the 100 000 ceramic pieces estimated to have constituted the original cargo (Flecker 2003, 2005–6). Based on ceramic styles and initial radiocarbon dating, the ship was thought to have sunk during the 13th century AD (the 68% probability range of the calibrated date is AD 1265–1310) (Brown 1997; Flecker 1997b).

The two main materials carried by the *Java Sea Wreck* vessel were ceramics and iron. Most of the ceramics were high-fired wares from China. Most of the Chinese ceramics were probably made at kilns in Fujian province, which produced mainly export wares at the time. A small set of finely made pieces with a light blue translucent glaze *(qingbai)*, however, is thought to have been made at kilns in Jingdezhen in Jiangxi province (Brown 1997; Niziolek 2015). Also among the cargo were numerous pottery pieces hypothesized to have been made in southern Thailand, including *kendis*, *kundikas*, hookahs, lids and pots (Brown 1997), some of which may have been intended to be used in the preparation of medicines or in ablution rituals (Respess and Niziolek 2016).

Almost 200 tons of iron were present at the wreck site (Flecker 2005–6), primarily in the form of bundles of iron bars (Bronson 1997; Flecker 2003). This material was probably manufactured in China for shipment to Java to be used in the production of weapons and agricultural tools. Although Javanese communities had access to local iron, it was more cheaply produced in large quantities in China and was exported from there to Indonesia (Christie 1999). Most of the iron was stored in the bottom of the ship. Over time, all but a few small pieces of wood disintegrated. The concreted iron formed a sort of map that could be used to estimate the ship's size and to reconstruct its structure (Flecker 1997b, 2003). Based on the type of wood used for the

construction of the ship (*Parastemon urophyllum*, or *mandailas*) and the likelihood of the vessel being of lashed-lug construction, the ship, which measured approximately 28 m long by 8 m wide, probably was built in South-East Asia (Flecker 2003).

The archaeological record tends to be biased towards non-perishable materials such as ceramics. Some items present in the *Java Sea Wreck* cargo, however, can be used to examine the trade of perishable materials, including ivory and solid resinous materials. A total of 16 pieces of ivory were recovered at the site and were found together in the area that would have been the starboard side of the stern (Flecker 1997a, b, 2003). During the Song dynasty (AD 960–1279), ivory was imported into China and used in art and decoration. It also was an important component in various folk medicines (Respess and Niziolek 2016).

The other major organic product frequently traded via maritime networks in East and South-East Asia and present at the *Java Sea Wreck* site is plant resin. During the recovery of the ship's cargo, eight pieces of resin were found scattered in the area believed to be the starboard side of the stern of the ship (Flecker 1997b) (the same general area where the ivory was found). Aromatic resin was often imported into China and, along with aromatic wood, was considered one of the most important commodities of the South China Sea trade up until the Southern Song dynasty (AD 1127–1279) (Miksic 1997). Typically, it was used in Buddhist rituals (Flecker 2003), but it also had medicinal applications and was used in perfumes and lacquers (Wang 1998). Some resins were also used as a caulking and waterproofing agent in the construction of boats in South-East Asia (Burger *et al.* 2010).

Resins are well documented in Zhao Rugua's 13th-century account of Chinese-Arab trade (Zhao 2012 [1911]). In the *Zhufan zhi* (*Record of foreign peoples*), Zhao, supervisor of foreign trade at and later prefect of Quanzhou (Fujian province), indicates that *ju-hiang* ('milk incense', or frankincense) came from three Arab or Persian countries – Ma-lo-pa (south-western Oman), Shï-ho (Yemen) and Nu-fa (southern Oman). Zhao's complete list includes 43 materials, the first eight of which seem most relevant to our study: camphor, frankincense, myrrh, dragon's blood, 'sweet benzoin', dammar, liquid storax and 'benzoin'. The remaining materials are exotic aromatics such as ambergris, gardenia flowers, patchouli, cloves, nutmeg and sandalwood, the main sources for which are the Middle East and South-East Asia (Wheatley 1959).

Determining the original sources of these treasured materials is not an easy task. An estimated 50 countries conducted overseas trade with China during the Song dynasty, including Gujara (Gujarat, India) and Japan (Wheatley 1959). In addition, trans-shipment took place, and the ports at which merchants procured trade items may have been far from the origins of these items; for example, frankincense from Hadhramaut on the southern part of the Arabian Peninsula was trans-shipped to Srivijaya on Sumatra for onward shipment to China. Further complicating the reconstruction of trade routes and identification of original product sources was the transportation of some products to multiple locations for processing. Wheatley (1959, 58) notes that 'in later periods Arab merchants shipped gum benjamin to India and the Middle East for adulteration with Indian gum-gugul [a type of myrrh] and Arabian frankincense, prior to carrying it back to the East for sale in China'. Information on the original sources of materials also was carefully guarded by merchants in some cases, so that they could maintain a monopoly on these products (Wheatley 1959).

At the time of the initial archaeological report on the recovery of the *Java Sea Wreck* (Mathers and Flecker 1997), the source and type of the resin found at the wreck site were not determined. Miksic (1997) hints at South-East Asian origins and notes that *Styrax benzoin*, found in Sumatra, Malaysia and western Java, was the most frequently traded type of resin. Flecker (2003) reinforces the idea that the resin is from South-East Asia, citing Sumatra as its likely origin.

MATERIALS AND METHODS

The two most common methods for structural elucidation of organic materials are nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry (MS) (Lambert *et al.* 2011). We have developed the NMR approach as an effective means to characterize both fossilized resin and modern plant exudates, but MS in its own right provides an excellent method (Lambert *et al.* 2008). NMR spectroscopy examines specific atomic nuclei within a molecule and characterizes their molecular environments according to the frequencies at which they interact with an applied magnetic field (Lambert and Mazzola 2004). The most useful nuclei for the examination of organic materials are hydrogen (also called 'proton' in this context and abbreviated as ^{1}H) and carbon-13 (^{13}C). Most common is the one-dimensional (1D) ^{1}H procedure, in which the various structural types of hydrogen atoms are characterized according to their frequencies by comparison with a standard (because of this comparison, the phenomenon is termed 'resonance'). The resonance frequency is plotted on the horizontal axis, and the vertical axis represents intensity, as determined by the proportion of that particular molecular species present in the sample. These spectra provide clear distinctions among the various types of plant materials that might have generated the resinous cargo.

SAMPLE SOURCES AND TREATMENT

All samples from the *Java Sea Wreck* were obtained from the anthropology collections of the Field Museum. Field Museum conservator Shelley Paine and author Niziolek removed approximately 100–150 mg each of the outer cortex and the interior material using a dental drill (samples from catalogue number 351444, due to its friable nature, had pieces broken off that obviated drilling).

For solid state carbon-13 (^{13}C) NMR measurements, samples were ground into a fine powder and were loaded into a Varian 5 mm general-purpose zirconia rotor, sealed with Vespel caps. The optimal sample load is about 150 mg of material, but smaller sample sizes (as little as 50 mg) required larger scan numbers. For solution state proton (^{1}H) spectra, approximately 55 mg of powdered exudate (recovered from ^{13}C analysis) was transferred to a small, glass vial. About 1 mL of deuterated chloroform-d_6 was added to each vial. The material was stirred at room temperature and allowed to sit overnight. The supernatant was pipetted out and transferred to the NMR tube.

DATA ACQUISITION

Solid state ^{13}C NMR data were recorded at Northwestern University on a 400 MHz Varian NMR system with a 5 mm T3 PENCIL probe. The magic angle spinning rate was set to 5000 Hz. The cross-polarization (CP) pulse sequence was used for normal ^{1}H decoupling. We used adamantane to adjust the Hartmann–Hahn matching condition for normal CP procedures and to adjust the observation pulse. A typical parameter set was as follows: spectrum frequency 100.544 MHz, spectral width 50 kHz, pulse width 3.4 μs for the 90° pulse for both ^{1}H and ^{13}C, contact time 2 ms, acquisition time 20.5 ms and scan number 256. Solid state ^{13}C spectra were referenced to an external adamantane peak at δ 38.3 and were converted to tetramethylsilane at δ 0.0.

The ^{1}H spectra were obtained at Trinity University on a Varian Inova-500 NMR spectrometer at room temperature, without spinning. Typical 1D parameters were as follows: spectral width 12 000 Hz, pulse width 60°, delay time 1.0 s, acquisition time 1.0 s and scan number 4. Spectra were referenced in $CDCl_3$ to TMS.

THE RESINOUS MATERIALS IN THE CARGO

All of the resin pieces are covered in a light brown, corky cortex. Below the surface, the material is harder, glassier, darker and reddish-brown in colour (Fig. 2). Some of the pieces are very friable. Flecker (1997a, 81) wrote in the archaeological report, 'There has been a bit of erosion, and the outer millimeter or so has become a soft powdery pale brown. But within, the solidified tree sap remains glassy, and the fragrance remains distinctive.' Table S1 provides the dimensions of the samples.

ARCHAEOLOGICAL INFERENCES CONCERNING THE SOURCE OF THE SHIP

Based on the quantity and types of ceramics found at the wreck site, it is hypothesized that the ship left from Quanzhou (Fujian province), one of China's major trading ports at the time, which

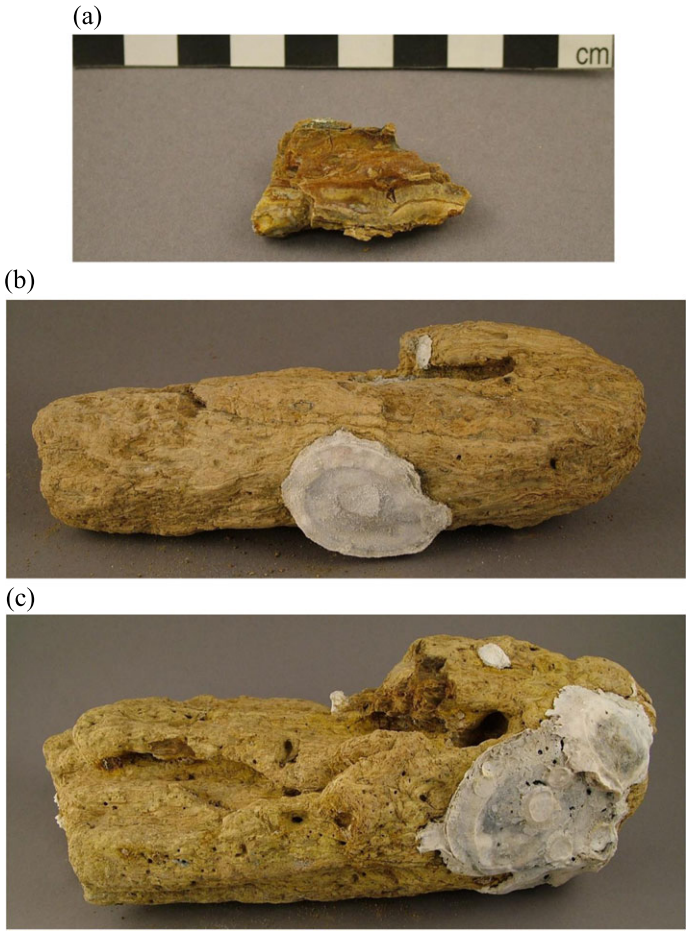

Figure 2 *(a) A small fragment of resin (Catalog No. 351381) from the Java Sea Wreck showing the fragile cortex (darker) and the glassy interior (lighter). (b) A piece of resin (25.5 cm long, Catalog No. 351442) showing evidence of having been cut prior to submersion. (c) A piece of resin (41.2 cm long, Catalog No. 351444). Both (b) and (c) have shells adhering to their surfaces and evidence of having been cut prior to submersion. (Photographs © The Field Museum.)*

was surrounded by kilns producing export wares similar to those in the *Java Sea Wreck* cargo (Flecker 2003). Its itinerary may have included Guangzhou (Guangdong province, an important Song-dynasty port in the south of China), peninsular Thailand (where the fine-paste earthenware pieces, such as the *kendis*, were added to the cargo), a port on Sumatra (where merchants would have traded their goods for natural products such as ivory and resin, to be taken back to China) (see Flecker 2003) and finally Tuban (one of Java's most prosperous ancient ports) (Mathers and Flecker 1997; Flecker 2005–6; Hall 2011). Merchants on board the vessel may have planned to trade the Chinese ceramics and iron for commodities such as spices and other forest and marine delicacies, which were highly desired in China during this period. Java, in fact, is identified by Zhao Rugua (2012 [2011]) as the origin for much of China's imported pepper in the 13th century. En route, however, the vessel, laden with copious quantities of trade goods, foundered and sank to the bottom of the Java Sea, where it remained for almost eight centuries.

NMR ANALYSIS OF THE RESINOUS MATERIAL

Analysis of the resinous materials had two objectives: (1) to determine the botanical type of exudate in the cargo of the *Java Sea Wreck*; and (2) to determine the source of the material. As already described, there were numerous types of resinous materials in active trade during the 13th century. These included frankincense, myrrh, storax (liquidambar), dragon's blood, dammar and 'gum benjamin' (also inaccurately called benzoin), as recorded by Zhao Rugua ([1911]). We can eliminate other aromatic materials as candidates for the cargo's resinous material, such as gardenia flowers, patchouli, cloves, nutmeg and sandalwood, which have characteristic morphologies or, in the case of patchouli, is a liquid essential oil. These materials are not capable of being processed into the types of blocks found in the cargo.

Up to this point, we have referred to this portion of the cargo as resin or resinous materials. In the field of plant exudates, the term 'resin' is restricted to materials derived from and composed of terpene constituents. As popular terms, however, 'resin' and 'resinous materials' are applied to any number of materials that resemble terpene-based resins in appearance but in reality are molecularly distinct. For the purposes of chemical analysis, it is appropriate to adhere to a classification based on molecular structure (Santiago-Blay and Lambert 2007; Lambert *et al.* 2008). Terpenes are predominantly hydrocarbons, composed of units of the simple material isoprene (CH_2==C(CH_3)—CH==CH_2). During the biosynthetic formation of exudates, this building block is functionalized and polymerized. Resins are highly soluble in organic solvents and insoluble in water.

Of the materials listed above, only dammars are true resins. Whereas resins are complex mixtures of terpenes, camphor is a single molecule of formula $C_{10}H_{16}O$ that is easily identified by modern spectroscopic methods. Gums are a second major group of exudates (Nussinovitch 2010). They are composed of units of carbohydrates, which have a very different spectroscopic signature from resins (Lambert *et al.* 2005). Gums tend to dissolve in water but are insoluble in organic solvents. None of the trade items listed above is a gum. Many plants exude a material that contains mixed gum and resin components. Such materials have been called 'gum resins' and include both frankincense and myrrh. Materials commonly called 'aromatic resins' constitute a third major group of plant exudates. In this context, the word 'aromatic' does not refer specifically to the olfactory properties of the material but, rather, to the presence of the molecular constituent that chemists call aromatic, signifying the presence of a functionalized benzene ring. In a chemical context, such molecular constituents are referred to as aromatic rings or aromatic functionalities. Because these

materials are not terpene-based, the term 'resin' is to be avoided, although it is commonly so used (Langenheim 2003). The exudates of eucalyptus trees provide one such example. They give uniquely characteristic spectral patterns, so we have referred to the class as 'kinos' (Lambert *et al.* 2007), a term used in South Asia for such exudates.

Figure 3 (a) presents the 1D ^{1}H spectrum of the cortex of sample 351380, dissolved in deuterated chloroform ($CDCl_3$). The spectrum is relatively simple, with strong peaks in the region δ 0.6–2.4 and a pair of closely spaced peaks at δ 5.5. In NMR spectroscopy, the Greek letter δ represents the resonance frequency unit in parts per million (ppm) of the magnetic field and is placed in front of the numbers. The region δ 0.6–2.4 corresponds to the frequencies at which hydrogen atoms bound to saturated carbons (those without multiple bonding) occur, so it is called the saturated region. Such functionalities are expected in a terpenoid (hydrocarbon) structure. The peak at δ 5.5 falls in the unsaturated region, in which hydrogen atoms attached to double bonds resonate. Its presence indicates that a small portion of the carbon atoms in the sample are doubly bonded. The peak at δ 0.0 is from tetramethylsilane, [$(CH_3)_4Si$, the standard used to provide an agreed-upon zero frequency]. The peak at δ 7.3 is from undeuterated solvent, $CHCl_3$, an

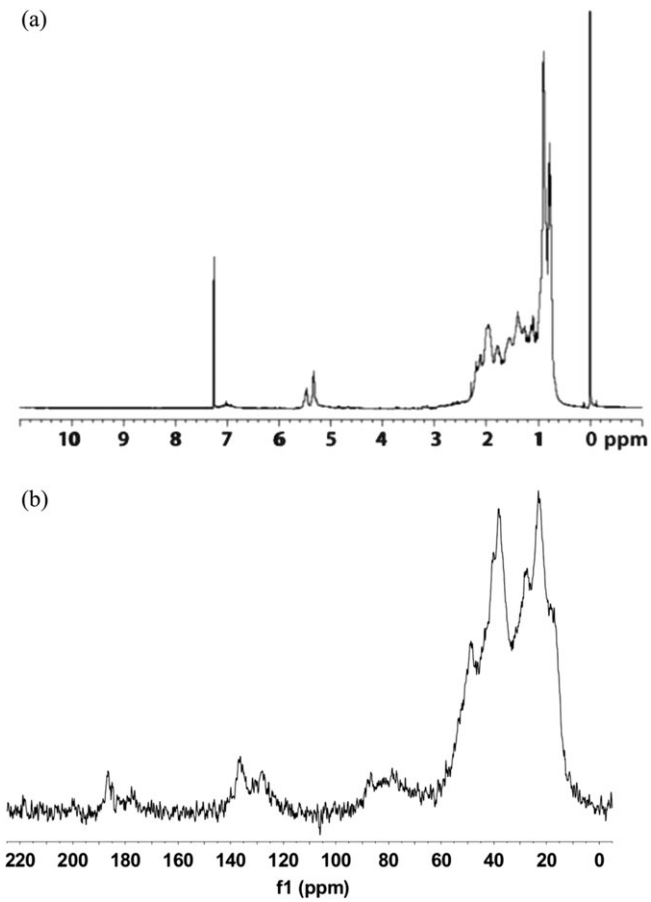

Figure 3 *(a) The 1D ^{1}H spectrum of a sample from the cortex of block 351380 from the Java Sea Wreck, dissolved in $CDCl_3$. (b) The solid state ^{13}C spectrum of the same sample, taken with magic angle spinning and cross-polarization.*

impurity in the commercial deuterated chloroform. This spectrum demonstrates that the resinous materials in the *Java Sea Wreck* indeed are true (terpene-based) resins.

The carbon spectrum of the same sample from the cortex of block 351380 is illustrated in Figure 3 (b). Carbon resonance frequencies also are reported in ppm of the magnetic field as designated by the symbol δ. The large set of resonances in the range δ 20–60 represent the NMR response of saturated carbon atoms. In ^{13}C NMR spectroscopy, unsaturated carbon nuclei fall in the region δ 110–150, and there are small resonances in this region. Their particular frequencies indicate that they come from internal (as opposed to exocyclic or terminal) double bonds. Unsaturated atoms characteristically produce so-called spinning side bands in solid state ^{13}C spectra, occurring on either side of the normal band at the spinning frequency, in this case at δ ~ 80 and 180. These artefacts are to be ignored. The spectra in Figure 3 are typical for a resin.

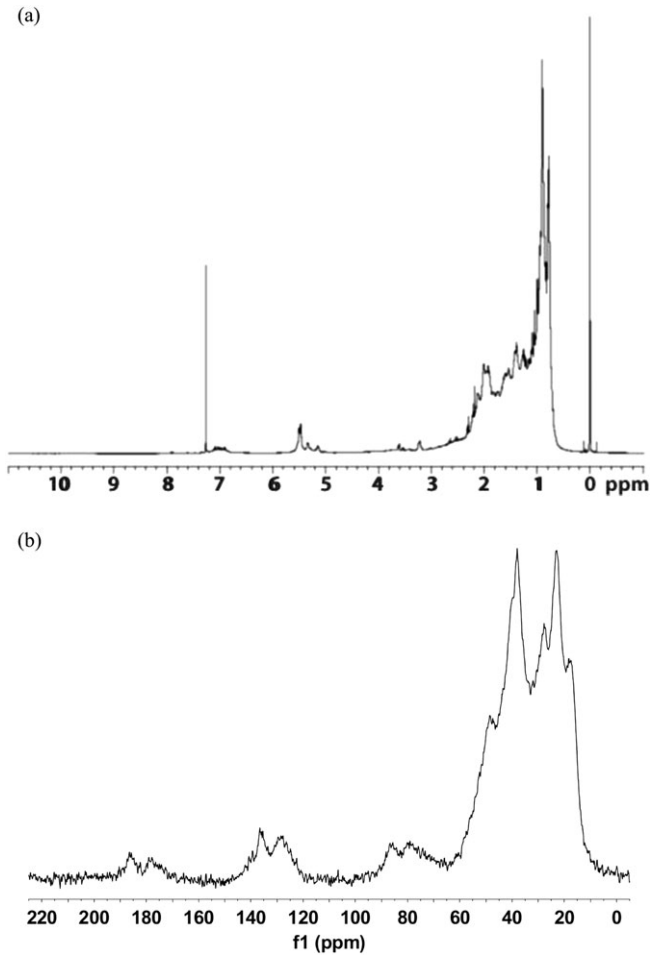

Figure 4 *(a) The 1D ^{1}H spectrum of a sample from the Museum of Comparative Zoology, Agassiz Museum, Harvard University, labelled sample C in the original source but identified as sample 1578 in the Trinity collection, said to be from Arkansas, dissolved in $CDCl_3$. (b) The solid state ^{13}C spectrum of the same sample, taken with magic angle spinning and cross-polarization.*

THE BOTANICAL IDENTITY OF THE RESINOUS MATERIAL

The spectra illustrated in Figure 3 resemble those of amber from Arkansas in the United States (USA) (Fig. 4). In the ^{1}H spectrum (Fig. 4 (a)), the saturated region is very similar to that in Figure 3 (a). In addition, even the small peaks at δ 3.2 and 5.5 are replicated. There are minor differences, including small resonances at δ 5.2, 5.4 and 7 in Figure 4 (a) (the last peak is in the aromatic proton region, δ 6.5–8.0, which contains resonances from molecules with benzene rings). The ^{13}C spectra in Figures 3 (b) and 4 (b) also are nearly identical.

The similarity of the spectra in Figures 3 and 4 relate the *Java Sea Wreck* resins to Group B, a worldwide amber class first characterized in 1990 by NMR from a sample from Arkansas (Lambert *et al.* 1990) and broadened into an amber class based on NMR spectral patterns by comparison with Australian and related Pacific ambers in 1993 (Lambert *et al.* 1993, 2008). The parallel MS Class II was defined by Anderson *et al.* (1992) at about the same time, based on the identification of specific molecular markers.

Identification of the *Java Sea Wreck* resinous material as related to Group B resins, based on a terpenoid molecular structure, eliminates gums, kinos and gum resins. Gums have the characteristic resonances of carbohydrates, with just two resonances, one close to δ 75 from carbon atoms attached to one oxygen atom and one close to δ 105 from carbon atoms attached to two oxygen atoms (the so-called anomeric carbons in carbohydrate nomenclature). Gum resins contain both these gum resonances, as well as the saturated, terpenoid resonances characteristic of resins. The materials from the *Java Sea Wreck* lack such characteristics, so frankincense and myrrh can be eliminated from consideration. Kinos are dominated by aromatic resonances (δ 6.5–8.5), entirely lacking in the spectra of the *Java Sea Wreck* materials.

In addition to these main classes of exudates, we must consider less common materials, such as those listed by Zhao Rugua in his 13th-century account of Chinese-Arab trade (Zhao 2012 [1911]). Exudates from the genus *Styrax* of the Styracaceae solidify to a solid that variously has been called styrax resin, benzoin resin, gum benzoin, gum benjamin and balsamic resin. Our analysis of the NMR spectra of several such samples (Lambert *et al.* 2013b, figs 7 and 8) demonstrated that these materials are neither resins (lacking terpenoid resonances) nor gums (lacking carbohydrate resonances), so neither of these terms is appropriate for them, negating all the common terms for these materials. Rather, the spectra are dominated by the resonances of aromatic carboxylic acids such as benzoic and cinnamic acid. Previous usage suggested that exudates from *Styrax* best be called balsams (Lambert *et al.* 2013b). The *Java Sea Wreck* materials clearly are distinct from balsams, eliminating the suggestion of Miksic (1997).

Dragon's blood is a term applied to many solidified exudates, but probably most widely to that of one species of rattan palms from the Arecaceae, *Daemonorops draco*, as well as to species from other genera, such as *Croton*, *Dracaena*, *Pterocarpus* and *Calamus* (Langenheim 2003). We have examined all these materials and found them in general to consist of phenolic functionalities, similar to kinos but with a quite distinct NMR profile (Lambert *et al.* 2015a, fig. 15). The absence of aromatic resonances in the spectra of cargo from the *Java Sea Wreck* eliminates dragon's blood as a candidate.

The term 'storax' mentioned by Zhao presumably refers to liquidambars, which are not liquid after they mature; nor are they amber. To avoid confusion between styrax and storax, we use the terms 'balsam' for styrax and 'liquidambar' for storax (Lambert *et al.* 2013b, 2015a). We have examined several samples of liquidambar from the family Altingaceae and found them to be terpene-based resins. The ^{1}H and ^{13}C patterns, however, are quite different from those from the resinous materials of the *Java Sea Wreck* (Lambert *et al.* 2015a, figs 20 and 21).

Unlike all other traded resinous materials, dammars provide a match with the *Java Sea Wreck*. The term 'dammar' most widely refers to the solid exudates from the Dipterocarpaceae (Langenheim 2003). Unfortunately, the term is applied to resins from the Burseraceae as well. The two families both are angiosperms of the type known as eurosids, but dipterocarps are from the order Malvales and the Burseraceae are from the order Sapindales. They have distinct NMR spectra, so that they should not be conflated. Resins from the Burseraceae should not be referred to as dammars. Several genera from the Dipterocarpaceae generate exudates with very similar NMR spectra, including *Dipterocarpus*, *Hopea*, *Shorea* and others (Lambert *et al.* 2013c). Although the family is pantropical, extending from Africa to northern South America to Asia, the resin-producing genera, including the three principal ones just mentioned, are found today from India through South-East Asia to Australia. We have previously commented on the similarity of the spectra of these dipterocarps with those of Group B ambers (Lambert *et al.* 2013a); Stout (1995) used MS methods to demonstrate the similarity of fossilized South-East Asian amber (NMR Group B) with modern dammar. Figure 5 presents the ^{1}H and ^{13}C spectra of the exudate

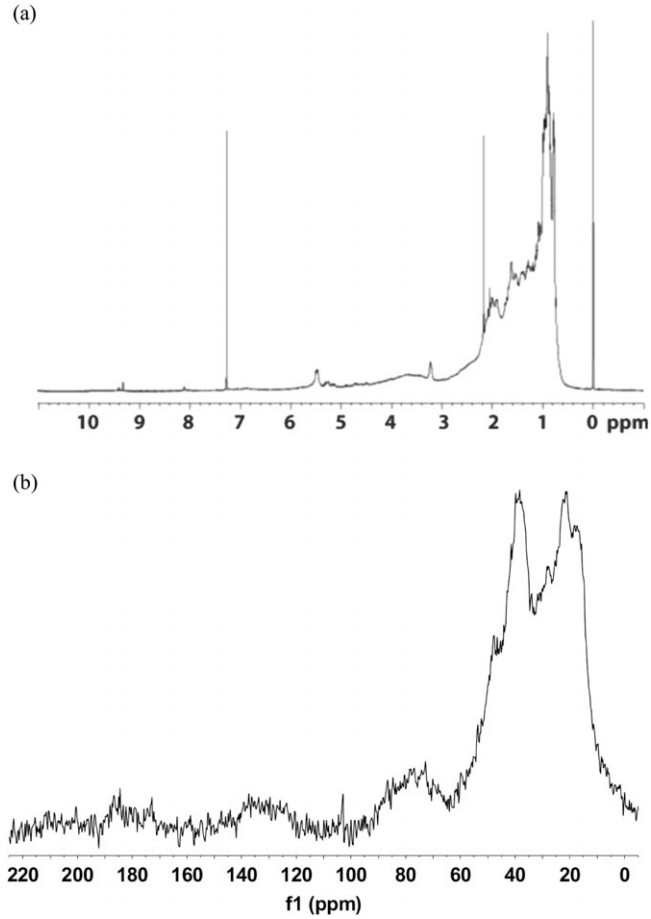

Figure 5 *(a) The 1D ^{1}H spectrum of a sample of Shorea robusta provided by the National Museum of American History, Material Medica Collection no. 142061, sample 1093 in the Trinity collection, dissolved in $CDCl_3$. (b) The solid state ^{13}C spectrum of the same sample, taken with magic angle spinning and cross-polarization.*

from *Shorea robusta* of the Dipterocarpaceae. The ^{1}H spectra of the resinous material from the wreck (Fig. 3 (a)) and Group B amber (Fig. 4 (a)) clearly resemble the spectrum of the modern resin closely (Fig. 5 (a)). They have in common the alkenic peaks at δ 5.5, the small peak at δ 3.2, the group of saturated protons at δ 2, the relatively level area at δ 1.2–1.6 and the dominant saturated protons at δ ~ 1 (the sharp spike at δ 2.2 in Figure 5 (a) is an impurity, probably from unintended acetone). The spectra in Figures 3 (a) and 5 (a) are by no means identical. We have examined the ^{1}H spectra of many dipterocarps and have seen a wide variety of details, within the same spectral theme (Lambert *et al.* 2013c). Analogously, the ^{13}C spectra of the wreck resin (Fig. 3 (b)) and of Group B amber (Fig. 4 (b)) closely resemble that of *S. robusta* (Fig. 5 (b)), although the last spectrum has a higher noise level. These spectral comparisons leave no doubt that the resinous materials from the *Java Sea Wreck* derive from a dipterocarp whose exudates have commonly been called dammars, as is true in general for Group B amber.

DELINEATION OF THE SOURCE OF THE RESINOUS MATERIAL

We have identified Group B amber in several locations in the USA, but dipterocarps have gone extinct there. The major current sources extend from South Asia through South-East Asia to the Pacific. It is safe to eliminate the Americas as the source of the resinous component of the cargo, but the remaining sources need to be considered. To date, we have identified Group B amber from India, Thailand, Australia, Papua New Guinea (Lambert *et al.* 1993), Japan, Indonesia, Malaysian Borneo (Lambert *et al.* 2013a) and possibly Burma (Poinar *et al.* 2007) (countries without references represent previously unpublished results). Dipterocarps are common in all these areas today. Conspicuously missing from the list are South-West Asian (Middle Eastern) sources. Amber is well known in the region from Lebanon through Iraq to Iran and Azerbaijan. Without exception, however, these materials have proved to be Group A ambers, which derive from a conifer source and are quite distinct molecularly and spectroscopically from Group B ambers. Although frankincense and myrrh do have primary sources in the Middle East, the resinous materials from the *Java Sea Wreck* are not gum resins. Thus Middle Eastern sources of the resin are safely eliminated. There remains, however, a large swath of territory from India to Japan, which produces Group B amber and the plants from which it is derived.

It is a likely possibility that the resin had been obtained from a source in Indonesia or Borneo close to the find site of the wreck (Fig. 1), to serve as trade material. We have carried out an extensive study of amber and its precursors from Indonesia (Lambert *et al.* 2013a). Although spectra of the Indonesian materials indeed represent Group B and are very similar to those of the resinous cargo, there is one definitive difference. Figure 6 provides the ^{1}H spectrum of one of 17 samples examined from four different Indonesian islands plus Malaysian Borneo. Although the saturated spectral region is reasonably similar to that of the cargo resins illustrated in Figure 3, there are consistent differences in the unsaturated (alkenic) region. All 15 of the cargo resin samples exhibit a simple doublet at δ 5.5, whereas all 17 of the Indonesian/Borneo samples exhibit a singlet at δ 5.5 and another, larger, singlet at δ 5.3. These distinct differences appear to eliminate any part of Indonesia or Borneo as sources of the resinous cargo. This conclusion can be negated by either of two circumstances: (1) the particular source of the wreck resins is atypical and corresponds to none of our 17 samples; or (2) Indonesian resins degrade uniquely to produce the alkenic bands found in Figure 6 (a) at δ 5.3 and 5.5. The latter circumstance is feasible. In our examination of Indonesian ambers, we included one sample of a material labelled ‘green amber’. Its ^{1}H spectrum (Lambert *et al.* 2013a, fig. 6) contains only the simple alkenic doublet at δ 5.5, as well as numerous small peaks, but lacks the singlets at δ 5.3 and 5.5 found in Indonesian ambers

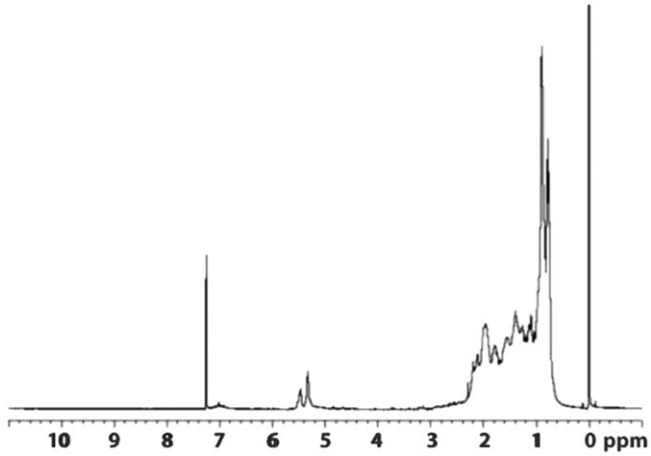

Figure 6 *The 1D ^{1}H spectrum of a sample of fossil resin from Kuala Tungkal, Jambi, Central Sumatra, Indonesia, provided by M. Iskandar bin Marzuki, sample 1418 in the Trinity collection, dissolved in $CDCl_3$.*

(Fig. 6). Thus it is possible that all our Indonesian ambers are considerably more degraded than the wreck resins.

The remaining Asian sources of Group B fossilized resins are Australia, Papua New Guinea, India, Japan and Thailand. None of these samples exhibit the peculiar alkenic pattern that characterizes Indonesian amber, so they all are candidates, at least from a spectroscopic point of view. The spectra of the samples from Australia and Papua New Guinea show the largest differences from the cargo resin (Figs S1 and S2). In the spectra from Australia and New Guinea, the alkenic resonances appear as a doublet at δ 5.5, but with much reduced intensity. In addition, the details of the respective saturated regions are quite different. These differences are probably sufficient to eliminate this region as the source of the resinous cargo. There also are significant differences in the saturated resonances in the Thai sample (Figs S3 and S4).

Both the Japanese and the Indian samples show strong similarities to the cargo resins. In Figure S5, the spectra from these respective sources are compared to those of the interior of block 351352 from the *Java Sea Wreck*. Although the Indian sample is unpublished, we recently reported the Japanese sample and commented on its unusual nature, since all other Japanese ambers are Group A (Lambert *et al.* 2015b). The spectra from both sources show strong similarities to that of the cargo resin. In particular, the alkenic doublet is an almost perfect overlay in both cases. The aldehydic resonances at δ 9.3 are weaker in both source spectra. The complex saturated region also shows remarkable similarities in both cases. It is difficult to attempt to choose a preference. Figures S6 and S7 provide an expansion of the saturated regions. Both sources are attractive from a maritime point of view. Gujarat is on the north-west coast of India, on the Arabian Sea and the border today with Pakistan, less than 1000 miles from Oman. It was a common port between the Middle East and Indonesia. Japan is at the opposite extreme on the trade route, a possible stopover point between China and Indonesia.

THE MATURATION LEVEL OF THE RESINOUS MATERIAL

Maturation describes the extent of cross-linking, oxidation and other chemical processes involved in the fossilization of resin. Although never truly finished, maturation is sufficient after

about a million years for a resin to be considered amber (Schlee and Glöckner 1978), although some authors consider that as little as 40 000 years suffice (Vávra 2009). A preliminary carbon date of the resinous material in the cargo was AD 1265–1310 (Brown 1997; Flecker 1997b), so the resin was relatively new at the time of the voyage and indeed still retained its odour in the interior. The appearance of the ^{1}H NMR spectra (Fig. 3 (a)), however, is suggestive of mature material, because of its close resemblance to the spectra of Arkansas resin (Fig. 4 (a), Eocene, Saunders *et al.* 1974) and that of Japanese resin (Fig. S5 (a), green). The Japanese sample is from Mizunami in Gifu Prefecture, materials from which have been considered to be from the Pleistocene or even younger (Hiura and Miyatake 1974). Less mature resins in particular exhibit significant peaks in the aldehyde region ($\delta \sim 9.3$) and additional fine structure in the saturated region. Modern resins and dammars exhibit such characteristics (Lambert *et al.* 2013a). Other conditions, however, can simulate maturation. In unpublished experiments, we have demonstrated that artificial heating can bring about NMR spectral changes that resemble the effects of maturation.

The resinous cargo was exposed for 700–800 years to the saline environment of the sea, whose effects are unknown. We considered the hypothesis that the saline environment would have a greater effect on the external (cortical) portion of the resin blocks than on the internal portion. Figure S8 compares the ^{1}H spectra of the interior and exterior resins from block 351445. Whereas the spectrum of the internal resin resembles that of less fossilized materials, that of the external resin resembles that of more fossilized materials. In particular, saline maturation results in loss of the aldehyde resonances at δ 9.3, a decrease in intensity of the main alkenic peak at δ 5.5, the loss of the alkenic filigree at δ 4.5–5.4 and 5.8–5.9, a decrease in intensity of the ever-present small peak at δ 3.2, simplification of the entire saturated region (δ 0.6–2.2) and alteration of the relative intensities of the two strongest peaks in the spectrum at δ 1.2 and 1.3. Overlays of expansions of the alkenic and aldehydic regions emphasize these changes (Figs S9 and S10).

CONCLUSIONS

Based on ceramic styles and preliminary ^{14}C dating, the *Java Sea Wreck* probably sank during the late 13th century AD (Brown 1997; Flecker 1997b). The type of wood used in the construction of the ship and the mode of construction suggests that the ship was probably built in South-East Asia (Flecker 2003). The cargo contained eight pieces of resinous material scattered over the presumed starboard side. Miksic (1997) hinted that the material had a South-East Asian origin, such as the exudate of *Styrax benzoin*, found in Indonesia and Malaysian Borneo, and Flecker (2003) supported the idea that the resinous cargo was from South-East Asia, with Sumatra a likely source. Alternatively, frankincense and myrrh were commonly imported from South-West Asia.

In order to clarify the nature of the resinous cargo and to delineate its source, we have carried out the NMR analysis of samples from seven of the resinous blocks and related materials, a total of 16 samples. Material was sampled from the surface and from the interior of each block. Both ^{1}H (Figs 3 (a) and S8 (a)) and ^{13}C NMR (Fig. 3 (b)) spectra were recorded. These were quite distinct from the suggested materials, such as frankincense, myrrh, *S. benzoin* (balsam, also called styrax resin or gum benjamin) (Lambert *et al.* 2013b) or other trade exudates, such as dragon's blood or liquidambar (Lambert *et al.* 2015a). Rather, it was a type of resin (a terpenoid polymer) known as dammar (Langenheim 2003), derived from plants of the Dipterocarpaceae (Lambert *et al.* 2013a). The spectra of the resinous cargo closely resemble those of, for example, the dipterocarp *Shorea robusta* (Fig. 5).

Fossilized ambers can derive from either conifers or flowering plants (Lambert *et al.* 2008) and have been found to fall into at least five groups distinguished by the botanical source. The spectra of the resinous cargo proved to be related to the variety we have called Group B (Fig. 4), which is found in North America, the Pacific, South Asia, South-East Asia and East Asia. The resinous cargo thus could not have come from the Middle East (South-West Asia). Although the spectra of the resinous cargo were distinct from that of mature resins from Indonesia (Fig. 6), Australia (Fig. S1), Papua New Guinea (Fig. S2) or (less so) Thailand (Figs S3 and S4), they showed similarities with those from Japan and India (Figs S5-S7).

Comparison of the spectra of samples from inside the resinous blocks with those from the surface (Figs S8-S10) demonstrate that exposure to the saline environment of the Java Sea for 700–800 years had clearly resulted in a process of maturation that is similar to the effects of age or heating. The spectra of, in particular, the cortical portions of the samples bore a strong resemblance to those of mature Group B amber. Although the spectra of the wreck resins did not resemble those of known Indonesian amber, they did resemble those of Indonesian green amber (Lambert *et al.* 2013a), which is a more age-appropriate comparison. Because of the ambiguities of maturity, no definitive statement at this time can be made concerning the geographical source of the resinous cargo.

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SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this paper at the publisher's web-site:

Table S1. Dimensions of resin pieces recovered from the Java Sea Wreck
Figure S1. The one-dimensional ^{1}H spectrum of a sample of amber from Cape Patterson, Australia, provided by G. O. Poinar, Jr. and W. Birch (Early Cretaceous), sample 151 in the Trinity collection (green), compared with that of a sample from the interior of block 351352, sample 1553 in the Trinity collection (red), dissolved in $CDCl_3$.
Figure S2. The one-dimensional ^{1}H spectrum of a sample of amber from Sudest Island of Papua New Guinea, provided by G. O. Poinar, Jr., and M. Bradshaw (unknown age), sample 139 in the Trinity collection (green), compared with that of a sample from the interior of block 351352, sample 1553 in the Trinity collection (red), dissolved in $CDCl_3$.
Figure S3. The one-dimensional ^{1}H spectrum of a sample of amber provided by the Department of Paleobiology, National Museum of Natural History, Smithsonian Institution, Jennifer Strotman, Mark S. Florence, Conrad Labandeira, "resin from Siam from turpentine resin gum collection, Department of Botany, University of Iowa, 1975," sample 1650 in the Trinity collection (green), compared with that of a sample from the interior of block 351352, sample 1553 in the Trinity collection (red), dissolved in $CDCl_3$.
Figure S4. The saturated regions of the one-dimensional ^{1}H spectrum of the same sample as in Figure S3 (Thai sample 1650 in green, resin cargo sample 1553 in red), dissolved in $CDCl_3$.
Figure S5. The ^{1}H spectrum of the interior of block 351352 in red (sample 1553 in the Trinity collection) overlaid with those of amber (a) from Mizunami, Gifu Prefecture, Japan (sample 1643, provided by T. Ueno), and (b) from Gujarat, India (sample 194, provided by G. O. Poinar, Jr.) in green.
Figure S6. Overlay of the saturated region of the ^{1}H spectra of the interior of block 351352 (sample 1553, in red) with that of amber from Mizunami, Gifu Prefecture, Japan (sample 1643, provided by T. Ueno).
Figure S7. Overlay of the saturated region of the ^{1}H spectra of the interior of block 351352 (sample 1553, in red) with that of amber from Gujarat, India sample 194, provided by G. O. Poinar, Jr.).
Figure S8. Comparison of the one-dimensional ^{1}H spectra of internal (a) and external (b) resinous materials from block 351445, respectively samples 1555 and 1554 in the Trinity collection, dissolved in $CDCl_3$.
Figure S9. Overlay of an expansion of the alkenic region of the one-dimensional ^{1}H spectra of internal (turquoise) and external (red) portions of resinous block 351445, respectively samples 1555 and 1554 in the Trinity collection, dissolved in $CDCl_3$.
Figure S10. Overlay of an expansion of the aldehydic region of the one-dimensional ^{1}H spectra of internal (turquoise) and external (red) portions of resinous block 351445, respectively samples 1555 and 1554 in the Trinity collection, dissolved in $CDCl_3$.