CHARACTERIZATION OF "GREEN AMBER" WITH INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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A peridot-like bright greenish yellow to green gem material called "green amber" has recently appeared in the gem market. It is produced by treating natural resin (amber or copal) with heat and pressure in two stages in an autoclave. Differences in molecular structure between untreated amber and copal as compared to treated "green amber" were studied by FTIR and ^{13}C NMR spectroscopy, using powdered samples. Regardless of the starting material, the FTIR spectrum of "green amber" showed an amber pattern but with a characteristic small absorption feature at 820 cm^{-1}. Solid-state ^{13}C NMR spectroscopy of the treated material indicated a significantly lower volatile component than in the untreated natural resin, evidence that the treatment can actually "artificially age" copal. A new absorption observed near 179 ppm in the NMR spectra of all the treated samples also separated them from their natural-color counterparts.

I t has been known for quite some time that amber and copal may be treated with heat and pressure in an autoclave—or treated at high temperature with linseed oil—to improve their brownish yellow color, transparency, or hardness (e.g., O'Donoghue, 2006). These treatments have focused on amber from the Baltic Sea region (which includes localities in Poland, Scandinavia, Russia, the Baltic Republics [Estonia, Latvia, and Lithuania], and Germany), and also young amber and subfossilized copal mined in Latin America. In recent years, it appears that such treatments have been refined to produce a new product.

In May 2006, a gem material called "green amber" (figure 1) debuted at the Hong Kong Jewellery & Watch Fair, where it was offered by Treasure Green Amber Ltd., Hong Kong. Dealers from Poland (Amber Gallery Export-Import, Amber Line) and Lithuania (Amber Trip Lithuania) presented this material at the International Jewellery Tokyo (IJT) show in January 2008. It also appeared at the Tucson gem shows in February 2008, where it was sold by amber dealers and distributors under names such as "natural green Caribbean amber" or "very rare Baltic amber" (Pedersen, 2008). This material, which has a peridot-like bright greenish yellow to green color, displays a distinctive deeper green component than previously seen in amber, even in the rare green material from Mexico.

Author AA visited Treasure Green Amber Ltd. in June 2007 and was provided with information on the material by general manager Hung Chi and sales manager Steven Wai. They stated that their "green amber" is obtained from natural amber—allegedly of Brazilian, Baltic, or other origin—that has been treated by a two-stage procedure involving long time intervals under controlled heat, pressure, and atmosphere, in an autoclave developed in Germany for heat treatment. The green color of the treated

Figure 1. The 9.0 ct briolette and carved beads shown here are examples of "green amber" from Treasure Green Amber Ltd. Photo by Robert Weldon.

material reportedly becomes deeper as the number of heating stages increases. During treatment, volatile components are evidently emitted from the material, causing it to become harder and more stable. They further explained that the treatment process was derived from a traditional enhancement technique frequently used to improve the color, transparency, or hardness of amber in Germany, Russia, Poland, and Lithuania. This process was refined by Hans Werner Mueller of Facett Art in Idar-Oberstein, Germany, to produce "green amber." Treasure Green Amber Ltd. purchased the technique and installed more than a dozen autoclaves at its factory in Guangzhou, China. It subsequently improved the heating process to achieve a higher yield of fine green color.

Dr. Lore Kiefert of the former AGTA-GTC laboratory visited Facett Art in 2007 and reported that this company mainly treated amber from Ukraine to alter the color to green. She concluded that no synthetic resin such as plastic was detectable in the material (Kiefert, 2008).

At the 2008 IJT show, there was considerable discussion among amber dealers from Poland and Lithuania around the contention by some that the starting material for "green amber" also came from Poland, and that all the "green amber" for sale had been produced from copal. As a result, many laboratories and amber dealers in Japan became suspicious of "green amber" because of the possibility that amber was not used as the starting material.

Amber and copal can usually be separated with basic gemological testing because of differences in their physical properties (e.g., hardness and resistance to acid; O'Donoghue, 2006) and their infrared spectra (Brody et al., 2001; Guiliano et al., 2007). It appeared possible, however, that the "green amber" treatment could change the structure of the original starting material so identification was not as straightforward. Hence, we collected samples of amber and copal from various localities and performed heat-treatment experiments with the assistance of Treasure Green Amber Ltd. Using Fourier-transform infrared (FTIR) spectral analysis and high-resolution solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy (box A), we studied the differences in molecular structure among "green amber," untreated amber, and untreated copal, as

BOX A: NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

NMR spectroscopy is one of the most advanced techniques for structural studies of liquids and solid-state analysis of organic compounds. This instrumentation (figure A-1) gives detailed information about atomic environments based on the interactions of nuclear magnetic "moments" with electromagnetic radiation.

NMR spectroscopy is appropriate only for atomic nuclei that have an odd number of protons and/or neutrons and a nuclear magnetic moment. The nuclear spin takes two orientations that have different energy levels when a magnetic nucleus such as ^1H, ^{13}C, ^{15}N, or ^{31}P is placed in the magnetic field. Solid-state NMR spectroscopy is performed by placing the sample in a magnetic field and observing its response to pulses of energy in the radio frequency (RF) portion of the spectrum. The technique requires samples to be ground to a fine powder and loaded into a small capsule, called a rotor. The rotor is then placed into a probe, which is loaded into a large apparatus housing a very strong magnet. Depending on the quality of data desired, a technique called magic-angle spinning (MAS) may be employed. This technique involves rapidly spinning a sample within the magnetic field at an angle of 54.7°, which averages out orientation-dependent magnetic effects that blur spectra. The sample is then exposed to pulses of RF energy, and the frequencies it re-emits are collected by a spectrometer.

During an NMR experiment, the energy emitted in response to the RF energy is measured as a function of time, producing a time-domain spectrum. A Fourier-transform function is applied to the spectrum, producing a frequency-domain spectrum where relative intensity is shown along the Y axis and energy is shown along the X axis. The energies are measured relative to a standard material in which the bonding environment of a nuclide and the RF energy it emits are known. Because the energy difference between the standard material and the sample is very small, X-axis values are typically reported in parts per million (ppm), or chemical shift, with 0 ppm representing the characteristic energy of the standard. Peaks in these spectra correspond to various atomic environments, and in the case of ^{13}C NMR spectroscopy, their position depends on the carbon bonding site energy in the sample relative to that of the reference standard.

NMR spectroscopy has important applications in organic chemistry, and it may also find potential
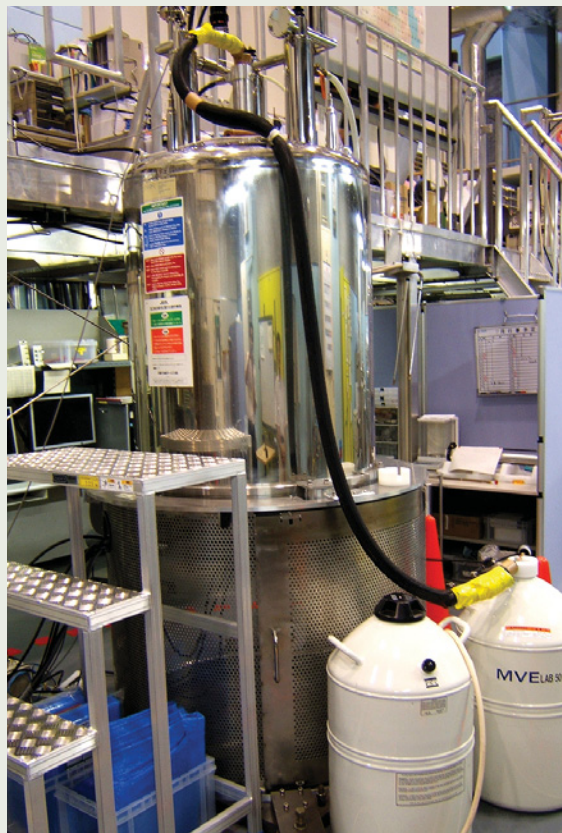
Figure A-1. This JEOL ECA-500 spectrometer is the NMR instrument used at the National Institute for Materials Science (NIMS) in Tsukuba, Japan, for this study. Photo by A. Abduriyim.

new uses in gemology. Unlike FTIR spectroscopy, NMR identifies unique atomic sites in organic molecular units or in the crystal lattice of a material. With further research, this technique may prove useful, in certain situations, for determining the relative age and the geographic origin of organic gems. NMR can be applied with minimal damage (i.e., it uses a small sample size, and chemical dissolution is not necessary). However, due to the high cost of the instrumentation (ranging from $355,000 to more than $5 million) and the potentially destructive nature of the method, it will likely see only limited application to gemology.

NEED TO KNOW

- Both copal and amber have been treated to produce "green amber."

- A two-stage heating process, in an autoclave, is used.

- The treatment "ages" copal so that its gemological properties resemble amber.

- Analysis of "green amber" with FTIR and ^{13}C NMR spectroscopy revealed diagnostic features at 820 cm^{-1} and near 179 ppm, respectively.

- The presence of "Baltic shoulder" features in the FTIR spectrum of a treated sample indicates that the starting material was amber; their absence cannot be used to identify the starting material.

- The green color appears to result from light scattering from fine clouds of inclusions.

Figure 2. Millions of years are required for tree resin to become amber. It first hardens to become copal, such as this sample from Madagascar (21.53 ct). Photo by Hideaki Fukushima.

well as the structural changes that occurred as the result of heat treatment. Following a discussion of the results of these studies, this article also covers the nomenclature for describing this material on laboratory reports.

BACKGROUND

Amber is fossilized tree resin. Resin is a semisolid amorphous organic hydrocarbon secreted by all plants. Amber forms when resin from certain trees hardens and fossilizes gradually over time (Schlee, 1984; Grimaldi, 1996; Lambert, 1997). The resin first hardens by losing volatile components such as alcohol and grease to become copal (figure 2), which then undergoes further devolatilization during burial in sediments to become amber.

Not all tree resin can become amber. In general, resins that fossilize to amber are secreted by trees in the families Araucariaceae (figure 3) and Fabaceae (the latter is commonly known as the legume family). In contrast, trees belonging to the family Pinaceae (i.e., the pine family) typically do not produce resin that fossilizes to amber (Kimura et al., 2006a). To become amber, the resin must contain a macromolecule called a diterpene, which is a type of hydrocarbon that is part of natural resin (Anderson and Winans, 1991; Anderson et al., 1992). Ozic acid, a diterpenoid, is a major component of resins produced by plants belonging to the family Fabaceae. Copal from Colombia, Tanzania, and Madagascar, as well as amber from the Dominican Republic, originates from trees that belong to this family. In contrast, communic acid is a major component of resin from trees in the family Araucariaceae, which may produce Baltic and Ukrainian amber.

Polymerization of organic hydrocarbon molecules (each of which has a similar "skeleton" of carbon atoms) changes the resin to copal, and a cross-linkage reaction between chains of these hydrocarbons produces amber (Clifford and Hatcher, 1995; see appendix A). In nature, this cross-linkage reaction proceeds very slowly at elevated temperature and pressure during sedimentation and burial of organic sediments; in fact, it takes about 17 million years to reach the halfway point (Kimura et al., 2006a). This means that copal requires tens of millions of years to change into amber. However, these reactions can be significantly accelerated by exposing copal to an alternative set of pressure and temperature parameters in the laboratory.

Methods that can be used to study the molecular

Figure 3. Baltic amber, such as these samples (11.20 and 14.77 ct), formed from the resin derived from trees of the family Araucariaceae. The darker color of the sample on the right is due to natural oxidation in the ground. Photo by A. Abduriyim.

structure of amber and related materials include FTIR spectroscopy, NMR spectroscopy, and pyrolytic gas chromatographic (Py-GC) mass analysis. However, all these techniques require destructive experimental procedures (including FTIR, when applied to amber and copal).

MATERIALS AND METHODS

A total of 44 samples were used in this study, with a weight range of 0.81–67.20 ct (table 1). The samples included 14 pieces of treated "green amber" provided by Treasure Green Amber Ltd. (originally from Brazil), Facett Art (from Ukraine), and Amber Gallery Export-Import (locality unknown); a representative piece of untreated copal from each of four sources (Colombia, Brazil, Madagascar, and Tanzania); and a representative piece of untreated amber from each of five sources (Kuji in Japan, the Baltic Sea region, Ukraine, the Dominican Republic, and

Mexico). All the untreated samples were examined first in their untreated state and then after heat treatment (see below). The amber samples from the Baltic Sea region, the Dominican Republic, and Mexico were not sliced prior to heat treatment, while the other samples (both copal and amber) were cut into two portions so that one piece could be used for heat treatment and the other portion retained in its untreated state. In addition, for further heat-treatment experiments, the untreated portion of the Colombian copal was cut into several additional pieces (one more slice and 14 beads).

Heating Experiments. With the cooperation of Treasure Green Amber Ltd., heating experiments were performed in the same autoclave (figure 4) and under the same conditions used previously by this company to produce "green amber" (Hung Chi, pers. comm., 2007). All the untreated amber and copal samples, except for Col-03–17, were placed on trays

TABLE 1. Properties of untreated and heated amber and copal samples.

Material	Location	Sample no.	No. of samples	Treatment	Weight (ct)	Color	UV fluorescence		RI	SG	Age
							Long-wave	Short-wave			
Amber	Kuji, Japan	Kuj-01	1	Untreated[a]	1.29	Brown	Dark green	Dark green	1.55	1.05	83–89 Ma (Kimura et al., 2006b)
		Kuj-02	1	Treated	0.81	Dark brown	Whitish blue	Dark green	1.55	1.06	
Amber	Baltic Sea region	Bal-01	1	Untreated	14.79	Brown-yellow	Bluish green	Dark green	1.54	1.06	35–55 Ma (Kimura et al., 2006b)
		Bal-01H		Treated	14.35	Yellowish green	Whitish blue	Dark green	1.54	1.06	
Amber	Ukraine	Uk-01	1	Untreated	25.05	Yellowish brown	Dark green	Dark green	1.54	1.08	30–38 Ma (Perkovsky et al., 2003)
		Uk-02	1	Treated	15.50	Green	Whitish blue	Dark green	1.54	1.06	
Amber	Dominican Republic	Dom-01	1	Untreated	6.46	"Honey" yellow	Dark green	Dark green	1.54	1.05	15–45 Ma (Rikkinen and Poinar, 2001)
		Dom-01H		Treated	5.73	Yellowish green	Whitish blue	Dark green	1.54	1.05	
Amber	Mexico	Mex-01	1	Untreated	8.34	Greenish yellow	Whitish blue	Dark green	1.54	1.04	22–26 Ma (Cattaneo, 2008)
		Mex-01H		Treated	8.09	Yellowish green	Whitish blue	Dark green	1.54	1.04	
Copal	Colombia	Col-01	1	Untreated	67.20	"Lemon" yellow	Dark green	Dark green	1.55	1.06	400–600 years (Kimura et al., 2006b)
		Col-02	1	Treated	12.28	Green	Whitish blue	Dark green	1.54	1.05	
		Col-03	1	Treated	10.42	Brown	Dark green	Dark green	1.55	1.06	
		Col-04-17	14	Treated	1.03–1.05	Yellowish brown	Dark green	Dark green	1.54	1.05	
Copal	Madagascar	Mad-01	1	Untreated	19.47	Pale yellow	Dark green	Dark green	1.52	1.05	50–60 years (Kimura et al., 2006b)
		Mad-02	1	Treated	12.07	"Golden" yellow	Whitish blue	Dark green	1.53	1.03	
Copal	Tanzania	Tan-01	1	Untreated	2.53	Pale yellow	Dark green	Dark green	1.53	1.05	Unknown
		Tan-02	1	Treated	1.42	Brownish yellow	Whitish blue	Dark green	1.53	1.05	
Copal	Brazil	Bra-01	1	Untreated	8.33	"Honey" yellow	Dark green	Dark green	1.54	1.06	Unknown
		Bra-02	1	Treated	8.46	Green	Whitish blue	Dark green	1.54	1.05	
Amber	Brazil[b]	TR-001-005	5	Treated	1.20–5.49	Green	Whitish blue	Dark green	1.55	1.06	Unknown
Amber	Unknown	BR-001	1	Treated	14.49	Green	Whitish blue	Dark green	1.54	1.05	Unknown
Amber	Unknown	BR-002-003	2	Treated	6.88, 9.46	Yellowish green	Whitish blue	Dark green	1.54	1.05	Unknown
Amber	Unknown	BR-004	1	Treated	40.98	Greenish yellow	Whitish blue	Dark green	1.54	1.05	Unknown
Amber	Ukraine[c]	FA-001-004	4	Treated	1.40–4.69	Yellowish green	Whitish blue	Dark green	1.55	1.06	Unknown
Amber	Ukraine[c]	FA-005	1	Treated	3.92	Greenish yellow	Whitish blue	Dark green	1.55	1.06	Unknown

[a] The presence of sun spangle–like inclusions suggests that this "untreated" sample may have been exposed to a previous heating process.
[b] Origin of untreated starting material, as reported by Treasure Green Amber Ltd.
[c] Origin of untreated starting material, as reported by Facett Art.

with chalk powder on their surfaces to prevent adhesion if melting occurred during heat treatment. A vacuum atmosphere was created in the sample chamber of the autoclave and then a small amount of nitrogen gas was introduced. The temperature was raised to 150°C, and the pressure was gradually increased to ~14 bars. This pressurization prevented the samples from liquefying. After the samples were heated for 30 hours in this environment, the temperature and pressure were slowly reduced to ambient conditions. The sample chamber of the autoclave was kept closed and the process was repeated, but during the second run the temperature was raised to 200°C and the pressure was ~22 bars, with a heating period of 20 hours. The temperature and pressure were again slowly lowered and the samples were left in the chamber until ambient conditions were restored.

We used the same autoclave to conduct another set of experimental heating experiments on Colombian copal samples Col-03–17, in which we lowered the maximum temperature (since the 200°C used above is close to the melting point of copal under pressure). We tested two variations: (1) Col-04–17 underwent a two-stage heating process at 180°C and 20 bars for 20 hours at each stage, and (2) Col-03 was subjected to a one-stage heating process at 180°C and 20 bars for one hour. The latter treatment process has also been used routinely by Treasure Green Amber Ltd. to induce a yellowish brown color in amber and copal.

Gemological Testing. Standard gemological methods were used to document the samples' color, hardness (by the fingernail scratch test), refractive indices (the spot method was used on curved surfaces), specific gravity (by hydrostatic weighing), fluorescence to long- and short-wave ultraviolet radiation, and inclusions (examination with a gemological microscope). In addition, we performed: (1) an alcohol test, by placing a drop of ethanol on the surface of the sample and noting any reaction after it had evaporated; (2) a brine test, in which the sample was placed in a saturated salt solution (SG of 1.1) made by adding 4–5 teaspoons of salt to 200 ml water; (3) a hot point test, by positioning a heated needle near the surface of the sample; and (4) a static electricity test, by briskly rubbing the samples with a cloth and then seeing if they attracted small pieces of paper. We conducted all tests on all the commercial "green amber" and on all the amber and copal samples before and after the heating experiments. To determine the depth of the green color, we sliced three pieces of the commercially treated "green amber"
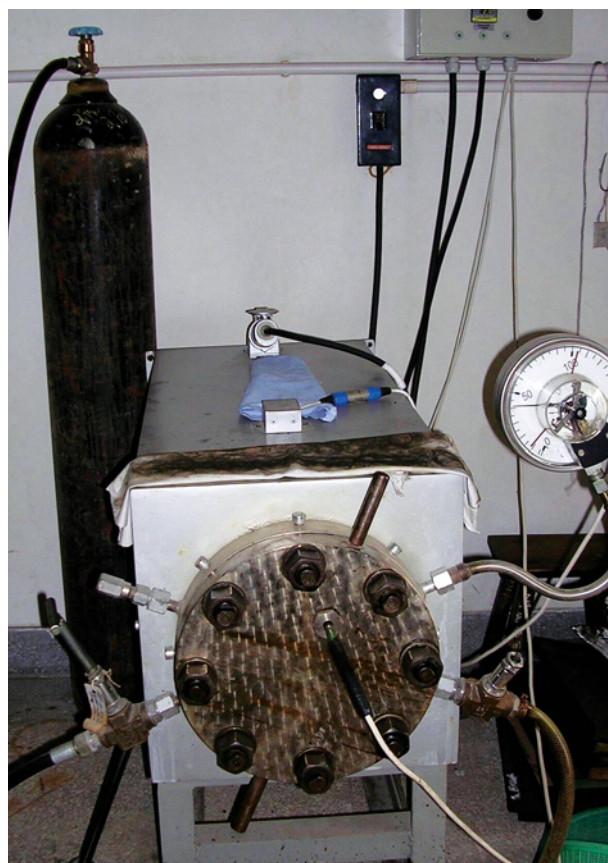
Figure 4. This autoclave was used for the treatment experiments in cooperation with Treasure Green Amber Ltd. It is equipped with a gas input system, and the temperature, pressure, and heating-time parameters can be carefully controlled. Photo by Hung Chi.

(TR-001–003) into thin sections. To check for color instability, we observed the coloration of all the commercially treated "green amber" samples after storing them in the dark for several months.

FTIR Spectroscopy. Infrared spectral analysis was performed on all samples with a Shimazu IR Prestige-21 FTIR spectrometer with a KBr beam splitter and DLATGS detector in the range 5000–400 cm^{-1}, with a resolution of 4.0 cm^{-1} and 100 scans. KBr tablets were prepared for each sample by evenly powdering several milligrams from each. The infrared beam was focused on the powdered sample holder in diffuse reflectance mode. All the spectra were normalized for differences in path length. It was necessary to use powdered samples because the FTIR absorption bands due to stretching and deformational vibrations in the various molecules of amber and copal cannot be resolved in spectra obtained using nondestructive transmittance or diffuse reflectance modes.

Figure 5. Representative amber and copal samples from various localities were used for the standard two-stage heating experiments. For each pair, the untreated samples are shown on the left, and those after heating are shown at the right. Colombian (Col-02) and Brazilian (Bra-02) copal turned bright green. Pale yellow copal from Madagascar (Mad-02) and Tanzania (Tan-02) turned intense yellow with a slight green hue. Kuji amber (Kuj-02) turned dark brown. Amber samples from the Baltic Sea region (Bal-01H) as well as from Ukraine (Uk-02), the Dominican Republic (Dom-01H), and Mexico (Mex-01H) generally turned green, although the color of the Dominican and Mexican material was not highly saturated. Photos by Masaaki Kobayashi.

NMR Spectroscopy. Thirty-three samples, including one representative sample of commercial "green amber" from each company and all amber and copal samples before and after the heat treatment experiments, were measured with solid-state ^{13}C CP-MAS (cross polarization–magic angle spinning) NMR spectroscopy (again, see box A). Analyses of the commercial "green amber" and other known amber samples were performed using a Bruker Avance DRX-600 spectrometer at Tsukuba University. NMR spectra of the copal samples were obtained with a JEOL ECA-500 spectrometer at the National Institute for Materials Science (NIMS) in Tsukuba City. Powdered samples weighing ~280 mg were analyzed. A description of the experimental parameters can be found in the *G&G* Data Depository at www.gia.edu/gandg.

Figure 6. A yellowish brown color resulted from treating 14 beads of "lemon" yellow Colombian copal (1.03–1.05 ct) with an experimental two-stage heating process (180°C and 20 bars, at 20 hours for each stage). Photo by A. Abduriyim.

RESULTS

Gemological Testing. *Commercial "Green Amber" Samples.* Most of the commercial "green amber" samples were yellowish green to green (some with uneven color distribution). The samples from Treasure Green Amber Ltd. had excellent transparency, with only a few inclusions (see below). The green color permeated the small pieces (1.20 and 1.31 ct) almost entirely, but it was limited to just near the surface of the largest one (5.49 ct). After the "green amber" samples were kept in the dark for several months, the green hue of two of them (i.e., TR-005 and BR-001) faded slightly.

The hardness of all the commercially treated samples was similar to that of amber (Mohs ~2–2.5), which—unlike copal—cannot be scratched with a fingernail. The SG was 1.05–1.06 and RI measurements ranged between 1.54 and 1.55, again similar to amber (see table 1; O'Donoghue, 2006). They fluoresced whitish blue and dark green to long- and short-wave UV radiation, respectively. They were warm to the touch and exhibited conchoidal surface fracture.

Samples Heat Treated for This Study. Unless stated otherwise, the information given for heat-treated samples in the remainder of the Results section

refers only to the standard two-stage heat treatment process used to produce "green amber" for this study.

After the standard heating, a "lemon" yellow Colombian copal and a "honey" yellow Brazilian copal turned bright green. Pale yellow copals from Madagascar and Tanzania turned "golden" yellow and brownish yellow, respectively, with a pale green tint. Brown Kuji amber turned dark brown. Amber samples from the Baltic Sea region as well as those from Ukraine, the Dominican Republic, and Mexico turned green and yellowish green, but the colors of the Dominican and Mexican ambers were not highly saturated (figure 5).

After the two-stage heating with shorter time intervals, the 14 beads of "lemon" yellow Colombian copal (Col-04–17) turned yellowish brown (figure 6). Single-stage heating of a "lemon" yellow Colombian copal (Col-03) also yielded a brown color (figure 7).

Before heating, all copal samples could be scratched with a fingernail; the amber samples could not be scratched. After heating, none of the samples could be scratched with a fingernail. No change was seen in the RI or SG values of any of the samples after heating. However, the long-wave UV fluorescence reactions were markedly different. The

Figure 7. This 10.42 ct "lemon"-yellow Colombian copal (left) was treated by a one-stage heating process (180°C and 20 bars for one hour) that has been used routinely by Treasure Green Amber Ltd. to induce a yellowish brown color in amber and copal, as was the result here (right). Photos by A. Abduriyim.
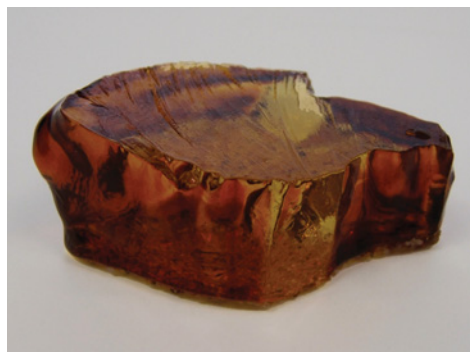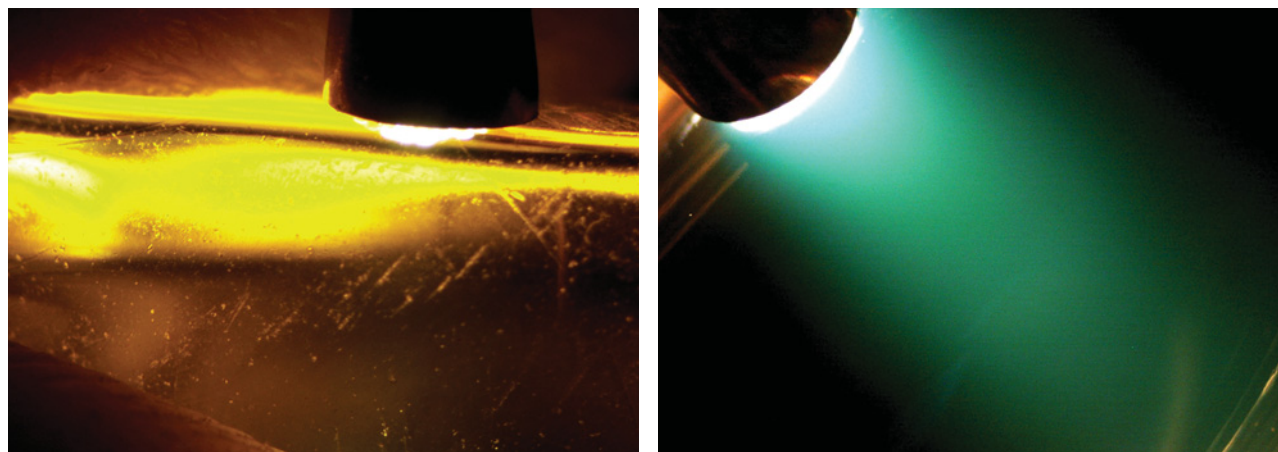
Figure 8. On the left, microscopic examination of untreated Colombian copal with fiber-optic illumination reveals no cloud-like inclusions. On the right, a fine granular cloud is illuminated in a piece of Baltic amber (Bal-01H) after heat treatment. Photomicrographs by A. Abduriyim; magnified 25× (left) and 15× (right).

untreated amber and copal fluoresced dark green or bluish green before heating, but this changed to a strong whitish blue after treatment (similar to that seen in natural "blue" amber). One exception to this was the Mexican amber, which fluoresced whitish blue to long-wave UV, both before and after heating. All samples fluoresced dark green to short-wave UV, regardless of whether they had been heat treated (again, see table 1).

Microscopic Observations. Before heating, some amber and copal samples contained small cracks or minute gas bubbles. Plant debris and insects were rarely observed. After the standard two-stage treatment, the cracks appeared larger and were disc-like (i.e., resembling the "sun spangles" or "glitter" seen in conventionally heat-treated material). The gas bubbles became smaller and migrated closer to the surface. The smaller plant debris and insects were broken up and reduced in size. A sample of milky white Ukrainian amber (Uk-02) became clear. Fine granular clouds could be seen with the use of a gemological microscope and strong fiber-optic illumination in all samples that underwent the two-stage treatment procedure (figure 8). The samples with a deeper green color contained more clouds.

Photomicrographs of various inclusions in "green amber" are available in the *G&G* Data Depository.

Alcohol Test. Before heating, all copal samples reacted to alcohol by losing their polish luster. Their surfaces became sticky and showed a finger-print after being pressed with a fingertip. None of the heated samples—like their heated and unheated amber counterparts—showed a reaction to alcohol.

Brine Test. In the saltwater solution, amber and copal from all localities floated before and after the heating, as did the commercial "green amber."

Hot Point Test. Before heat treatment, the copal samples started to melt, while gradually giving off white smoke, when a hot point was positioned close to their surfaces. After heat treatment, none of the samples showed any melting reaction, although they all gave off white smoke when the hot point was touched to their surfaces. Untreated copal released a sweet-sour resinous odor, while untreated natural amber gave off a pungent resinous odor. Treated "green amber" produced a weaker odor than the untreated natural amber.
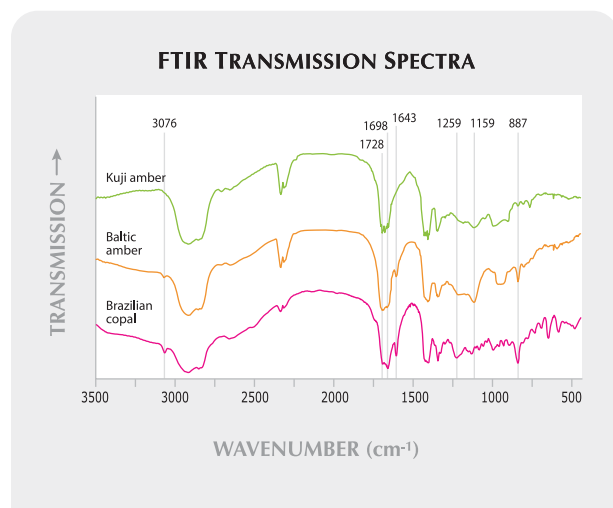
Static Electricity Test. All samples showed static electricity after they were rubbed with a cloth, as expected for natural resin.

FTIR Spectroscopy. The FTIR spectra of representative samples of untreated and treated amber and copal are presented in figures 9 and 10 according to their geologic age (see table 1 for ages). FTIR peak assignments are described in appendix A. The amber from Kuji in Japan represents the oldest and consequently the most structurally mature sample. Amber from the Baltic Sea region was selected for comparison in these figures because it has diagnostic spectral features for determining geographic origin (as described below and in appendix A). The Brazilian copal is shown because copal from this locality is often used as a starting material for commercial "green amber" treatment. FTIR spectra from all studied localities—and a table of FTIR spectral features

for amber and copal before and after heat treatment—can be found in the *G&G* Data Depository.

Untreated Amber. Most of the features visible in the amber spectra in figure 9 have been previously reported, including carbon single-bond absorption features near 2927 and 2867–2853 cm^{-1}, and at 1454, 1384, and 1024–975 cm^{-1} (Marrison et al., 1951; see appendix A for a discussion of the relationship between molecular structure and spectral features). The spectra of amber from the Baltic Sea region and Ukraine displayed the "Baltic shoulder"—a flat shoulder in the area between 1259–1184 cm^{-1} and an associated feature at 1159 cm^{-1}—that has been noted as characteristic of these materials in past studies (Beck et al., 1964; Langenheim, 1969). The Kuji spectrum resembled that of Baltic amber in general, but with a less-flat Baltic shoulder–like absorption at 1259–1184 cm^{-1}. Low-intensity asymmetric absorptions at 744, 698, 640, and 540 cm^{-1} may be related to aromatics or substitution in benzene rings (Broughton, 1974).

In the regions of carbon-carbon double bonding, an absorption was observed at 3076 cm^{-1}. A weak absorption at 1643 cm^{-1} was also seen, visible as a shoulder of a strong absorption at 1728–1698 cm^{-1}. In addition, there was a sharp absorption at 887 cm^{-1}.

Untreated Copal. The copal spectra (see, e.g., figure 9) contained major features at 3076, 1643, 1593, and 887 cm^{-1}, which indicate a high content of double bonds in these samples. Also, the absorption at 1698 cm^{-1} in the double-bonded carbon-oxygen region was relatively stronger than the absorption at 1728 cm^{-1}. Clearly separated small absorptions were recognized at ~2867 and ~1384 cm^{-1}. In addition, there were broad absorptions at 4720 and 4607 cm^{-1} (not shown in the figures), and intermediate-intensity absorptions at 744, 698, 640, and 540 cm^{-1}.

Heat-Treated Amber. The absorptions at 4720, 4607, 3076, 1643, and 887 cm^{-1} diminished or disappeared after treatment, while the appearance or increase in intensity of the 820 cm^{-1} absorption was observed for all amber samples (e.g., figure 10).

Figure 9. These FTIR spectra represent amber from Japan and the Baltic Sea region, and copal from Brazil, prior to heat treatment. They are arranged in order of geologic age, with the oldest sample on the top. Each spectrum is offset vertically for clarity. Features at 3076, 1643, and 887 cm^{-1}, which are attributed to carbon-carbon double bonds in exocyclic methylene groups, are detectable in the Ukrainian amber and Brazilian copal. Features at 1728 and 1698 cm^{-1}, and in the region from ~1260 to 1150 cm^{-1}, are due to carbon-oxygen double bonds and single bonds, respectively, in functional groups.

*Figure 10. These FTIR spectra were collected after a two-stage heating process was applied to the samples in figure 9. Note that the 3076 cm^{-1} and 1643 cm^{-1} features were not detected in the copal after heat treatment, indicating that exocyclic methylene groups were destroyed in these materials during treatment. A new feature at 820 cm^{-1}, marked with red circles, was observed in all samples after heat treatment.*
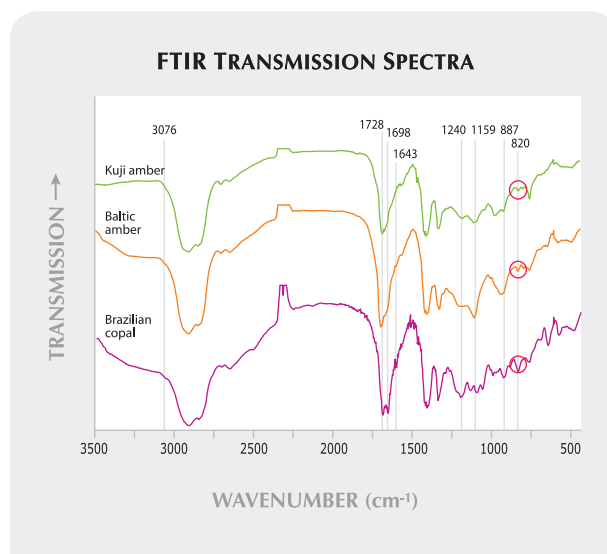
In addition, three peaks at 1172, 1147, and 1107 cm^{-1} tended to decrease and broaden in the Dominican sample. The diagnostic Baltic shoulder remained in the spectra of the Baltic and Ukrainian samples.

Heat-Treated Copal. The spectra of all copal samples showed significant changes after heating (e.g., figure 10): The absorption features at 3076, 1643, 1593, 887, 744, 698, 640, and 540 cm^{-1} were greatly diminished and those at 4720 and 4607 cm^{-1} disappeared. The absorption at 1698 cm^{-1} became notably weaker, while that at 1728 cm^{-1} became stronger. In the carbon single-bond region, the absorption at 1259 cm^{-1} shifted to 1242 cm^{-1} and three absorptions at 1172, 1147, and 1107 cm^{-1} appeared to decrease and broaden. After heating, the overall pattern of the copal spectra closely resembled those of amber but without the Baltic shoulder. Also, a small absorption formed at 820 cm^{-1} in all copal samples.

Following the experimental two-stage heating at 20 hours per stage, the spectral changes for the 14 yellowish brown copal beads (Col-04–17) were similar to those exhibited by samples for which the heating process produced a green color (see *G&G* Data Depository figure DD-6). The maximum absorption at 1698 cm^{-1} became weaker, while absorption at 1728 cm^{-1} increased, and the absorption at 1269 cm^{-1} shifted to 1242 cm^{-1}. The resulting absorption pattern resembled that of amber, except that the absorption at 820 cm^{-1} was not evident.

After the experimental one-stage heating process, copal sample Col-03 turned brown, while the absorption intensity at 4607, 4270, 3076, 1643, 1593, 887, 744, 698, 640, and 540 cm^{-1} decreased by about half. Therefore, the features that characterize it as copal could still be recognized (again, see *G&G* Data Depository figure DD-6).

Commercially Treated "Green Amber." The results for these samples were similar to the spectral patterns of the amber and copal samples after our heating experiment. Absorptions at 4607, 4270, 3076, 1698, 1643, 1593, 744, 698, 640, and 540 cm^{-1} were almost absent, a weak absorption at 887 cm^{-1} was observed, and a small absorption near 820 cm^{-1} was present in all samples (see *G&G* Data Depository figure DD-7). The spectrum of the sample from Facett Art (see FA-001 in figure DD-7) was distinctly different from those of the samples from the other two companies—Treasure Green Amber Ltd. and Amber Gallery Export-Import—with absorption features resembling a Baltic shoulder. The absorption seen at 975 cm^{-1} was stronger than that at 1024 cm^{-1}.

NMR Spectroscopy. The ^{13}C NMR spectra of amber from Kuji in Japan, amber from the Baltic Sea region, and copal from Brazil are shown in figures 11 and 12. NMR spectra from all the studied localities—and a table of NMR spectral features for amber and copal before and after heat treatment—can be found in the *G&G* Data Depository. NMR peak assignments are described in appendix A.

Untreated Amber. In general, the spectral patterns of amber from each locality were similar (again, see figure 11), though certain features showed some variation according to geologic age.

In the single-bonded region at 90–10 ppm, the ^{13}C NMR spectra showed a peak that had the largest signal intensity at 40–37 ppm. This peak is attributed to several carbon sites in the core structure of both amber and copal (Lambert and Frye, 1982) that are stable over tens of millions of years. Except for this feature, signals of carbon single-bonded to hydrogen were distributed in the 22–17 ppm range and those of carbon single-bonded to carbon were at 30–26, 36, 53–50, and 59–58 ppm. Line widths in this single-bonded carbon region tended to broaden with increasing age of the sample.

In the double-bonded carbon region at 155–105 ppm, four carbon signals were detected at 148, 139, 127, and 108 ppm. The signals at 148 and 108 ppm tended to be weaker in spectra from the older amber samples, and were absent from the Kuji amber spectrum (likely the oldest sample).

In the functional group region at 200–170 ppm, the ester group appeared only in Baltic and Ukrainian amber samples at 176–172 ppm. Note that the presence of an ester group in the amber structure is unique to material from Ukraine and the Baltic Sea region.

Untreated Copal. In the spectra of the untreated copal samples, the signals from single-bonded carbon at 49–47 ppm, 29–28 ppm, and 20–15 ppm were sharper than those of amber, and the spectral pattern of each signal was further divided into several small signals (e.g., figure 11). In the double-bonded carbon region, four main signals were resolved. The intensities of the signals at 148 and 108 ppm
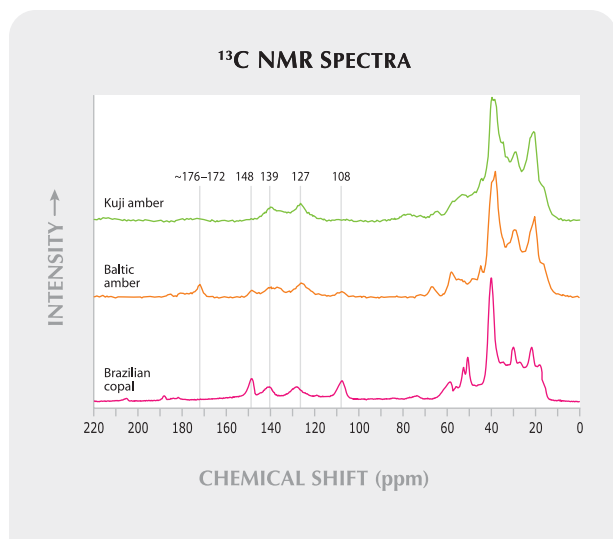
¹³C NMR SPECTRA

Figure 11. ¹³C NMR spectra are shown for representative amber from Japan and the Baltic Sea region, and copal from Brazil. Peaks related to carbon atoms in the carbon skeleton are located in the 90–10 ppm region. The peaks at 148 and 108 ppm in the Baltic amber and Brazilian copal are attributed to carbons in exocyclic methylene groups. The peaks at 139 and 127 ppm, which are attributed to carbon atoms in the structural core of diterpene units, were observed in all samples. The peak at ~176–172 ppm in the Baltic amber spectrum is attributed to an ester functional group, which is characteristic of Baltic and Ukrainian material.

¹³C NMR SPECTRA

Figure 12. Shown here are the ¹³C NMR spectra for the samples in figure 11 that were treated by the standard two-stage heating process with pressure. A new signal at 179 ppm, detected in all of these heated samples, is marked with red circles.

were stronger than the signals at 139 and 127 ppm. In the functional group region, the spectra of all the copal samples had a clear peak at 184–182 ppm related to carboxylic acid.

Heat-Treated Amber. After heat treatment, signal intensities at 57, 48, 44, and 28 ppm generally decreased and peaks broadened in the single-bonded carbon region of all amber samples (figure 12). In the double-bonded carbon region, the signals at 148 and 108 ppm almost disappeared in all treated amber samples, and the signals at 139 and 127 ppm in the spectra from some localities increased slightly and broadened. A new signal was observed in the functional group region at 179 ppm.

Heat-Treated Copal. Unlike the heat-treated amber described above, the carbon signals in the single-bonded carbon region changed from sharp peaks for the untreated copal to broader curves for the treated
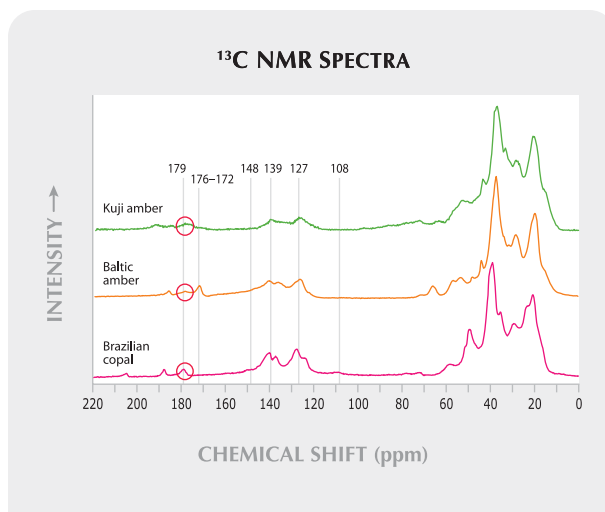
material. Even so, the peaks for the heat-treated copal were sharper than those in the spectra of the (untreated) geologically old Kuji and Baltic ambers and approximately the same as those of (untreated) young Dominican amber. The signal intensities at 148 and 108 ppm greatly diminished after heat treatment, while the signal intensities at 139 and 127 ppm generally increased. The carboxylic acid functional group signal at 184–182 ppm also disappeared after treatment, and a new signal appeared at 179 ppm (e.g., figure 12).

During the heating process using two stages with short time intervals, the spectral changes of the 14 samples of Colombian copal (Col-04–17) after treatment were almost the same as those of the Colombian sample (Col-02) heat treated with the standard set of experimental parameters, but the decrease in signal intensity at 148 and 108 ppm appeared smaller than that seen in sample Col-02 (see *G&G* Data Depository figure DD-10). In general, features in the three regions of the spectrum for Col-04–17 resembled those of unheated young amber, but with a faint signal at 179 ppm.

The Colombian copal sample (Col-03) that was heated in a one-stage treatment process showed no change in the single- and double-bonded carbon regions. In its spectra before and after heat treatment, the signal intensities at 148, 139, 127, and

108 ppm remained the same (again, see *G&G* Data Depository figure DD-10). However, the carboxylic acid functional group signal at 182 ppm disappeared and no signal was detected at 179 ppm.

Commercially Treated "Green Amber." Spectra of representative samples from the three producers are shown in *G&G* Data Depository figure DD-11. In the single-bonded carbon region, all the signals in the spectra from TR-001 and BR-001 resembled the spectrum of amber and copal samples after heat treatment, but the spectrum from FA-001 showed a less intense signal at 49–47 ppm than the spectra of those other two samples. In the double-bonded carbon region, signals at 148 and 108 ppm were barely detectable in any of these samples, and their patterns resembled the spectrum of the Kuji amber (the oldest sample studied) before and after heating. In the functional group region, a weak signal attributed to ester group carbons was detected at 172 ppm in the Facett Art sample. A signal at 179 ppm was detected in all the samples.

DISCUSSION

The main questions surrounding the green amber that has entered the market are: (1) is it "natural"; and (2) if not natural, is it produced from amber or the younger, structurally immature resin, copal? We know from the literature and our experience that green amber is extremely rare in nature and has not been reported to date in the deep peridot-like colors currently seen in the marketplace. In fact, several of the dealers offering the material readily acknowledged that it is produced by heat treatment. What is not readily apparent is whether the original material being treated is copal or its more valued fossilized counterpart, amber. We know from our heating experiments that a two-stage process involving long intervals under controlled heat, pressure, and atmosphere can produce green in both materials.

Gemological Properties. Compared to untreated amber, the heated "green amber" showed no observable differences in RI and SG, but its hot-point odor was weaker than that of natural untreated amber. The fluorescence reaction of amber and copal is potentially a very good indicator of heat treatment. A whitish blue reaction to long-wave UV radiation appears to signal treatment because, with

the exception of Mexican amber, it was observed only in amber and copal after heat treatment and in "green amber" samples that were represented as being heat treated. However, this fluorescence reaction cannot identify the starting material because heat-treated amber and copal samples had the same reaction. Destructive tests involving scratching, alcohol exposure, and a hot point may be useful for separating "green amber" from imitation amber (synthetic resin), but the reactions to these tests are not helpful in separating "green amber" from copal or amber, or in determining the starting material used to produce "green amber." The multi-stage heat treatment may improve the saturation of green color or the depth to which the color layer penetrates from the surface of the material. The green color is not always stable when the material is placed in a dark area.

Production of "green amber" in an autoclave is possible with either amber or copal, but it requires certain pressure, temperature, and time parameters. In addition, the optimal set of conditions may vary for individual starting materials, and in some cases may not exist at all. Using the Treasure Green Amber Ltd. autoclave and heat-treatment protocol, we produced "green amber" from Colombian and Brazilian copal and from amber from the Baltic Sea region, Ukraine, the Dominican Republic, and Mexico; both copal and amber samples from other localities turned greenish yellow or brown.

FTIR Spectroscopy. Our general observation of the FTIR spectra of the commercial "green amber" samples and our heat-treated "green amber" samples is that they resembled those from amber rather than copal, even when the starting material was known to be copal. Therefore, it is difficult to determine from FTIR spectra whether these "green amber" samples were originally copal or amber.

It is possible, however, that spectral features characteristic of certain localities may help identify the geologic origin of some samples and, therefore, the likelihood that the original material was copal or amber. For example, the presence of the Baltic shoulder in the FTIR spectrum indicates that amber from the Baltic Sea region or Ukraine is the likely starting material. All "green amber" samples from Facett Art showed an absorption similar to that of ester functional group carbons, which produces the Baltic shoulder in the range of 1259–1159

cm^{-1}. This feature was not seen in any of our copal material before or after heat treatment. In subsequent studies, we confirmed that several pieces of "green amber" from Treasure Green Amber Ltd. showed similar Baltic shoulder features in their FTIR spectra. These FTIR results provide supporting evidence that the Facett Art sample and at least some of the samples from Treasure Green Amber Ltd. were indeed Ukrainian or Baltic amber, as the companies claimed.

The FTIR spectra of copal from all studied localities showed peaks with strong intensities at 4720, 4607, 3076, 1643, 1541, 887, 744, 698, 640, and 540 cm^{-1}, which are related to unsaturated bonds. These peak intensities decreased after the heating protocol, which indicates that the unsaturated-bond content of the copal samples was reduced by the multi-stage heat treatment. Amber that is geologically older—or, more precisely, structurally more mature—is known to have a lower content of unsaturated bonds, since unsaturated bonds are converted to saturated bonds during fossilization processes (see appendix A). Also, after treatment the maximum absorption at 1698 cm^{-1} changed to 1728 cm^{-1} for these copal samples, causing their spectra to appear more like that of amber. This means that FTIR spectra provide evidence that the structural changes from polymerization occur in copal as a result of the multi-stage heat treatment. That is, this heat treatment essentially matures or "artificially ages" copal by causing it to undergo polymerization so that it resembles geologically older amber.

The absorption around 820 cm^{-1} was detected to varying degrees in all the amber and copal samples subjected to the standard multi-stage heat treatment and in the "green amber" from the three companies. It was not, however, present in the Colombian copal samples treated in the additional two-stage and one-stage heat treatment experiments. The presence of this signal may be a reliable indicator for multi-stage heat treatment, especially if higher-quality spectra with better signals are collected.

NMR Spectroscopy. In the ^{13}C NMR results for the commercial "green amber" from the three companies, the signals of the double-bonded carbons in the carbon skeleton at 139 and 127 ppm were comparable to those observed in amber and copal, but the signals of exocyclic methylene group carbons at 148 and 108 ppm were very weak or undetectable. However, the signals of carbon in samples from

Treasure Green Amber Ltd. and Amber Gallery Export-Import at 58–57, 49–47, 36–33, 29–28, and 20–15 ppm in the single-bonded carbon region did not appear as the broad, partially resolved peaks observed in older Kuji and Baltic amber samples. Instead, they resembled spectral features of the relatively young amber from the Dominican Republic. In the functional group spectral region, we observed a signal at 179 ppm in all "green amber" samples that generally was not seen in any unheated amber and copal or in traditionally heated materials. For the "green amber" from Facett Art used in this study, the signals at 57, 48, 44, and 28 ppm in the single-bonded region were low and broad, and in the double-bonded region the signals at 148 and 108 ppm were not detectable. A weak signal due to an ester functional group was detected in the Facett Art sample at 172 ppm; this characteristic spectral feature of Baltic and Ukrainian amber indicates that the sample was likely from one of these localities.

The untreated copal samples from all studied localities showed sharper peaks at 58–57, 49–47, 36–33, 29–28, and 20–15 ppm than were seen in the untreated amber. After heat treatment of copal, peaks in the single-bonded carbon region generally broadened but did not exactly replicate the line shapes in spectra of untreated older amber. Moreover, the line shapes in the copal spectra after treatment showed less variability than was seen in untreated amber.

In the double-bonded carbon region of the spectra from the untreated copal samples, the signal intensities of exocyclic methylene group carbons at 148 and 108 ppm were greater than the signal intensities of double-bonded carbons from the carbon skeleton at 139 and 127 ppm. In the spectra of untreated amber from the Baltic Sea region, Ukraine, and the Dominican Republic, the relative signal intensities at 148 and 108 ppm were lower than those at 139 and 127 ppm, and no signals were detected in this region of the Kuji amber spectrum. After heat treatment, signal intensities at 148 and 108 ppm decreased greatly in all the samples. The molecular structure of copal is partially polymerized, meaning that individual molecules are joined into polymer chains, but bonding between polymer chains is scant and the chains are separated. Thus, exocyclic methylene groups, which are consumed during cross-linkage reactions that join polymer chains (see appendix A), are present in natural copal and their carbons (with signals at 148 and 108 ppm) are detectable in

Figure 13. Ranging from greenish yellow (shown here) to green, commercial amounts of "green amber" have entered the marketplace. This necklace consists of faceted beads that range from 1.3 to 1.8 cm in diameter. Courtesy of HotRockJewelry.com, Solana Beach, California; photo by Robert Weldon.

the corresponding spectra. However, the multi-stage heat treatment process can induce these cross-linkage reactions (see appendix A, figure App-2).

An earlier study by Kimura et al. (2006b) proposed that this cross-linkage formation was related only to the age of the amber and not to its thermal history. However, we found in the present study that the cross-linkage formation in copal and amber can be produced by a multi-stage heating process under pressure, essentially artificially aging the sample during treatment. The polymer network formation that results from the artificial aging of copal following treatment appears to be less complex than that formed during the natural aging of amber, as suggested by the broader spectral pattern of single-bonded carbon signals in the ^{13}C NMR spectrum of treated copal as compared to untreated amber. Therefore, estimating the age of "green amber" produced by heat treatment is not possible by measuring the intensities of the 148 and 108 ppm signals alone.

Identification and Cause of Color. In the functional group region, a new ^{13}C NMR absorption was observed near 179 ppm in all multi-stage heated amber and copal, as well as in all the commercial "green amber" samples, thus providing a spectroscopic index for separating samples that have been artificially and naturally aged. However, this signal cannot be used to establish the identity of the starting material. The formation of the signal is likely due to the production of a new functional group from a devolatilization reaction during the multi-stage heating process.

The small absorption around 820 cm^{-1} in the FTIR spectra was detected in all the treated amber and copal samples (except those treated by the experimental double- and single-stage processes) and in all the commercial "green amber" samples. This feature can be used to identify the treatment. Spectral evidence of the Baltic shoulder indicates that the starting material was amber; however, the absence of this feature provides no conclusive information about the starting material.

The green color exhibited by the treated material is not directly related to the molecular structure of amber or copal; nor is it derived from fluorescence. Heat treatment produced fine granular cloud inclusions that were observed throughout the treated green samples with the use of magnification and a strong fiber-optic light (again, see figure 8). The green color is likely caused by colloidal dispersion (scattering of light) of the minute grains in these clouds, as is the case with the rare Mexican green amber (Cattaneo, 2008). The mechanism by which these fine grains formed is beyond the scope of this article.

NOMENCLATURE

The "green amber" color was produced in both amber and copal by heat treatment. As a result of this process, the heat-treated copal showed changes in physical properties, such as increased hardness and improved solvent resistance, that made it more

similar to untreated amber. The "green amber" obtained from copal by this treatment is physically almost identical to amber and extremely difficult to identify by standard gemological testing. Therefore, the Laboratory Manual Harmonization Committee (LMHC) concluded that effective June 1, 2009, if the identity as amber or copal cannot be made readily, then its variety should be called *amber* and the words "Indications of heating, this resin has been processed by heat and pressure and may have been derived from copal" placed in the comment column. This statement applies to green as well as to yellow-to-brown material.

As also noted above, the presence of the Baltic shoulder feature in the FTIR spectrum proves that the starting material was amber. Identification by this method, however, requires that several milligrams be ground to a powder. In some cases, the Baltic shoulder may also be identifiable by nondestructive diffuse reflectance FTIR spectroscopy. For heated samples exhibiting this feature, the LMHC has stipulated that the following comment be used on the report: "Indications of heating, this resin has been processed by heat and pressure." This statement applies to green as well as to yellow-to-brown material.

CONCLUSION

In recent years, greenish yellow (figure 13) to peridot-like "green amber" has been circulating in the gem market. The intense color of much of this material has not been seen in untreated amber, and it possesses excellent transparency with fewer inclusions than typical amber. The hardness, SG, and solvent resistance of "green amber" are typically greater than of copal. The odor given off when "green amber" is burned with a hot point is slightly weaker than that emitted by natural, untreated amber, but its other physical properties are quite close to untreated amber.

Employing an autoclave to perform a multi-stage heating process under pressure, we successfully produced "green amber" using amber from the Baltic Sea region, Ukraine, the Dominican Republic, and Mexico, as well as copal from Colombia and Brazil. Japanese amber from Kuji turned brown, and copal from Tanzania and Madagascar turned yellow with a slight greenish hue. However, only a limited number of samples were treated, so it is possible that other material from these localities would respond differently.

Spectral analysis with FTIR and ^{13}C NMR identified structural changes in the treated copal and amber. While identification of the treated material is possible using these techniques, the drawback is that they require destructive analysis. The cause of the green color in treated green amber is not clear, but it appears to be the result of the scattering of light by minute particle clouds formed during treatment.

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APPENDIX A: THE STRUCTURE AND SPECTROSCOPY OF AMBER AND COPAL

Resinites are a group of organic hydrocarbons (compounds made of carbon, oxygen, and hydrogen) that are derived from plant resin. Amber and copal are the fossilized and semi-fossilized forms of resinite, respectively. Fossilization of resin involves a series of polymerization and devolatilization reactions that change its composition and structure. The measurable differences in the physical properties of copal and amber are a direct result of the structural changes that occur during fossilization processes.

In nature, fossilization takes place over long periods of geologic time at elevated temperature and pressure conditions that result from sedimentation and burial of organic materials. Fossilization reactions can also be induced in the laboratory by subjecting a resinite material to specific temperature, pressure, and time parameters so that polymerization and devolatilization can occur on the timescale of an experiment. The structure of any resinite is therefore strongly dependent on both the age and thermobarometric history of the sample—that is, its *maturity* (Anderson et al., 1992). This is quite important, since the treatment processes used to make "green amber" involve the use of temperature and pressure conditions that artificially increase the maturity of copal and amber—making the treated material difficult to identify based on its physical and spectroscopic properties.

Molecular Structure. *Individual Structural Units.* On a molecular level, resinites are composed of structural units joined together in chains of varying lengths. The precursor units that make up resinites are macromolecules called labdanoid diterpenes, which are a class of hydrocarbons with the general chemical formula $C_{20}H_{32}$. Ozic acid is a major component of resin produced by plants from the genus *Hymenaea*. Copal from Colombia, Tanzania, and Madagascar, as well as amber from the Dominican Republic, originate from the Fabaceae family (which includes *Hymenaea*). In contrast, communic acid is a major component of Baltic Sea region amber that originates from plants that may belong to the genus *Araucaria*. Both communic and ozic acid possess labdanoid diterpene molecules with similar structures (Schlee 1984; Schlee and Ayuzawa, 1993; Kimura et al., 2006a). For the purposes of this article, this appendix will discuss several key points about the molecular structure of amber and copal.

A graphic representation of a labdanoid diterpene unit is shown in figure App-1. This line-angle structure diagram provides a simplified illustration of the core structure of an organic molecule (i.e., a labdanoid carbon "skeleton"). The diagram shows only the bonds between carbon atoms. A single line represents a single bond, also known as a *saturated* bond, and a double line represents a double bond, also known as an *unsaturated* bond. Carbon atoms are located at the ends of lines and at the intersections of two lines. It is assumed that in addition to the bonds shown, each carbon participates in enough single bonds with hydrogen (C-H) so that its total number of bonds is four. Where carbon and hydrogen atoms in groups are shown at termini, it is for informational purposes.

Note that most carbons are bonded to two other carbons in the core of the structure. These carbons are bonded to two or three additional carbons by single bonds, although one double bond occurs between two carbon sites (labeled 12 and 13 in the figure). In general, the carbons in the core of the structure are not involved in the polymerization and devolatilization reactions that occur as copal matures to amber.

Other carbon sites in the labdanoid diterpene unit are terminal carbons, which are bonded only to carbon in the structural core. These terminal carbons bond with other atoms in what is called a *terminal group*. These terminal carbons are quite important to structural differences between copal and amber because they are involved in maturation reactions.

A labdanoid diterpene unit contains three *methyl groups* in its structure, which are terminal carbon bonded to three hydrogens (annotated CH_3; shown in green). It also contains one *functional group* site (shown in blue) that involves a terminal carbon bonded in one of several arrangements. These include carboxylic acid (-COOH; shown) and ester (-COO-). Carboxylic acid is present in copal, but not in amber. It is widely known that only amber originating in the Baltic Sea region and Ukraine contains ester as the functional group, so it is a useful indicator of geographic origin.

Perhaps the most gemologically relevant functional group is the *exocyclic methylene group* (shown in red); it is this group that is involved in the polymerization and devolatilization reactions that turn copal to amber. Each labdanoid diterpene unit contains one exocyclic methylene group, denoted CH_2. It consists of a terminal carbon double-bonded to a carbon in the structural core of the unit, and to two hydrogens in single C-H bonds.

Polymerization of Individual Units. As mentioned above, polymerization reactions are an important part of the fossilization process. In general terms,
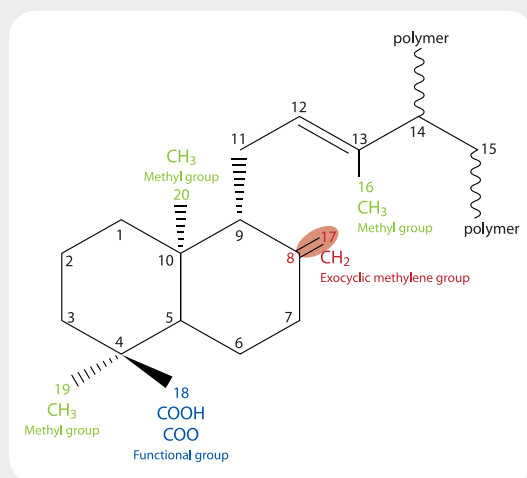
Figure App-1. This line-angle carbon skeleton structure diagram illustrates one of the macromolecules called a labdanoid diterpene that forms linkages in amber and copal. All bonds in the plane of the page are represented by straight lines. Dashed and wedged-shaped bonds are going into and out of the plane of the page, respectively. Bonds that connect individual labdanoid diterpene units to polymer chains are shown by wavy lines. Carbons that participate only in single bonds with other carbons are those labeled 1, 2, 3, 4, 5, 6, 7, 9, 11, 14, 15, 16, 19, and 20. Four of these occupy terminal sites; three of them belong to methyl groups (16, 19, and 20; shown in green), and one belongs to a functional group (18; shown in blue). Carbons involved in double bonds with other carbons are labeled 8, 12, 13, and 17. The only one of these to occupy a terminal position is part of an exocyclic methylene group (17; shown in red).

polymerization reactions involve the conversion of unsaturated (double) bonds to saturated (single) bonds. Initially, polymerization involves linking of individual labdanoid diterpene units (such as those shown in figure App-1) into polymer chains, which occurs at carbon sites 14 and 15 in immature resin. This requires breaking a double bond between sites 14 and 15 (not shown) to join individual units.

As polymerization proceeds, cross-linkage between chains of labdanoid diterpene takes place as copal changes to amber and continues as amber structurally matures (figure App-2). This cross-linkage occurs when the double bond between carbons 8 and 17 breaks, the exocyclic methylene group is destroyed, and a single bond re-forms between the carbon at site 8 and a carbon at site 12 in another labdanoid diterpene to form a three-dimensional polymer network. In copal, few cross-linkages exist and chains are separat-
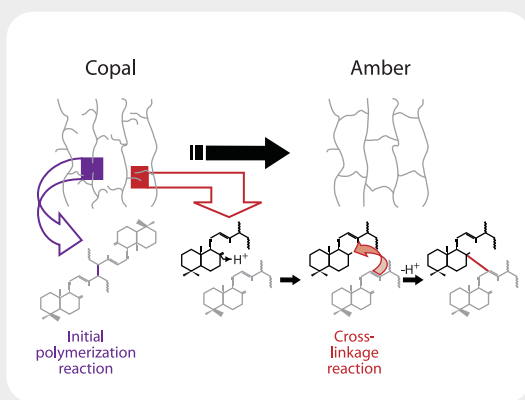

Figure App-2. This diagram illustrates the polymerization reactions involved in the formation of copal and the transition from copal to amber. During initial polymerization, individual labdanoid diterpene units in resin join together to form polymer chains and produce copal (shown in purple). Replacement of terminal exocyclic methylene groups in labdanoid diterpenes with bonds between them produces cross-linkages between polymer chains as copal matures into amber (shown in red).

ed, and thus the double bonds are present in this material. These bonds are replaced with saturated bonds as copal matures into amber. The amount of exocyclic methylene double bonds present in these materials is a rough indicator of their maturity.

Spectroscopic Methods for Investigating Structure. Fossil resins have been classified into several types (e.g., Lambert et al., 2008), using gas chromatography/mass spectrometry (i.e., Classes Ia, Ib, Ic, II, III, IV, and V) and NMR spectroscopy (Groups A, B, C, and D). These types are differentiated according to their macromolecular structure and whether they contain succinic acid within their structure. Equivalent types are Class Ia and Group C, Class Ib and Group A, Class Ic and Group D, and Class II and Group B.

FTIR and NMR spectroscopy are complementary techniques for studying the structure of amber and copal. Absorption lines in FTIR spectra correlate to bonds *between atoms*, so this technique provides information about the nature of bonds in the structure shown in figure App-1. In contrast, peaks in NMR spectra correlate *to atoms*, so this technique provides information about the individual sites shown in figure App-1.

FTIR Spectroscopy. A representative FTIR spectrum of amber studied for this article (i.e., of a Class

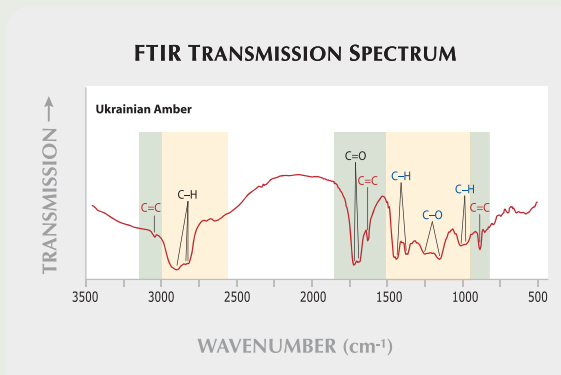## FTIR Transmission Spectrum

Figure App-3. In this representative FTIR spectrum of Ukrainian amber, regions corresponding to double and single bonds are shaded in green and tan, respectively. The colors of peak labels correspond to the color-coding used in figure App-1.

¹³C NMR Spectrum

Figure App-4. In this representative ¹³C NMR spectrum of Colombian copal, the region from 90 to 10 ppm corresponds to single-bonded carbon, from 155 to 105 ppm corresponds to double-bonded carbon, and from 200 to 170 ppm corresponds to a functional group. Peaks are numbered and colored according to the carbon site in figure App-1 to which they are attributed.

Ib/Group A resinite) is shown in figure App-3. It contains features that are important to distinguishing copal from amber, and to investigating the structural changes that occur as these materials mature.

One set of important features is attributed to bonds involving terminal carbons belonging to the exocyclic methylene group described above. Single bonds between carbon (site 17) and hydrogen in the exocyclic group correlate to absorptions at ~2927, 2853, 1470, and 1380 cm⁻¹, and a band from ~1050–950 cm⁻¹. Double bonds between carbons (sites 8 and 17) correlate with absorptions at ~3070, 1640, and 887 cm⁻¹.

The second set of important FTIR features is attributed to bonds involving terminal carbons belonging to the functional group site. Carbon (site 18)-oxygen double bonds in this group are correlated with
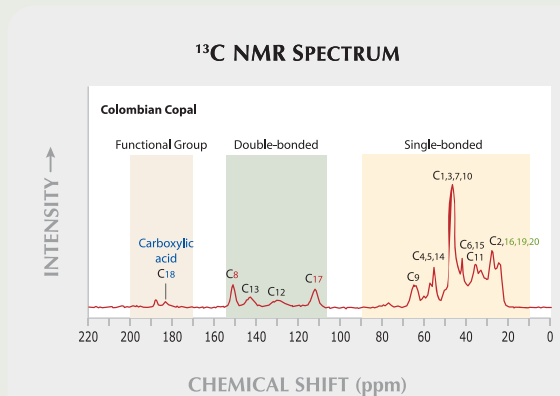
bands at ~1728 and 1698 cm⁻¹. Carbon (site 18)-oxygen single bonds are correlated with absorption features between ~1250 and 1150 cm⁻¹. When the functional group is an ester, as is the case with amber from the Baltic Sea region and Ukraine, this region displays what is termed the "Baltic shoulder." This refers to a broad horizontal shoulder from ~1250 to 1175 cm⁻¹, followed by a sharp absorption peak at ~1159 cm⁻¹.

The FTIR features correlated to the core structure of hydrocarbons comprising amber and copal are important for differentiating these materials. These features, which consist of low-intensity absorptions

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at 744, 698, 640, and 540 cm^{-1}, are due to single carbon-hydrogen bonds involving carbons in the hexagonal rings. The positions and intensities of spectral features related to these unsaturated bonds can be used to separate mature amber from immature copal.

NMR Spectroscopy. A representative ^{13}C NMR spectrum of copal studied for this article (i.e., of a Class Ic/Group D resinite) is shown in figure App-4. NMR spectra of amber and copal are divided into three regions irrespective of resin age: single-bonded carbon (-C-) in the region of 90–10 ppm, double-bonded carbon (>C=C<) in the region of 155–105 ppm, and a functional group [(-COO-) and (>COOH)] in the region of 200–170 ppm (Lambert and Frye, 1982; Lambert et al., 1985). Individual peaks in these spectra correlate to the specific carbon sites (numbered 1–20 in figure App-1) in the structure.

In the single-bonded carbon region, peaks distributed between 22 and 17 ppm correspond to methyl group carbons (16, 19, 20) that are single-bonded to hydrogen. Peaks correlating to carbons that are part of the "labdanoid carbon skeleton" are located at 30–26, 37–40, 36, 53–50, and 59–58 ppm. The 37–40 ppm peak is attributed to several carbon sites (1, 3, 7, and 10) in the core of the structural unit (Lambert and Frye, 1982), which is stable over tens of millions of years of fossilization. Thus, this peak is quite distinct in the spectra of amber and copal of all ages. In general, peaks in this single-bonded carbon region tend to be broader with increasing age of the sample.

Spectral patterns in the double-bonded carbon region from 155 to 105 ppm are important, because of how the two different double bonds (those between 8 and 17 vs. those between 12 and 13) are affected by maturation processes. In this region, four distinct peaks at 148, 139, 127, and 108 ppm correspond to the four double-bonded carbons, at sites 8, 13, 12, and 17, respectively (Clifford and Hatcher, 1995; Clifford et al., 1997; Kimura et al., 2006a). Sites 12 and 17 are bonded to hydrogen, whereas sites 8 and 13 are bonded to carbon. The double-bonded carbons (sites 8 and 17) in the methylene group signals at 148 and 108 ppm are broken during the transition from copal to amber, as described above. The relative intensities of these two signals decrease with increasing sample maturation because their double bonds break during the transition from resin to copal to amber, until they are virtually absent in very mature samples such as the Kuji amber in this study. In contrast, the relative intensities of the 139 and 127 ppm features do not vary much with the maturity of amber and copal since the double bonds between carbons 12 and 13 are not involved in fossilization processes. Therefore, one can infer the age of natural amber from its ^{13}C NMR spectrum by setting signal intensities at 139 and 127 ppm as a standard and defining the relative signal intensities that are observed at 148 and 108 ppm (Lambert et al., 1985; Clifford and Hatcher, 1995; Clifford et al., 1997; Kimura et al., 2006a,b).

The spectral region from 200 to 170 ppm contains features of the various functional groups. The core structural units of amber and copal possess different functional groups. A peak at 176–172 ppm is attributed to carbon (site 18) from an ester functional group, which is only observed in the spectra of amber from the Baltic Sea region (Lambert and Frye, 1982; Clifford and Hatcher, 1995). In general, amber samples from other localities do not display any features in the functional group spectral region. A peak at 184–182 ppm corresponds to carbon from a carboxylic acid functional group, which is only present in copal.

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