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Taphonomy of fossilized resins: determining the biostratinomy of amber

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ABSTRACT

Comparing the maturity of fossilized resins with that of their enclosing bedrock can provide information on the maturity, relative age and biostratinomy of amber and copal. A method to determine this is presented here with examples of amber and copal from the Dominican Republic. Maturity of the bedrock was determined by vitrinite reflection and that of the fossilized resin by FTIR analysis. Vitrinite oxidation values showed maturity states corresponding to lignite and sub-bituminous coal ranks. While the samples from some mines demonstrated that the maturities of the rock and fossilized resin were syngenetic, other samples indicated that recycling of the amber may have occurred. Darkening of the amber (from yellow to red) was correlated with increased oxidation/weathering. This method can be a useful tool for understanding the biostratinomy of fossilized resins.

Keywords: Amber. Copal. Taphonomy. Maturity. Relative age. Dominican Republic.

INTRODUCTION

Amber from the Dominican Republic is well-known for its range of biological inclusions (Poinar, 1992; Poinar and Poinar, 1999; Wu, 1996), thus providing a rare view of past life in a tropical habitat. However there are still a number of unknowns concerning the origin and age of Dominican amber. In fact, there now appears to be as many age estimates as there are investigators. The last two studies involved researchers from the American Museum of Natural History who published papers with differing age estimates, (Grimaldi, 1995 (23-30 million years); Iturralde-Vincent and MacPhee, 1996 (15-20 million years). Neither of these studies gave serious consideration to the 30-45 million year dates obtained earlier by Cepek (Schlee, 1990). One of the problems dating amber deposits by analyzing microfossils in the bedrock is knowing whether any of the amber underwent recycling or redeposition during its geological history. Some amber deposits, such as the Canadian Cretaceous amber in Alberta and the Hat Creek deposits in British Columbia (Pike, 1993; Poinar et al., 1999) occur in coal seams which indicates "in situ" production and the age of the amber would be the same as that of the coal. Other amber deposits, such as most of the Mexican and Dominican, are found in sedimentary rocks and have obviously undergone some transportation previous to burial, although how extensive and how long this process took is difficult

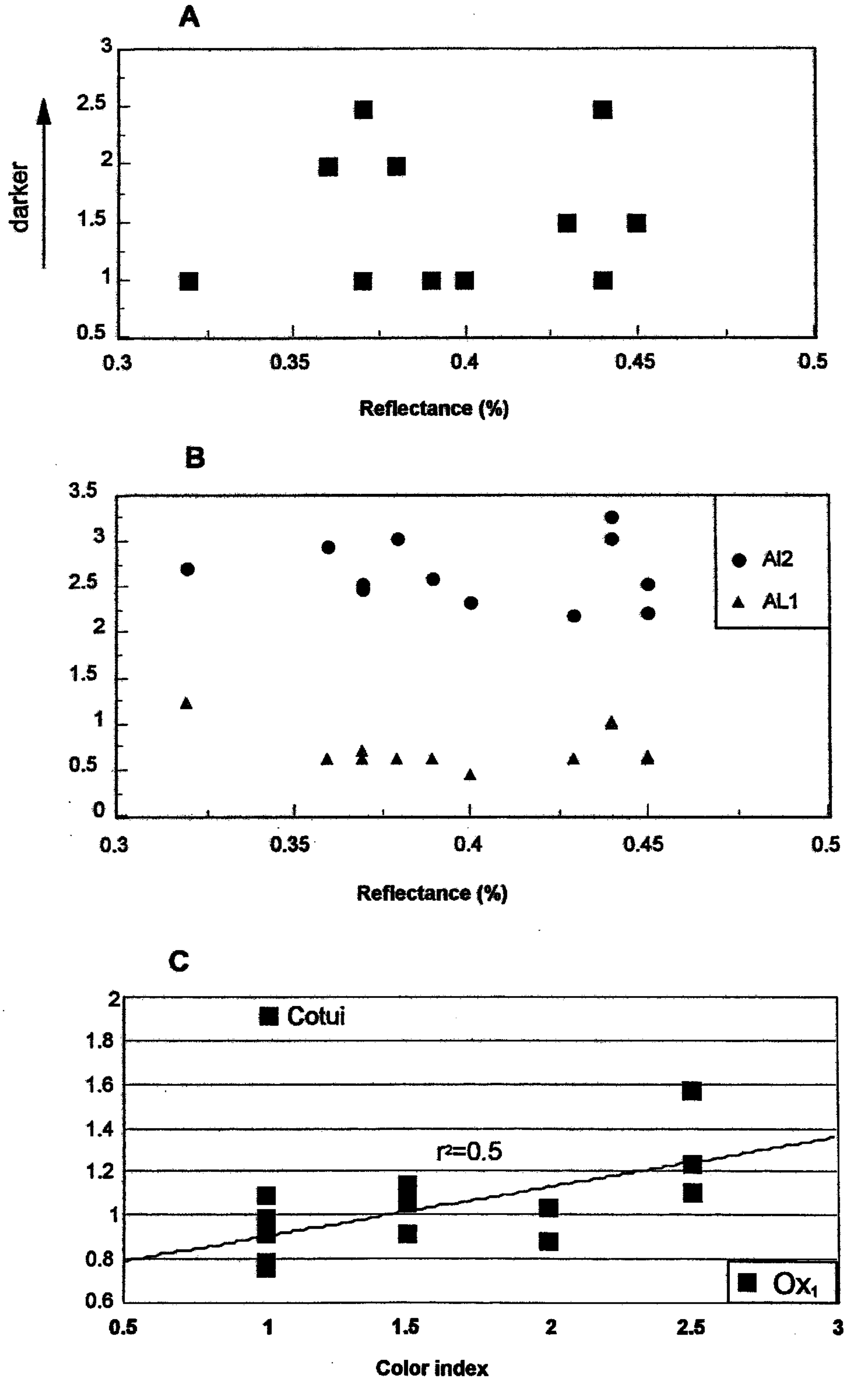

Figure 1. A. Relationship between vitrinite reflectance and a color index of amber; B - Vitrinite reflectance and FTIR-derived ratios: Al_1-CH_2/CH_3 in the 2800-3000 cm^{-1} stretching region and AL_2-CH_2/CH_3 in the 1300-1500 cm^{-1} aliphatic bending region. Note lack of correlation; C-A positive correlation between color index of amber and Ox_1 ($C{=}O_{1600\text{-}1800}/CH_2{+}CH_{3\ 2800\text{-}3000}$) index. Note Cotui amber not following the trend.

Sample	Vitrinite Ro (%)	Vox	Color index
Palo Alto High	0.43 (0.07)	0.7	1.5
Palo Alto Middle	0.39 (0.03)	9	1
Palo Alto Low	0.45 (0.06)	4	1.5
Cotui	5.90 (0.86)	17	1
El Hijo	0.37 (0.02)	1	2.5
El Valle	0.32 (0.02)	1.5	1
Palo Quemado I	0.44 (0.08)	1.5	2.5
Palo Quemado II	0.36 (0.07)	0.3	2
Palo Quemado III	0.49 (0.08)	nd	nd
Los Cacos	0.44 (0.08)	9	1
Las Aquitas	0.45 (0.08)	1	1.5
Cibao	0.38 (0.01)	0.25	2
La Toca ground	nd	2.4	2.5
La Toca 30	0.40 (0.01)	0.7	1
La Toca 128	0.37 (0.03)	0.4	1
La Toca 60	0.37	nd	nd
La Toca 50	0.49 (0.03)	nd	nd
La Toca 45	0.38 (0.04)	nd	nd
Note: Vox - vitrinite oxidation index, standard deviation for vitrinite reflectance given in brackets			

Table 1. Vitrinite reflectance (Ro, %), vitrinite oxidation index (Vox) of the samples studied and color index of the associated amber, nd- not determined.

to say (Poinar, 1992). Another method to determine the maturity and relative age of amber is to chemically examine the matrix. This was first accomplished in 1964 with the infra-red analyses (IRS) of resinites (essentially small bits of amber embedded in low grade coal seams) (Murchison and Jones, 1964) and amber (Beck et al., 1964; Savkevich and Shakhs, 1964). Although this method is suitable for fingerprinting the fossilized resin to identify its province, it cannot be used for dating purposes since the maturity level is dependent on the geothermal regime and not the absolute age (Murchison and Jones, 1964; Mustoe, 1985).

Nuclear magnetic resonance (NMR) spectrometry was also successfully used to fingerprint amber from various deposits (Lambert et al, 1985, 1989). The fingerprints obtained with NMR spectroscopy as well as with IRS essentially were a characterization of the plant group that produced the amber. An initial attempt to chronologically date Dominican amber using NMR spectroscopy was based on differences between the exomethylene resonances obtained from amber originating from different mines. An age range of from 15 to 30 million years was suggested for most of the ambers, however amber from one mine (La Toca) indicated a range of up to 40 million years (Lambert et al., 1985). The question that arose was whether these results reflected chronological age differences or maturity changes as a result of contact metamorphism. An additional study of exomethylene resonances in resin, copal and amber from New Zealand and Australia (Lambert et al., 1993) showed that exomethylene resonances could be used to indicate maturity but that a correlation between maturity and chronological exists only if two conditions are satisfied, namely that the resin originate from the same plant genus or species and that it undergo similar diagenetic processes. The first point, that of the resin originating from the same plant genus or species, is not a serious problem since the spectra can be used to identify the source plant or the identity of the plants have already been established. It is the second condition that causes concern since in many areas of amber burial, both regional and contact metamorphism result in the amber being subjected to differing amounts of heat and pressure, which would affect the exomethylene resonances. A likely example is provided when the amber of Mexico is compared with that of the Dominican Republic. Both amber originates from members of the genus *Hymenaea* (the Dominican amber tree has been identified

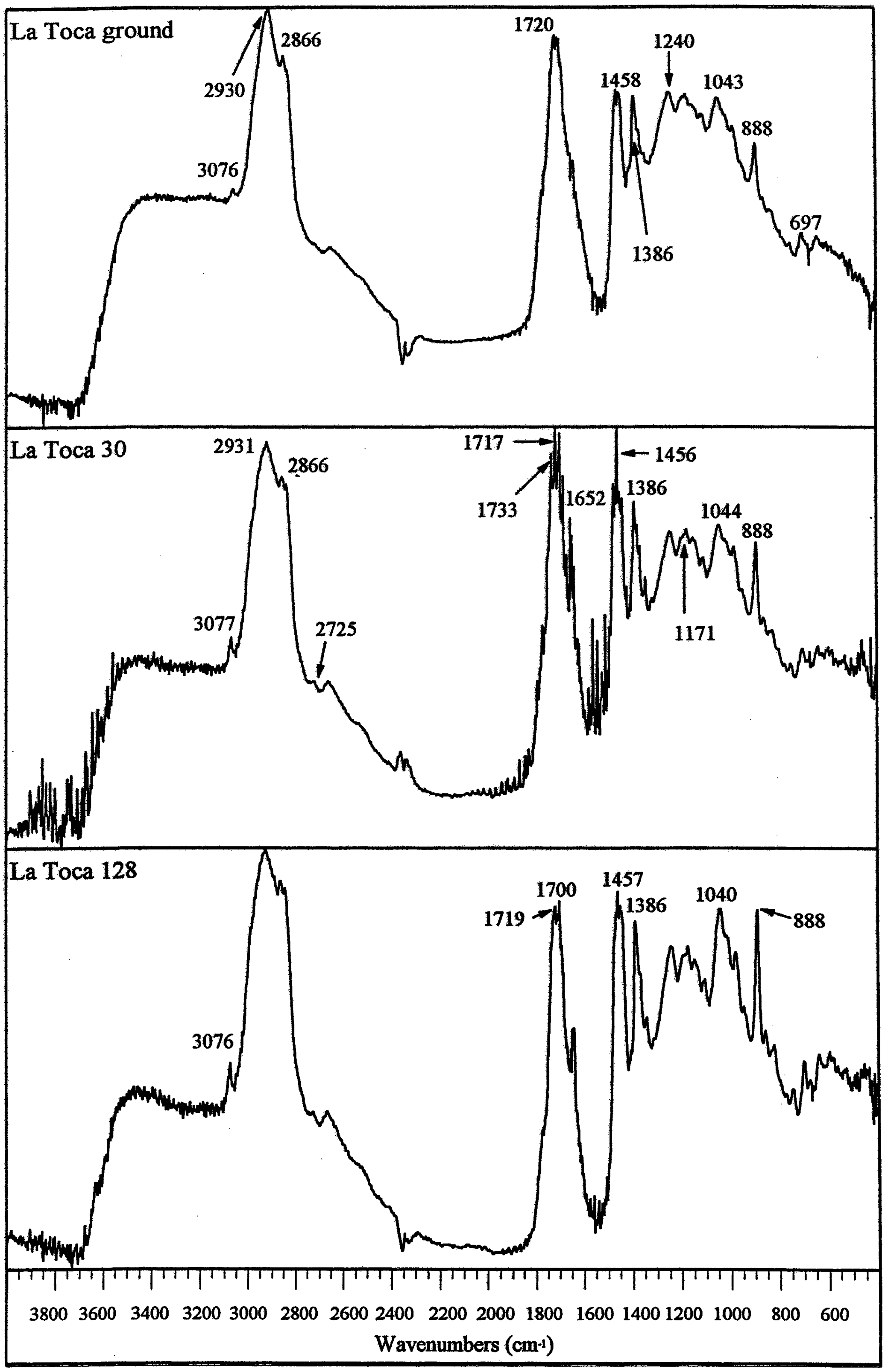

Figure 2. FTIR spectra of La Toca samples. Note varying intensitiy of bands assigned to exocyclic methylene groups (3076,888 cm^{-1}).

Sample	Color index	Al1	Al2	Ox1	Ox2
Palo Alto High	1.5	0.64	2.2	1.06	4.05
Palo Alto Middle	1	0.63	2.61	0.92	4.74
Palo Alto Low	1.5	0.65	2.54	1.14	5.84
Cotui	1	0.62	2.32	1.93	6.49
El Hijo	2.5	0.71	2.49	1.11	7.1
El Valle	1	1.25	2.73	1.1	4.81
Palo Quemado I	2.5	1.04	3.05	1.58	7.71
Palo Quemado II	2	0.62	2.95	0.88	4.17
Palo Quemado III	nd	nd	nd	nd	nd
Los Cacos	1	1.02	3.28	0.99	4.64
Las Aquitas	1.5	0.62	2.22	0.92	4.59
Cibao	2	0.63	3.04	1.04	4.58
La Toca ground	2.5	0.62	3.16	1.24	5.36
La Toca 30	1	0.46	2.34	0.76	4.36
La Toca 128	1	0.62	2.54	0.79	3.97
La Toca 60	nd	nd	nd	nd	nd
La Toca 50	nd	nd	nd	nd	nd
La Toca 45	nd	nd	nd	nd	nd

Table 2. FTIR-derived ratios of the amber: Al_1-CH_2/CH_3 in the 2800-3000 cm^{-1} stretching region; Al_2 - Al_1-CH_2/CH_3 in the 1300-1500 cm^{-1} aliphatic bending region; Ox_1 - C=O $_{1600-1800}$ /CH_2+CH_3 $_{2800-3000}$; Ox_2 - C=O $_{1600-1800}$/$CH_{2,3}$ $_{1450}$; nd: not determined.

as *Hymenaea protera* Poinar, 1991b). However it is apparent by the nature of Mexican amber (hardness, specific gravity) and by the fact that many insect inclusions actually show evidence of compression and shear pressure that much of the Mexican amber has been subjected to high levels of heat and pressure. Indeed there is still much volcanic activity today in the areas of the Mexican mines (Poinar and Poinar, 1994). Such contact metamorphism increases the rate of maturation, which probably explains why the exomethylene resonances of Mexican amber are less than those of Dominican amber (Lambert et al., 1985, 1989), assuming that the ages are roughly equivalent.

Studies on the taphonomy of fossilized resins are infrequent, yet this is an important aspect of amber studies. The sedimentary history or biostratinomy of fossilized resins can involve transport, mixing and sorting by various agencies. Amber transported by rivers into the sea or low lying deltas, which are later inundated by salt water, often end up in uplifted sedimentary sequences. During these processes, amber from different plant sources and different ages can become mixed, thus making dating and paleo-reconstruction difficult.

The present study was undertaken to determine the rate of maturity of amber from various "mines" in the Dominican Republic and compare them with the rate of maturity of organic matter in the rock matrix containing the amber. It was hoped that such analysis would provide information on the maturation of the amber in relation to the rock and indicate whether the fossilized resins were in a primary or subsequent depositional site (evidence of recycling).

MATERIALS AND METHODS

Rock samples containing amber from several locations in the Dominican Republic (Table 1) were collected by the senior author and others during a University of California Research Expeditions Program in 1987 (Poinar and Poinar, 1994). The samples had been stored at room temperature since that period. With the exception of the samples from Cotui and El Valle, all of the mines were located in the Cordillera Septentrional roughly between Santiago and Puerto Plata in the Northern Portion of the country. These localities lie in the Altimira facies of the El Mamey Formation (Upper Eocene) which is shale-sandstone interspersed with a conglomerate of well-rounded pebbles (Eberle et al, 1980). The El Valle source originates in the eastern portion of the Dominican Republic while the Cotui site is located in a valley between the Cordilleras Central and Septentrional. The numbers following the La Toca samples indicate the distance in feet

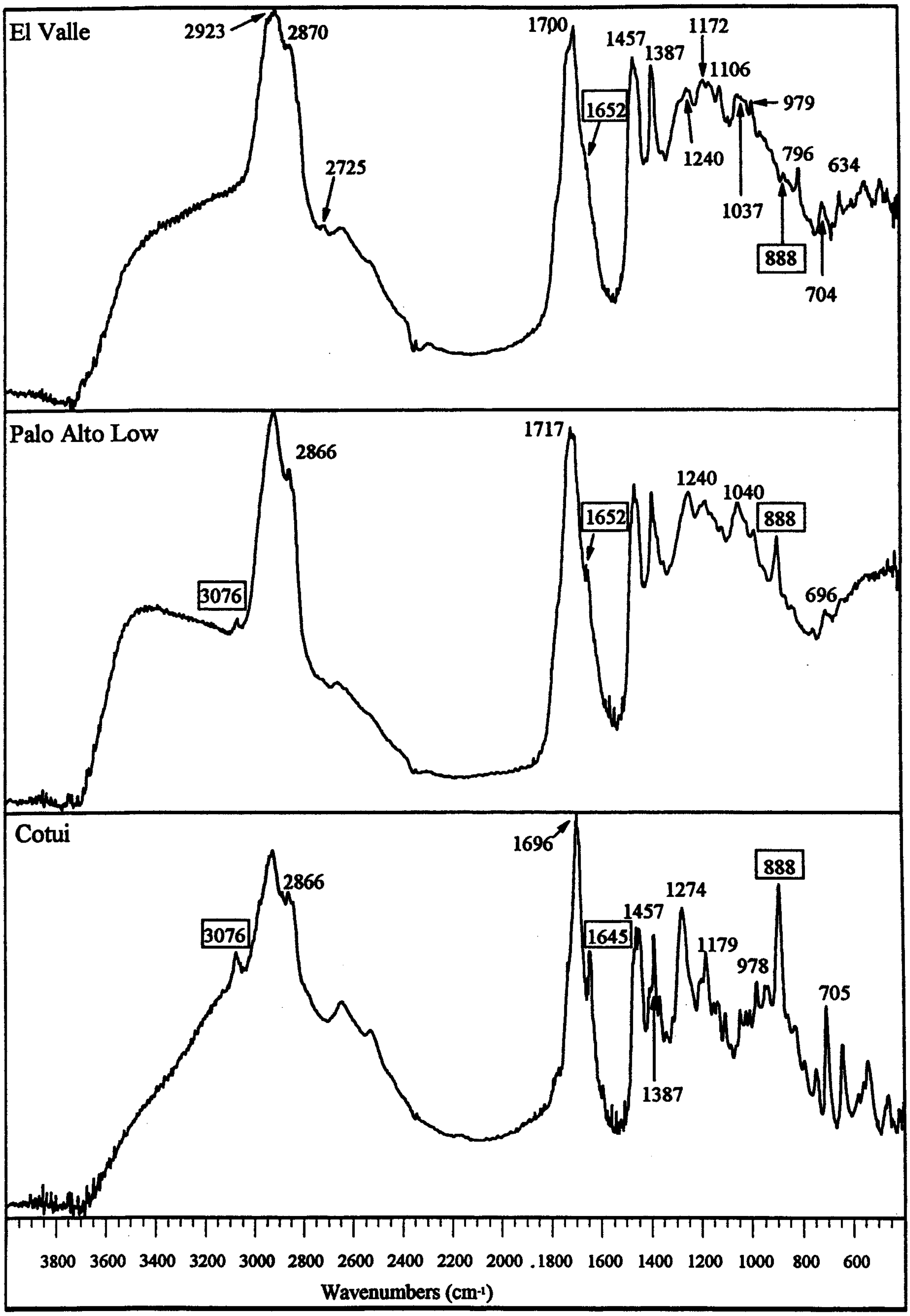

Figure 3. FTIR spectra of El Valle, Palo Alto Low and Cotui ambers. Note differences in exocyclic methylene groups (3076, 1645-1652, and 888 cm^{-1}), with the strongest in Cotui to almost undetectable in El Valle.

Sample	3081	1644	888	E/Al2800-3000	Group
Cotui	S	S	S	0.28	A
La Toca 128	S	S	S	0.1	A
Las Aquitas	S	S	S	0.08	A
La Toca 30	M	M/S	M/S	0.06	A
Cibao	M	M	M	<0.01	B
Palo Alto High	W/M	W	M/S	<0.01	B
Palo Alto Middle	W/M	W	M	<0.01	B
Palo Alto Low	W	W	M	<0.01	B
Palo Quemado II	W	W	M	<0.01	B
El Hijo	W	W/A	M	<0.01	B
La Toca ground	W	W	M	<0.01	B
Los Cacos	W/A	W/A	W	<0.01	C
Palo Quemado I	W/A	W/A	M	<0.01	C
El Valle	A	A	A	<0.01	C
Note: S - strong, M - medium, W - weak, A - absent					

Table 3. Relative intensity of exocyclic methylene groups (with peaks at 3081, 1644, and 888 cm^{-1}) and their ratio to CH_2 and CH_3 in the aliphatic stretching region (E-integration area of exocyclic methylene groups).

of various amber locations along the slope of a mountain. It appeared that these represented different veins that transected the mountside.

Rock samples were prepared as polished blocks following standard petrography procedures (Bustin et al., 1985). A Leitz MPV-2 microscope was used to identify organic matter types and to measure random vitrinite reflectance in oil. Vitrinite particles were recorded as either unoxidized, slightly oxidized or strongly oxidized and a vitrinite oxidation index (Vox) was calculated as a ratio of oxidized to unoxidized vitrinite based on no fewer than 20 vitrinite particles per sample. Random vitrinite reflectance was determined from 10 to 25 measurements, depending on the availability of material.

Amber separated from the host rock was first given a color value, based on a scale from 1 to 3: 1- light yellow, 1.5- yellow, and yellow with orange edges, 2- dark yellow to light orange, 2.5- dark orange to light brown and 3- brown. This index would be correlated with other parameters. For analysis of the fossilized resin, crushed amber or copal was subjected to Fourier Transform infrared analysis (FTIR) and analyzed with a Nicolet 20SXC spectrometer equipped with a DTGS detector and diffuse reflectance accessory. With this procedure, a small amount of amber (ca 2 % by weight) was mixed with finely ground KBr and loaded into the compartment of a diffuse reflectance attachment. Spectra were obtained in reflectance mode at a resolution of 8 cm^{-1} with 1,024 scans collected from each specimen.

The IR signal was recorded in the region of 400 to 4000 cm^{-1} wavelength. Bands were identified by comparison with published assignments (Painter et al., 1981; Wang and Griffith, 1985; Goodarzi and McFarlane, 1991; McFarlane et al., 1993). The following ratios were calculated: CH_2 /CH_3 in the 2800-3000 cm^{-1} stretching region (AL_1), CH_2 /CH_3 in the 1300-1500 cm^{-1} aliphatic bending region (AL_2), $C{=}O_{1600\text{-}1800}$/ CH_2 +CH_3 $_{2800\text{-}3000}$ (Ox_1), and $C{=}O_{1600\text{-}1800}$/$CH_{2,3\ 1450}$ (Ox_2). For selected samples, a ratio of exocyclic alkenes/ CH_2 + CH_3 $_{2800\text{-}3000}$ was also calculated. These ratios utilize band integration areas rather than absolute concentrations of functional groups.

RESULTS

Organic petrography of the rock matrix

The amount of organic matter in the rock matrix ranged from traces to several percent. It was dominated by vitrinite that occurred as variable size fragments. The vitrinite often showed remnants of woody cell structure, although homogenous telocollinite was also present, often in association with framboidal pyrite. In some specimens, the vitrinite showed little signs of oxidation while in others it was oxidized, with prominent relief and weath-

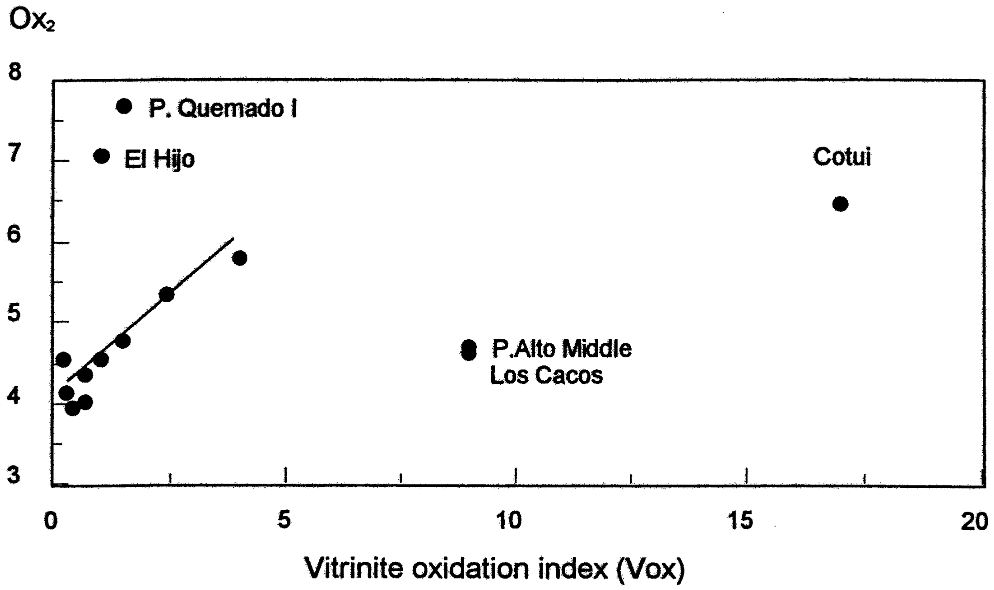

Figure 4. Relationship between vitrinite oxidation index (Vox) of amber-bearing rocks and Ox_2 ($C{=}O_{1600\text{-}1800}/CH2,_{3\ 1450}$) for the amber studied. Line shows a linear trend between vitrinite oxidation index of the rock matrix (Vox) and oxidation index of amber (Ox_2) for the majority of samples.

ering cracks. The Vox index ranged from 0.25 to 17 (Table 1) , with the least oxidized vitrinite coming from Cibao, Palo Quemado II, La Toca 128, La Toca 30 and Palo Alto High and the highest from Cotui, Palo Alto Middle and Los Cacos. Macerals of the liptinite group represented by often yellow fluorescing liptodetrinite (probably of pollen and algal origin) were dispersed in the samples.

With one exception, the maturity of the organic matter in the rock corresponded to a lignitic or sub-bituminous coal rank, as inferred from the vitrinite reflectance range of 0.36% to 0.49%. The exception was the sample from Cotui where the vitrinite showed a reflectance ranging from 3.2% to 6%. The organic particles were often porous and vesiculated, highly oxidized and resembled those found in thermally altered zones near volcanic intrusions.

Amber samples

The color of the amber obtained from the rock matrix, which varied from light yellow (1) to dark orange-brown (2.5) (Table 1) did not show a correlation with the vitrinite reflectance of the matrix rock (Fig. 1A). Nor did the vitrinite reflectance always show a correlation with FTIR-derived ratios (Fig. 1B). The color index did show a significant correlation with oxidation indices (Ox_1, Ox_2) ($r^2 = 0.5$) indicating that the color darkens as these ratios increase (fig. 1C).

FTIR analysis of the ambers showed distinct differences between them with regard to the distribution of functional groups. Figure 2 presents FTIR spectra of three amber samples occurring in close proximity to each other. The spectra are dominated by signals from aliphatic groups (2800-3000 cm^{-1} and 1350- 1480 cm^{-1}) and oxygenated groups (1600-1800 cm^{-1}). The closer spectral analysis shows differing intensities of CH_2 and CH_3 groups between individual amber specimens. The proportion of CH_2 to CH_3 (reflecting the length and branching of aliphatic chains {Lin and Ritz, 1993}) is highest in El Valle, Palo Quemado 1 and Los Cacos (Table 2), suggesting that the longest chain and least branched aliphatic structures occur in these three samples. This proportion is expressed by Al_1 (aliphatic stretching region) and Al_2 (bending mode region). Ratios Ox_1 and Ox_2 include aliphatic and oxygenated groups in the equations and usually reflect the oxidation level of the organic matter: CH_2 and CH_3 are known to be consumed during oxidation with the C=O groups being formed (Kister et al., 1988; Vasallo et al., 1991; Pradier, 1992). These and similar ratios have been used as a measure of oxidation (Gethner, 1987; Lynch et al., 1988; Goodarzi and McFarlaine, 1991). Assuming that CH_2 and CH_3 were equally abundant in the fossilized resin, the least oxidized ambers would be from

La Taco 128 and La Toca 30 and the highest oxidized would be samples from Cotui, Palo Quemado 1, El Hijo and La Toca ground.

The concentration of exocyclic alkenes in diterpenoid form also differentiates the various fossil resins. These compounds are represented by bands at 3076, 1645 and 888 cm^{-1} (Streibl et al., 1976). Based on the intensity of bands representing these compounds, the fossilized resins studied can be divided into three groups (Table 3) comprising those of high intensity (A)(characterized by a ratio of isocyclic alkenes/CH_2 + CH_3 2800-3000 higher than 0.01), medium intensity (B) and low intensity (C). The samples with intense exocyclic alkanes were Cotui, La Toca 128, Las Aquitas and La Toca 30. Those with medium intensity were Cibao, Palo Alto high, Palo Alto middle, Palo Alto low, Palo Quemado II, El Hijo and La Toca ground. Those with low intensity were Los Cacos, Palo Quemado 1 and El Valle. Figure 3 shows examples of FTIR spectra of ambers representing each of these groups, clearly demonstrating the most distinct bands at 3076 and 888 cm^{-1} in Cotui and almost undetectible in El Valle. Other notable bands belonged to aldehydes (2725 cm^{-1}) which are usually weak to absent except in La Cacos, Cibao and La Toca 30. No aromatic compounds were detectable.

Amber specimens of group A were the most heterogeneous with significant variations in functional groups observed. The Cotui sample was especially unique and had the exocyclic alkenes much more intense than in the others (almost three times higher in the Cotui sample) (Fig. 3 and Table 3). The Cotui sample also revealed an intense band at 1274 cm-1 that could represent aryl-O-aryl functions (Osawa and Shih, 1971). This band did not appear in any other samples. Also found in the Cotui sample was a dominant band at 1696 cm^{-1} (Fig. 2) which could be assigned to stretching vibrations of the -COOH group with the carbonyl group conjugated with C=C in the ring (Bellamy, 1980).

DISCUSSION

The present study indicates that the maturity of the dispersed organic matter in the rock matrix containing samples of amber from the Dominican Republic corresponds to lignitic and subbituminous coal ranks as expressed by vitrinite reflectance values ranging from 0.32 % to 0.49 % (see Teichmuller and Teichmuller, 1982). In his study of resinites and associated coals, Murae et al. (1995) showed that at a vitrinite reflectance of about 0.4 %, exocyclic alkenes began to disappear. This stage of maturity is not surprising since many of the amber deposits (including resinites) found world-wide today occur in similar ranking coal deposits (Poinar, 1991a, 1992). In fact there are no reports of recognizable amber or resinites associated with anthracite coals since carbonization associated with the increase in maturity will result in resinite fluidity and migration which can occur even in some bituminous coals (Poinar, 1991a). In a study of resinites and amber associated with coal deposits of known age in New Zealand, it was possible to find amber in sub-bituminous deposits dating from the Miocene, Oligocene, Eocene and Cretaceous and in lignite beds dating from the Miocene and Oligocene (Poinar, 1991a; Sherwood, 1986).

The present study also showed that in most samples a similar level of maturity occurred in the amber and the enclosing rock matrix, suggesting that the two matured together. One of several exceptions to this trend was the sample from Cotui which in contrast to all others, showed a lower degree of maturity than that found in the matrix rock. Here the vitrinite in the host rock showed increased maturity (as expressed by vitrinite reflectance), while the amber showed very low maturity as indicated by intense exocyclic methylene groups (Fig. 3). This could be explained if the Cotui sample originated from a different plant genus or species or if the Cotui material had a different biostratinomy. Differences between Cotui material and amber from other areas of the Dominican Republic was also noted in an earlier study on the NMR spectra of amber (Lambert et al., 1985). The spectra of Cotui material obtained in the latter study differed from all others enough for it to be placed in a separate category. Later C^{14} dating studies revelaed that the Cotui material is under 1000 years old (Schlee, 1990; Poinar, unpublished results). However, in the age analysis of Dominican amber based on exomethylane resonance peaks, it was assessed with the amber samples (Lambert et al., 1985). This resulted in a biased estimate of the Cotui age (15-17 million years) which was based on the assumption that all of the material originated from the same *Hymenaea* tree species. A recent analysis of the Cotui copal indicates that the plant source is the extant *Hymenaea courbaril* (Mastalerz and Poinar, unpublished observations) while all of the amber samples probably originated from the extinct species *Hymenaea protera* Poinar (1991b). This difference in plant origin may explain why an anomalous date of these deposits was obtained in a previous study using nuclear magnetic resonance (Lambert et al., 1985). The Cotui material probably represents deltaic deposits which were incorporated into sediment typical of that region resulting in a high maturity host rock contrasting with the low maturity copal. Although Grimaldi (1995) stated that Burleigh and Whalley (1983) and Schlee (1984) carbon-dated other deposits of Dominican amber (from Bayaguana) Burleigh and Whalley did not include any samples from the Dominican Republic in their study and Schlee only carbon-dated Cotui deposits.

The importance of diagenetic factors in modifying the infra-red spectra of amber and resinites has already been discussed by Mustoe (1985) and Murchison and Jones (1964), respectively. Changes in infrared spectra of coal as a result of increased oxidation has also been established (Gray and Lowenhaupt, 1989).

In the present study, aside from the Cotui sample, four other amber samples did not show a maturation at the same level as the rock matrix (Fig. 4). The amber from El Hijo and Palo Quamado 1 showed a higher degree of oxidation than would be expected from the analysis of organic matter in the rock matrix. This suggests that the ambers had either been exposed to severe weathering before lithification or that they had been re-cycled. The sample from El Hijo was obtained from strata in a wet clay deposit along a river and may have undergone some exposure, but the Palo Quamado 1 sample came from rock strata that had not previously been exposed and may have been recycled. In addition, amber from La Cacos and Palo Alto Middle show relatively low oxidation in contrast to the high oxidation index of the organic matter in the rock matrix (Fig. 4). This suggests that either some mixing occurred, resulting in more recent amber being mixed with carbon remains from earlier deposits or that the organic matter from the rock matrix was strongly oxidized before deposition.

This study also shows that the color of the amber samples can have no relation to maturity. Some colors like red, clear yellow and blue are characteristic of certain amber mines and several reasons for this have been proposed, such as differences in hardness, age, and weathering (Poinar, 1992). In fact dealers in the Dominican Republic told the senior author that in order to make yellow amber red, simply place it in the oven at 500 F for 15 minutes. While the present study shows that there is no correlation between color and most functional groups, there is a significant correlation between color and the Ox_1 and Ox_2 ratios. These ratios, especially Ox_1, are considered indices of oxidation or weathering (Goodarzi and McFarlane, 1991) and thus strongly indicate that weathering brought about the darker color. Also it is a general phenomenon that young amber or copal is lighter in color than mature amber produced from the same genus of trees. This is quite clear in comparing Dominican amber with Colombian copal (dated at < 1000 years; Poinar, 1996), both from *Hymenaea* trees. So there can be a general correlation between the maturity of fossilized resin and color, but as this study shows, amber of the same age group can vary in color as a result of differential weathering.

The present investigation demonstrates that it is possible to compare the maturation of amber with that of dispersed organic matter in the embedding rock matrix. It should be emphasized that what is being measured here is the degree of maturation which has no bearing on the chronological age of the deposits. In fact Given (1964) already stated in regards his chemical study of coal macerals that " the correlation between the degree of metamorphism and geological age is not close". This study also demonstrates the usefulness of comparison of oxidation indicators for both host rock and amber. Such a comparison can provide an understanding of the pre-depositional history of not only amber but also other types of organic matter.

While the methods employed here are fairly standard, advanced analytical techniques could provide further information on this topic. Such studies are useful in understanding amber biostratinomy, especially in relation to the origins of their biological inclusions.

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