by each Cu within the [Cu₂O₂] core. Upon inspection of the crystal structure of the fully reduced form of ascorbate oxidase (I1), the three trigonally ligated Cu(I) centers (average Cu-Cu distance, 4.5 Å) appear geometrically predisposed toward accommodation of O₂ and formation of a [Cu₃O₂] cluster. However, no current spectroscopic studies of the metastable oxygen intermediates of multicomponent oxidases and their derivatives support the existence of an intensely absorbing o xo-Cu(III) chromophore, and no unusually short Cu-O bond distances such as those observed in 2 are indicated (12, 13, 32). In accordance with these studies, however, the facile reaction of three Cu(I) monomers with O₂ to form the mixed-valence bis(μ₄-oxo)Cu(II)/Cu(II) Cu(III) species 2 does suggest that O₂ bond cleavage at trinuclear Cu sites requires full 4e− reduction of O₂. In the case of native laccase, the fourth electron is provided by the remote “blue” Cu center, whereas in 2, the extra electron must be obtained at the cost of further oxidation of one of the Cu sites.

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14. The (1R,2S)-cyclohexanediol backbone was chosen both for its preorganized nature and its chirality. In its synthetically preferred conformation, with the two amine substituents equatorially positioned, this ligand is preorganized for binding a single metal. The enantiomeric purity of the ligand significantly reduces the probability of forming clathromes complex.

15. Although 1 has not been structurally characterized, its 1H NMR spectrum in the diamine ligand region is nearly identical to that of the structurally characterized trinuclear complex (Cu₂PPPh₂)₂(CF₃SO₂)₂ which is formed upon addition of PPh₃ to a solution of 1. The N-perethylated analog of 1, [(L')Cu₂(H₂O)₃]Cl(NO₃) [L' = NNNV.N'-tetraethyl-trans-(1R,2S)-cyclohexanediamine], with bound CH₂CN has also been structurally characterized as a trigonal planar species (18).

16. Reported concentrations and molar absorptivities are uncorrected for the thermal contraction of CH₂CN at below-ambient temperatures, consistent with other reports.

17. The product of oxygenation depends on the concentration of 1. Solution of reactions at or below 1 mM in water generates a different species X with extremely intense electronic and vibrational transitions (per Cu atom; absorbance ε = 10,000 M⁻¹ cm⁻¹ at wavelength λmax = 295 nm, ε = 13,000 M⁻¹ cm⁻¹ at 392 nm; resonance Raman features at 607 and 583 cm⁻¹ for 1₇O₂− and 1₈O₂− derived species, respectively). The close spectroscopic resemblance of X to the structurally characterized dimer [BN₂TACN]Cu₂O₂]− (SbF₆)₂ recently reported (J. A. Hallen et al., Science 271, 1597 (1996)) suggests that it is a similar 2:1 CuO₂ complex (BN₂TACN)Cu₂O₂ = 1,4,7-tris(2,4,6-triazacyclononane).

18. Supporting information is available from the author or at the Science Web site http://www.sciencemag.org/ science/feature/beyond/#code. Included are synthetic procedures and spectroscopic characterization data for all new compounds and x-ray structural information, including tables of crystallographic parameters, positional and thermal parameters, and interatomic distances and angles.

19. Isolated yield, 50%. The x-ray crystal data is available (18).

20. Crystal data for [1R,2S]-CH₂CN·browromatic rhombic blocks from cold (−40°C) CH₂CN·ether; monoclinic C2 (no. 5), a = 29.303(1) Å, b = 16.8004(3), c = 15.3762(2) Å, β = 119.158(1)°, V = 6332.2(1) Å³, Z = 4; 14,745 reflections were collected and appropriately averaged (18), 9779 of which were unique (150 S, S′ < 28 < 46); 1124 reflections [F(>4σ(F))] yield R = 7.4 and R1 = 7.6.

21. Although the two clusters are crystallographically unique, they are isostroic within to a root-mean-square (rms) deviation of 0.162 Å (0.093 Å)

Age and Paleogeographical Origin of Dominican Amber

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The age and depositional history of Dominican amber-bearing deposits have not been well constrained. Residues of different age exists in Hispaniola, but all of the mainamberiferous deposits in the Dominican Republic (including those famous for yielding biological inclinations) were formed in a single sedimentary basin during the late Early Miocene through early Middle Miocene (15 to 20 million years ago), according to available biostatigraphic and paleogeographic data. There is little evidence for extensive reworking or redeposition, in either time or space. The brevity of the depositional interval (less than 5 million years) provides a temporal benchmark that can be used to calibrate rates of molecular evolution in amber taxa.

In the Dominican Republic, amber (1) occurs in commercially exploitable quantities in two zones (Fig. 1): north of Santiago de los Caballeros (the “northern area”) and northeast of Santo Domingo (the “eastern area”). Amber from the northern area has been suggested to be as old as Early Eocene or as young as Early Miocene (2–7); estimates for the eastern area are more diverse, ranging from Cretaceous to Recent (2–4, 6–9). Age spreads of this magnitude are implausible, but to date no resolution of the age of Dominican amber has met with wide acceptance. The resolution offered here is based on a synthesis of available biostatigraphic and paleogeographic data from several parts of Hispaniola (Fig. 2).

In the eastern area, amber-bearing sedi-
ments occur in the ~100-m-thick Yanigua Formation (Fm), composed of organically rich laminated sand, sandy clay, and some intercalated lignite layers up to 1.5 m thick. Plant debris is found at low frequency throughout. Isolated beds of gravel and calcarenite occur, but true alluvial sediments are absent. Amber pieces are found embedded in lignite and sandy clay. In addition to indicative sedimentary features, the character of the invertebrate and vertebrate fossils from these beds (thin-shelled mollusks, foraminifera, and ostracods; crocodiles, sirenians, and turtles) imply that deposition occurred in a near-shore context, probably in coastal lagoons (8, 10) fronting low, densely forested hills (11). Microfossil assemblages (12) and zone definitions (13) indicate a late Early to early Middle Miocene age for this formation.

In the northern area, the amber-bearing unit comprises the upper 300 m of the La Toca Fm, a 1200-m-thick Oligocene to Middle Miocene suite of clastic rocks (14–16). The amberiferous unit is composed of sandstone with occasional conglomerate that accumulated in a deltaic to deep-water environment. Individual beds—thick, coarse, and tail-graded or massive at their base—grade into amber-containing sandstone with parallel lamination, rarely presenting ripplemarks. Amber fragments from these sands show few surface signs of transport and can reach lengths of 30 to 40 cm. Lignite occurs in the form of thin lamellae within the sandstones; carbonized wood fragments are also common. These rocks grade into flyschoid, deeper water deposits containing detrital amber (17) underlain by thick conglomerate (14, 16). Microfossils (18) in the amber-bearing unit correlate with faunal zones of Early to Middle Miocene age (5, 14–16).

Paleogeographically, the eastern and northern areas were part of the same sedimentary basin that was later disrupted by movements along major faults (Fig. 1). Paleocurrent analysis (19) of amber-bearing rocks of the northern area indicates that the sediment source was located toward the southeast, so the only plausible source of resin input would have been forests surrounding the depositional basin (Fig. 1). In the eastern area, slope-wash carried resinites into nearby coastal lagoons, where they were apparently concentrated in lenses or pockets. Resinites in the La Toca Fm were probably slope-washed into river channels cutting the ancestral Cordillera Central, then transported with sand and silt into the deltaic and deep-water environments of the basin. Hydrodynamic experiments (20) indicate that Hymenae resin and copal float in fast-moving fresh water but sink when the current is slow or negligible. Fresh resin floats in saline water, but copal and amber may float or sink depending on the density of the individual specimen. Therefore, fresh resin and copal entering high-energy marine environments would probably have been widely dispersed.

Outside the major mining areas, amber occurs in small quantities in turbiditic facies of the Early to Middle Miocene Sombrero Fm (21), south of the Cordillera Central in an area of Plateau Central–San Juan. Trace amounts have also been reported from lateral lignite-bearing sediments of the early Middle Miocene Maissade Fm in Haiti (22). These occurrences represent an external temporal control for the age of the amber-bearing deposits north of the Cordillera Central (Figs. 1 and 2).

In combination, these data indicate that the amber-bearing deposits of the Dominican Republic are uniformly late Early to middle Miocene in age (15 to 20 million years ago). However, this conclusion does not agree with efforts to date amber through the use of exomethylene resonance signatures visualized by nuclear magnetic resonance spectroscopy (NMRs) (7). In order to derive an age assessements, their present separation results from post-Oligocene left-lateral displacement along the SF and RGF (compare with insert and (15, 32)). The northern and eastern areas formed a protected embayment on the north coast of Hispaniola, wherein sediments could accumulate rapidly. Fig. 2 (right). Stratigraphic columns of selected Tertiary regions in Hispaniola and eastern Cuba, compiled from various sources (6, 8, 10, 13, 15, 16, 29, 31), with additional information on stratigraphy and age obtained for this report. Formational names are for reference; chronostratigraphic framework after (33).
ment by this method, resistance intensity must first be calibrated against NMR results for specimens of known age. The only published calibration curve (7) relevant to the dating of Dominican amber is based on two data points: (i) amber from Palo Alto mine (northern area), accepted as Early Miocene because sediments yield microfossils of that age (5), and (ii) a sample of resin from a Recent representative of *Hymenaea*. Age estimates based on this curve are said (7) to indicate a Late Eocene age for amber recovered from mines at La Toca and Tamboril in the northern area and a Middle Miocene age for specimens from Bayaguana and Cotui in the eastern area. Microfossil evidence supports a Miocene age for amber-bearing sediments in the mines at Bayaguana (10), but microfossils as distinctly as clearly established that the La Toca mines are also Miocene (18), which contradicts the NMR results. If amberiferous sediments at La Toca, Palo Alto, and Bayaguana are paleontologically equivalent in age, then the exomethylene decay curve does not produce meaningful results, as has been pointed out by others for example, (3).

It has been suggested that occurrences in the Dominican Republic may have been emplaced by redeposition, so that they may be older than the sediments that bear them (5, 7, 8). Several considerations make this interpretation unlikely. First, amber has not been reported in rocks older than Miocene anywhere in the Dominican Republic (Fig. 2); therefore, they cannot be the source of older amber, if such existed. Second, plants and animals preserved in Dominican amber can almost always be allocated to extant groups at low hierarchical levels and often seem to differ little from relatives living in Hispaniola today (see, for example, 2, 3, 5, 23). Third, if Dominican amber derives from a single species of *Hymenaea* (24), as is strongly indicated by infrared spectroscopy pyrolysis gas chromatography (25), then the resin source was probably highly confined, both geographically and temporally (26). Fourth, the fact that individual pieces of amber may either float or sink in saline waters could have facilitated dispersion during reworking but not the formation of concentrated ore bodies. For all these reasons, it is logical to conclude that Dominican ambers are the same age as the sediments that contain them, that is, that the reappearance of ambers of different ages has not occurred.

The fact that the major occurrences of Dominican amber can be so narrowly constrained in age should open up new possibilities for investigation, such as estimating rates of genetic change from ancient DNA in amber inclusions (27). Genetic material appears to be unusually well preserved in Dominican amber (27, 28), suggesting that it may be an ideal material for this kind of study.

**REFERENCES AND NOTES**

1. Resinoids derived from plants differ widely in their chemical composition and physical characteristics (2). Copal and amber are often difficult to distinguish by inspection, but differ in their resistance to heating and organic solvents. Less resistant copal is conventionally interpreted as an unfossilized version of amber, although the relation between age and the complex diagenetic changes that yield true amber is not well understood. Dominican copal, allegedly of Holocene age (9), is not discussed in this report because we were unable to examine its original depositional context, it is noteworthy that hard copal is sometimes with biological inclusions, can be recovered in the litter under Hymenaea trees today.


11. Amber-bearing sediments in the Dominican Republic usually contain lignites (Fig. 2 [8, 9]), as do amberiferous localities elsewhere in the world (2). Cenozoic lignite deposits are not rare regionally (Figs. 1 and 2), being known from the Oligocene in Puerto Rico (30), Early to Late Miocene in Hispaniola (Fig. 2) (31), and Early to Middle Miocene in Cuba (13). Lithologic similarities in the amber-bearing Yagua Fm. in Hispaniola are the lignite-bearing Maisaire Fm. of central Haiti and the Arabos Fm. of eastern Cuba (Figs. 1 and 2), which are composed of shales, marls, and sands, containing mixed marine and brackishwater animals. Their amber potential, if any, has never been tested.

12. The Yagua Fm. localities we investigated (Colonia San Rafael, Sierra del Agua, Bayaguana, and Yagua) contain identical microfossil assemblages that correlate with the late Early Miocene Miohippus-Soritidae benthic fauna zone (13) (M. antilleana, Sorites margaritatus, and Archais angustulatus) and other formations of Early Miocene through early Middle Miocene age (Ammonia beccari parvomomota, A. b. omata, Archais trilobus, Catapsydrax haveri, Cytherella sp. aff. C. miocenica, H. occipitalis; E. antiquus, E. janetia, E. pusilla, E. sarsi, E. calcarata, E. trilobus, E. linguiformis, E. microspina, E. sp., and E. sp. aff. E. linguaformis); and the Oligocene (28, 30, 32). None of these explanations why, in the Greater Antilles, large amounts of amber occur only in restricted Miocene deposits and their preservation as amber (2, 8, 24). None of these explanations why, in the Greater Antilles, large amounts of amber occur only in restricted Miocene deposits and their preservation as amber (2, 8, 24). None of these explanations why, in the Greater Antilles, large amounts of amber occur only in restricted Miocene deposits and their preservation as amber (2, 8, 24). None of these explanations why, in the Greater Antilles, large amounts of amber occur only in restricted Miocene deposits and their preservation as amber (2, 8, 24). None of these explanations why, in the Greater Antilles, large amounts of amber occur only in restricted Miocene deposits and their preservation as amber (2, 8, 24). None of these explanations why, in the Greater Antilles, large amounts of amber occur only in restricted Miocene deposits and their preservation as amber (2, 8, 24). None of these explanations why, in the Greater Antilles, large amounts of amber occur only in restricted Miocene deposits and their preservation as amber (2, 8, 24).

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