by each Cu within the [Cu$_4$O$_2$] core. Upon inspection of the crystal structure of the fully reduced form of ascorbate oxidase (I), the three trigonally ligated Cu(I) centers (average Cu—Cu distance, 4.5 Å) appear geometrically predisposed toward accommodation of O$_2$ and formation of a [Cu$_4$O$_2$] cluster. However, no current spectroscopic studies of the metastable oxygen intermediates of multicopper oxidases and their derivatives support the existence of an intensely absorbing oxo-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 O$_2$ to form the mixed-valence bis(μ-oxo)Cu$_2$(II)Cu(II)Cu(III) species does suggest that O$_2$ bond cleavage at trinuclear Cu sites requires full 4e$^-$ reduction of O$_2$. 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.

REFERENCES AND NOTES

14. The (1R,2R)-cyclohexadienamine backbone was chosen both for its preorganized nature and its chirality. In its energetically 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 diastereomic complexes.
15. Although it has not been structurally characterized, its $^1$H NMR spectrum in the diamine ligand region is nearly identical to that of the structurally characterized trigonal planar complex [Cu$_2$(PPH$_3$)$_2$]($\text{CO}_2$), which is formed upon addition of PPh$_3$, to a solution of 1. The $N$-peracetylated analog 1, [1,1′-boc-CH$_2$(CH$_3$)$_2$(CN)]($\text{CO}_2$) [L] = N,N,N′-tetraethyl-trans-1,2-cyclohex-

22. The structure of 2 bears a strong structural resemblance to that of a previously reported macrocyclic bis(μ$_3$-hydroxo-μ$_2$-oxocopper(II)) species; however, this thermally stable cluster exhibits full threefold symmetry, has normal Cu(II)-O and Cu(II)-N distances, and carries an overall charge of +4 (+[U. Comarmond, B. Dietrich, J. Lehn, R. Louis, Chem. Commun. 1988, 74 (1985)]).
24. Formulation of 2 as a μ$_3$-hydroxo-μ$_2$-oxocopper(II) species would also be consistent with an overall charge of +3 but fails to rationalize the short Cu—O bonds exhibited by the unique Cu site.
27. Ferromagnetic interactions in Cu$_3$O$_2$ cores have been reported previously [for example, P. Chauaudri et al., Angew. Chem. Int. Ed. Engl. 24, 57 (1985)].
34. We thank the University of California Mass Spectrometry Facility (Department of Pharmaceutical Chemistry, San Francisco); Z. Hou and V. Mahe- hadar for experimental assistance; and F. Hol- lander for use of the Siemens SMART diffracto-
35. 22 April 1996; accepted 5 August 1996

Age and Paleogeographical Origin of Dominican Amber

Manuel A. Iturralde-Vinent* and R. D. E. MacPhee

The age and depositional history of Dominican amber-bearing deposits have not been well constrained. Residues of different ages exist in Hispaniola, but all of the main amberiferous deposits in the Dominican Republic (including those famous for yielding biological inclusions) were formed in a single sediment 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, sirensians, and turtles) imply that deposition occurred in a near-shore context, probably in coastal lagoons, 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 ripple marks. 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 lenslike 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 *Hymenaea* 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 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 the area of Plateau Central–San Juan. Trace amounts have also been reported from lagoonal lignite-bearing sediments of the early Middle Miocene Maissant 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 early 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 (NMR) (7). In order to derive an age-assess-

---

Fig. 1 (left). Ancestral western Greater Antilles (future Cuba and Hispaniola) in the latter half of the Early Miocene (16 to 18 million years ago). Existing coastlines (interrupted where necessary) provide orientation. SF, Septentrional fault zone; RGF, Rio Grande fault zone. (Inset) Present-day Hispaniola, showing location of the main mining districts (northern and eastern areas) and distribution of the latest Eocene through Pliocene rocks (shaded). In the early Neogene, the terranes that comprise Hispaniola were located west of their current positions, closer to present-day southeastern Cuba (note alignment of Altamira and Guantánamo rocks, latest Eocene to Oligocene in age) (14, 15, 32). Their present separation results from post-Oligocene left-lateral displacement along the SF and RGF [compare with inset 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 (23).
REFERENCES AND NOTES

1. Resinines 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 conventional reconstructed version of amber, although the relation between age and the complex diagenetic changes that yield true amber is not well understood. Dominican copal from Cotub, 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 copals and amber from biology, Dominican Republic, and the sediments in the amber can be recovered in the litters under Hymenaea trees today.


11. Amber-bearing sediments in the Dominican Republic usually contain lignites (Fig. 2) (8, 25), as do amber-bearing localities elsewhere in the Caribbean. 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). Lithologically very similar to the amber-bearing Yangua Fm in Hispaniola are the lignite-bearing Las Mañosa Fm of central Haiti and the Arabos Fm of eastern Cuba (Fig. 2) (25, 32, 33), and sands, containing mixed marine and brackish-water faunas (13, 22). Their potential, if any, has never been tested.

12. The Yanigua horizons that we investigated (Colonia San Rafael, Sierra del Agua, Bayaguana, and Yanigua) contain identical microfossil assemblages that correlate with the late Early Miocene Mioypsina-Soritiidae benthic foraminifera zone (12) (M. antillensis, Sonete marginals, and Archaias angulatus) and other forams of Early Miocene through early Middle Miocene age (Ammonia beccari parkinsonii, A. b. ornata; Amphistegina sp.; Arcaia angustata; S. marginals; Elphidium cf. A. advenum, E. concadens, A. lenta; E. psammon, E. puercolens, E. sagra; and Quinqueloculina polycera). This correspondence is in agreement with the chronology (10) from mines at Bayaguana and Laguna (Ania galerita; Bandia spp.; Catleia spp. aff. C. mariae; Cushmania howeri; Cytherea spp. aff. C. pulchra; Eucytherea spp.; Euplectiscus spp.; Paracytheridea spp.; A. angulatus; A. b. ornata; Paracytheridea spp. aff. P. hispa; Paranaensis antillensis; Floculina sp.; Paradiaphus spp.; A. antillensis; A. angulatus; A. b. ornata; Procythereis deformis; Pseudopammosicythere ex gr. vickburgi; and Uronerbeis sp. 1).


