

Lovelock's "Gaia Hypothesis" (2) and other reports that have appeared in *Science* (3, 4), these results merit further investigation. Berner and Landis indicate that during the Late Cretaceous [75 to 95 million years ago (Ma)] the O₂ content of the atmosphere was "greater than 30 percent," whereas in the Eocene-Oligocene values were 21%, as today.

Lovelock (2) asserts that "at 25% oxygen even damp twigs and grass of a rainforest would ignite," and at above 30% O₂ the danger would be even greater.

Wildfires at the Cretaceous-Tertiary (K-T) boundary (65 to 66 Ma) are suggested by Wolbach *et al.* (3) on the basis of clay samples from this boundary in Denmark, New Zealand, the North Pacific, and Spain, all of which contain graphitic carbon. These workers suggest that the amount of biomass burned to produce the graphite in the boundary clay represents 10% of present biomass of carbon, or 4% of precivilization values.

If atmospheric O₂ values in the entire Late Cretaceous (95 to 65 Ma) were greater than 25 to 30%, then widespread fires should have been common; graphitic carbon should be found throughout this time, particularly in areas of low rates of sedimentation. If this is not found, then perhaps the data of Berner and Landis (1) should be questioned. If abundant graphite is found, then perhaps the interpretation of Wolbach *et al.* (3), and for that matter, that of Alvarez *et al.* (4), should be questioned.

Alternatively, perhaps the high O₂ level found by Berner and Landis (1) and the threshold that Lovelock (2) cites for highly probable fires suggest that the globe was "poised" for massive conflagration during the Late Cretaceous. Either meteor impact-induced fires (3, 4), or some less dramatic event, might have touched off such fires. Obviously, a large meteor impact or other similar phenomenon occurring today would have grave consequences. However, one interesting negative consequence of considering the Alvarez *et al.* theory (4), the Berner and Landis (1) and Wolbach *et al.* (3) data, and the Lovelock (2) assertion together is the realization that the present time may lack one important component (O₂ > 25%) to trigger a recurrence of the events that have been hypothesized to have caused the massive extinctions at the K-T boundary.

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1. R. A. Berner and G. P. Landis, *Science* **239**, 1406 (1988).
2. See, for example, J. E. Lovelock, *Gaia: A New Look at the Earth* (Oxford Univ. Press, Oxford, 1979).
3. W. S. Wolbach, R. S. Lewis, E. Anders, *Science* **230**, 167 (1985).
4. See, for example, L. W. Alvarez, W. Alvarez, F. Asaro, H. V. Michel, *ibid.* **208**, 1095 (1980).

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Berner and Landis (1) believe that concentrations of the major gases N₂, O₂, and CO₂ have existed in amber since its formation and that the ratios of these components can be used to establish atmospheric O₂ levels during Cretaceous and Tertiary times. These conclusions require that oxygen and the other gases be stable in amber with respect both to chemical reaction and loss by diffusion over geological times of the order of millions of years. In a recent presentation at a national meeting (2), we reported much lower O₂ contents in amber and pointed out that, because the N₂/Ar ratio in amber was near the solubility ratio of these gases (3), the atmospheric ratios could not be deciphered, even if, as we then thought, the occluded gases might be as old as the enclosing amber. In the interim we have performed numerous experiments on amber which show that (i) O₂ is not chemically stable in amber, and (ii) the "diffusive residence time" of gases in amber is only a few years, so that unfortunately nothing can be learned about ancient atmospheres.

Although we have analyzed more than 20 samples of ambers, copals, gums, and resins from four continents for atmospheric gases, hydrocarbons, and isotopic composition of CO₂, we report here only those experiments dealing directly with the question of the antiquity of O₂ and other gases. First, we measured O₂ consumption by reacting freshly ground ambers and copals with O₂ in a closed system at various temperatures. Figure 1 shows the results obtained with Baltic amber at 107°C: the reaction is first order with a half-time (in our experiment; see caption) of 1 day for O₂ consumption. Similar results were obtained with amber and copal at 114°, 64°, and 23°C. At 23°C, 0.44 g of amber consumed 3.5 cc at standard temperature and pressure (STP) of O₂ from air during a period of 31 days, with production of only 0.13 cc(STP) of CO₂. These experiments, and similar results at higher temperatures, showed that less than 10% of the O₂ consumed by amber appears as CO₂, that the activation energy for O₂ consumption is about 8.8 kcal/mole (much less than expected for simple oxidation), and that the mean-life for O₂ exposed to fresh amber at room temperature is about 67 days in our experiments. Although solid free

radicals are formed in amber by grinding, these radicals are also observed in unground samples and, after grinding, they decrease in number with a half-life on the order of 1 week (4). Part of the O₂ consumption in our experiments is due to reaction with fresh surfaces; however, amber exposed to air for several months after crushing contained only small amounts of O₂ relative to N₂ and Ar that equilibrated with air by diffusion. Clearly, most of the O₂ that had diffused in to the amber fragments had been consumed within the matrix of the amber itself.

Second, measurements of N₂ and Ar concentrations in a variety of ambers show that these gases are present in two phases: as dissolved gases in the matrix of the amber, with N₂/Ar ~ 39, and in bubbles with the air ratio N₂/Ar = 83.6 (these results are derived from the relation of concentrations and ratios). The atmospheric equilibrium solubility of N₂ in amber was found to be ~56 × 10⁻³ cc(STP) (= 56 mcc) per gram, on the basis of diffusion experiments described below and on the maximum concentrations observed with the air solubility N₂/Ar ratio. The highest N₂/Ar ratios, 60.7 and 53.2, were for Baltic bone amber containing large numbers of microscopic bubbles. About one-third and one-half of the N₂ in these two samples, respectively, is dissolved in the matrix; the remainder is in bubbles that, however, contain essentially zero O₂ in crushed samples. Excluding bone and "mist-ed" or "cloudy" ambers, all of our other ambers have an N₂/Ar ratio that ranges from 39 (the approximate air solubility ratio, which is very similar to the ratio in water) to maximum values of about 45, corresponding to about 30% of the N₂ being present in bubbles. In all of these ambers and copals, including two different Canadian Cretaceous ambers and one Canadian Tertiary amber, the O₂/Ar ratio ranges from zero to a maximum of 1.1, as compared with ratios of about 21 expected for both air and solubility values (2). We also measured CO₂ concentrations after gas-chromatographic purification from hydrocarbons (such as ethane, propane, and acetylene); the mean CO₂/Ar value in our amber samples (including the Canadian ambers) was 13.6, with a range from 6.4 (Canadian Cretaceous amber) to 50.4 in an amber from Israel. We find no correlations of any of these gases that would allow us to derive an original O₂ ratio to N₂ or Ar from the O₂ and CO₂ relations with N₂ and Ar (5).

Third, we find that the gases in amber are replaced so rapidly by diffusion from the atmosphere that they cannot be of geological antiquity. We carried out experiments on crushed ambers of various origin and particle sizes that had been pumped on in vacu-

um and then "soaked" by exposure to air for times up to several months. Our initial experiments were done by "soaking" air-equilibrated amber in pure Ar at atmospheric pressure. We found that soaking particles of 1.3-mm mean diameter for 6 days reduced the N₂/Ar ratio from the initial value of 39 to 1.30. Further, soaking our smallest

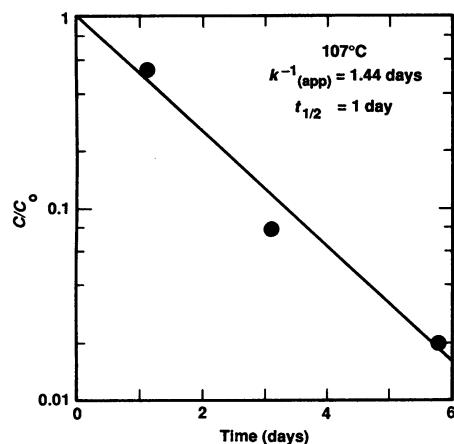


Fig. 1. O₂ consumption by freshly ground Baltic amber at 107°C in a closed system with air. The ordinate shows the concentration of O₂ in the tube versus that at the start, plotted versus time. The consumption rate is first order with a reaction (plus diffusion) "apparent" half-time of 1 day. The "apparent" rate constant $k = k^* \cdot A \cdot M$, where A is the specific area (equal to $6/\rho d$ for spheres, where ρ is the density and d is the mean diameter), and M is the mass of amber used. In these experiments d is estimated to have been ~ 50 μm , and M was 0.10 g; thus $A \cdot M \approx 116$ cm^2 and the actual rate constant $k^* \approx 1/167$ days cm^2 .

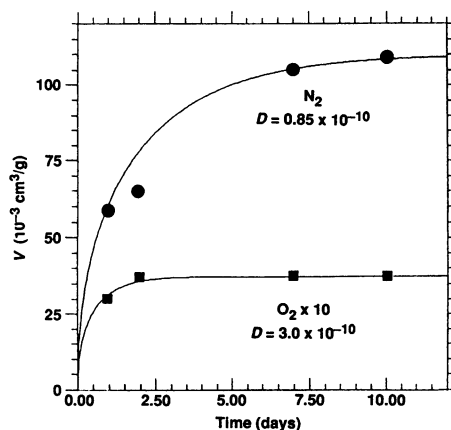


Fig. 2. Diffusion coefficients, D , in Baltic amber at room temperature. Data points are the volumes of gas (V) diffusing out of air-equilibrated crushed amber (40-80 mesh, mean diameter 0.276 mm) into an evacuated sealed glass tube, plotted as cumulative amounts versus time. The curves are calculated (6) for spherical fragments exsolving gases to vacuum. The total O₂ content [3.75×10^{-3} cc(STP)/g] is only 8.5% of that expected from the N₂ and Ar values (see text), indicating removal of O₂ within the amber by oxidation reactions. Argon data (not shown) gave a value of D equal to that for N₂: note that $D(\text{O}_2)$ is ~ 3.5 times larger than $D(\text{N}_2)$ in amber.

grains (less than 0.18 mm) in Ar for 4 days reduced the ratio from 39 to a value as low as 0.45. Soaking the amber to solubility equilibrium, followed by vacuum extraction in successive stages, provided accurate measures of the diffusivities of the gases. Thus amber fragments soaked in air for several months after crushing were used for diffusion measurements by sealing the fragments in glass tubes after rapidly pumping off the air, and then reopening the tubes periodically with a flexible vacuum tube-breaker, collecting the exsolved gases, and resealing the tube.

Figure 2 shows the results of one set of measurements on N₂ and O₂ in Baltic amber fragments over 10 days. The curves are calculated for spheres of the mean diameter exsolving gas by diffusion into vacuum (6). These fragments are heterogeneous media, as indicated by the total N₂ concentration (110 mcc/g), approximately twice the atmospheric-equilibrium solubility, which, from the correlation with the measured N₂/Ar ratio of 52.4, corresponds to half the total N₂ being present in bubbles. Note that the O₂ content, 3.75 mcc/g, is much less than the concentration expected from the N₂ and Ar contents, 44 mcc/g. That is, even after soaking in air for several months, less than 10% of the O₂ that has diffused into the amber can be re-extracted by diffusion. We interpret this as indicating that O₂ is actively consumed within the amber grains as well as on the surfaces.

Even more significantly, the experimental results in Fig. 2 show that the diffusion coefficients, on the order of $D \sim 10^{-10}$ cm^2/s , are much too high for the gases in amber to be antiques. From the diffusion equation for spheres (6) we define an e -folding "mean-diffusion time" (that is, the time for reducing the gas contents of the particles to $1/e$ of the initial values) $\tau = d^2/71.7D$, where d is the mean diameter. Thus τ is an effective time constant for considering the diffusive interchange of gases between spherical lumps of amber and the surrounding medium. For times on the order of 50×10^6 years, we require $\tau \sim 2 \times 10^8$ years in order to preserve most of the gas. For a 10-cm diameter piece of amber, we require D as low as 2×10^{-16} , about six orders of magnitude smaller than the value found for O₂ (Fig. 2, lower curve). In this case we require a ball of amber about 116 m in diameter to preserve the initial gases!

This calculation is extreme, of course, because we assumed zero gas pressures in the external medium, although this is nearly the case for amber buried in seawater for most of its existence. Nevertheless, these results show that the air in amber is very young. While the diffusion coefficients are

not yet completely understood with respect to the heterogeneous nature of the amber (7), the orders of magnitude are clear. With D for air $\sim 10^{-10}$, the air inside a 10-cm ball of amber is about 440 years old; in a 1-cm ball it is only about 4 years old. Regardless of the stability of O₂ in bubbles, gases in amber cannot tell us anything about air older than a few centuries. If amber is "forever" (8), its occluded air supply, unfortunately, is not.

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REFERENCES AND NOTES

1. R. A. Berner and G. P. Landis, *Science* **239**, 1406 (1988).
2. Y. Horibe and H. Craig, *Eos* **68**, 1513 (1987).
3. The atmospheric N₂/Ar ratio is 83.6: the ratio at atmospheric solubility equilibrium is 38 in water and, as we determined, ~ 39 in amber.
4. T. Urbanski, *Nature* **216**, 577 (1967).
5. Berner and Landis identified gases in two phases in amber, but they assumed that gases in these phases (matrix and bubbles) are completely independent entities. However, our data on diffusion rates show that gases in bubbles will be in equilibrium with gases dissolved in the matrix, barring very rapid chemical reactions. Their finding that Dominican amber bubbles contained gases at pressures of 10 atm was based on total extraction of gases from pieces in which large bubbles of measured volume were observed. However, the N₂/Ar ratios show that only about half the gas is in bubbles, and most of the gas must be in bubbles too small to measure as well as dissolved in the matrix. Since they did not report gas concentrations, we cannot explain their results in detail.
6. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford Univ. Press, London, ed. 2, 1959), case IV, p. 235.
7. For example, measurements on another piece of Baltic amber in which the N₂/Ar ratio showed that no bubbles were present gave $D(\text{N}_2) = 2 \times 10^{-10}$, whereas we would expect that with no bubbles D would be less than the value for the bubble-rich sample in Fig. 2.
8. K. Winsor, *Forever Amber* (Macmillan, New York, 1945).
9. Supported by National Science Foundation grant OCE87-18060. We thank T. Cerling, D. Burtner, and C. Nilson for assistance and discussion.

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Response: Since publication of our report (1), we have conducted more than 300 gas analyses on 15 ambers and resins that range in age from lower Cretaceous to recent time and are geographically distributed from many of the known world occurrences. We find that by our successive crush technique (1) we can usually see mixing trends between two or more compositionally different gases in amber, with one end member containing high values of O₂ and N₂, and the other end members being generally anoxic and enriched in CH₄, CO₂, H₂, and

In Reply: Is the Air in Amber Ancient?

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