Technical Comments

Is the Air in Amber Ancient?

Reports regarding ancient air "trapped" in amber have motivated an alternative analysis and explanation of the observations reported by Berner and Landis (*1*, *2*) and by Horibe and Craig (*3*). Our results indicate that, far from being a sealant, amber dissolves and transports molecules that are even larger than atmospheric components and therefore amber cannot trap ancient air in its clearly visible bubblelike inclusions.

Gravimetric absorption experiments on cryo-ground Dominican amber powder (10-μm characteristic particle diameter) were performed in our laboratories with a Cahn recording electrobalance in a high-vacuum system. This amber has been dated by nuclear magnetic resonance (NMR) analysis as varying from lower Miocene to upper Eocene (*4*). Propane was selected as the penetrant of choice because it is molecularly larger than all of the air gases and therefore the demonstration of absorption and diffusion of propane in amber would provide a critical test of the capacity of amber to transport and exchange air gases. Because propane is more condensible than the air gases, the gravimetric response is highly accurate and a single, simple experiment provides direct experimental evidence for the capacity of amber to dissolve, transport, and exchange low molecular weight atmospheric components.

These experiments revealed that Fickian diffusion with a characteristic half-time ($t_{1/2}$) on the order of 100 min controlled both the absorption and desorption of propane. The amber powder absorbed 0.89% by weight in contact with 589 torr propane pressure at 35°C, which is comparable to the sorption typically observed for propane in common synthetic polymers under similar conditions (*5*). The estimated diffusion coefficient for propane transport in the amber powder was in the range from 10^{-13} to 10^{-12} cm^2/s, also on the same order of magnitude as the propane diffusivity determined in conventional polymeric glasses (*6*). These observations complement reports that amber is an amorphous polymeric glass with mechanical, dielectric, and thermal features common to amorphous polymeric glasses as a class of materials (7). These composite results suggest that the values of component diffusivities and solubilities determined in common glassy polymers provide reasonable estimates of the diffusion and solubility coefficients for the respective penetrants in amber. Most important, these results indicate that amber cannot trap gases in bubblelike inclusions.

Recognizing that the diffusivity value determined from a sorption experiment in cryo-ground powders is compromised by the distributed particle size of the powdered sample, we performed complementary absorption experiments on uniform ultramicrotomed amber microflakes (1 μm by 3 mm by 3 mm) with a McBain balance in a high-vacuum system. The detailed results of the absorption experiments performed with these uniform, 1-μm-thick microflakes under otherwise comparable conditions are presented in Fig. 1. The kinetic response is identical in form to ideal diffusion kinetics predicted for Fickian absorption in thin platelets, whereby the amount absorbed varies linearly with $t^{1/2}$ over the first half of the sorption process and a clearly defined equilibrium value is achieved at relatively long times.

The results with the microflake sample confirmed the qualitative and quantitative conclusions revealed by the experiments with the cryo-ground samples. Specifically, the equilibrium absorption in the microflakes was 0.80, which is similar to the absorption observed in the cryo-ground sample. The similarity in amounts of sorption observed in the two samples, which differ significantly in surface area to mass ratio, geometric form, and characteristic dimensions, confirmed that diffusive absorption rather than surface adsorption controls the observed mass uptake. This conclusion is further supported by the observed kinetics. The marked difference in geometric form and characteristic dimension between the samples resulted in a large difference in diffusion half-times, $t_{1/2}$. The $t_{1/2}$ values are 160 and 15 min for the powder and flakes, respectively. These very different half-times (resulting from the different geometries and characteristic dimensions between the samples) correspond, however, to very similar diffusion coefficients of 8×10^{-13} and 5×10^{-13} cm^2/s for the powder and flake samples, respectively.

The half-time for diffusive absorption or desorption of components into or from slabs and spheres is given by $t_{1/2} = (0.049\ l^2/D)$ and $t_{1/2} = (0.00766\ d^2/D)$, respectively, where D is the diffusion coefficient, d is the diameter of the sphere, and l is the thickness of the slab (*6*, *8*). Diffusion coefficients for small molecules in amorphous, polymeric glasses decrease by more than ten orders of magnitude as the molecular size of the penetrant increases from helium to hexane (*6*). In that regard, the diffusion coefficients for O_2 and N_2 are typically four orders of magnitude higher than the diffusivities characterizing propane transport (*6*). If we assume that the diffusion coefficients for O_2 and N_2 are on the order of 10^{-8} cm^2/s, as commonly determined in glassy polymers (*6*), $t_{1/2}$ for desorption from, for example, a chunk 2 cm in diameter would be ~35 days. Therefore, a negligible fraction of O_2 or N_2 would be released from the matrix during "5 to 8 hours" (*1*) of degassing as performed by Berner and Landis. However, once the sample is crushed under vacuum, slivers with a characteristic dimension of 10 μm, for example, would require less than 5 s to release half of the O_2 and N_2 dissolved in the amber matrix.

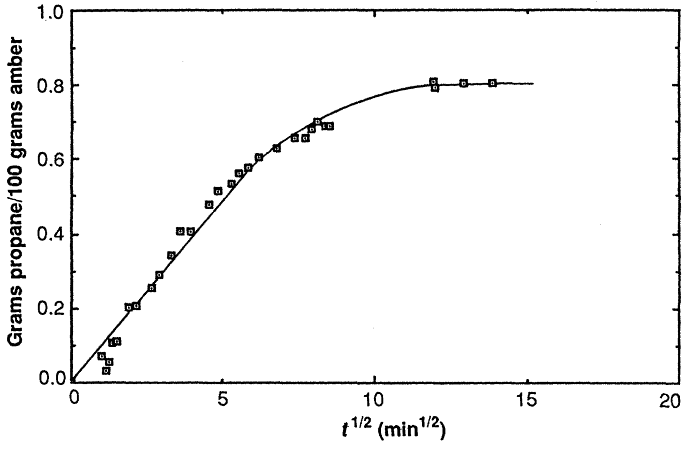

Fig. 1. The experimentally determined diffusion kinetics of propane sorbed in 1-μm-thick Dominican amber microflakes at 35°C. The amber was in contact with 630 torr propane throughout the experiment after degassing of the amber to a constant weight in high vacuum. The line represents a plot of the predicted Fickian diffusion kinetics with a diffusion coefficient of 5×10^{-13} cm^2/s and an equilibrium absorption of 0.80% by weight.

Berner and Landis state explicitly that during the last stages of crushing, small particles are formed that release "dissolved matrix gas." The only difference between the original amber samples and the fragments that result from crushing is size, per se. The characteristic diffusion times, which vary with the square of the characteristic dimension of the sample, revealed that amber fragments can release matrix gas in seconds and that amber chunks found in nature exchange atmospheric components over the course of months. Once Berner and Landis acknowledged that the latter crushes release dissolved matrix gas, they implicitly reveal that diffusion controls transport in amber and, in turn, that amber cannot trap "ancient air" in bubblelike inclusions.

Horibe and Craig (*3*) observed that ball-milled Baltic amber released approximately 0.07 cc(STP)/g (cubic centimeter at standard temperature and pressure per gram) of noncondensible "air" gases. Although they explicitly consider these gases to be "trapped in occluded bubbles," their observed value of 0.07 cc(STP)/g is similar to the dissolved capacity of air amber calculated to be 0.06 cc (STP)/g. This estimate is based on the simple dissolution of O_2 and N_2 from air as we now know it, without taking into account the absorption of Ar and CO_2 that would, of course, complement the absorption of O_2 and N_2 from air. The predictions are made with the use of solubility coefficients for O_2 and N_2 in amorphous hydrocarbon polymers, which are on the order of 0.1 and 0.05 cc(STP)/cc atm) for O_2 and N_2, respectively (*5*).

The calculated value of 0.06 cc(STP) "air" gases per gram of amber is larger than the largest amount of gas released in the experiments by Berner and Landis (*2*). They reported that a maximum of 10^{-7} mole of gas was released per gram of amber, which corresponds to only 0.002 cc(STP)/g. This difference suggests that the larger particles in the particular particle size distribution resulting from their crushing protocol did not release all of the dissolved gas during the arbitrary experimental time scale for crushing and gas collection.

Berner and Landis calculated a bubble pressure of 10 atm by assuming that all of the gas released upon crushing was previously trapped in the known volume of bubblelike inclusions and that none of the gas released had been previously dissolved in the amber. Their conclusion that amber can maintain bubbles for thousands of millennia at superatmospheric pressures depends on their explicit assumption that the gas collected from the amber was exclusively recovered from bubbles. Clearly, as recognized by Berner and Landis, the dissolved matrix gas is "much more abundant," and very few small amber particles produced by the crushing could desorb the large amount of gas that was detected experimentally and that led to the calculation of a superatmospheric bubble pressure.

For example, one amber microsliver, 10 μm by 200 μm by 200 μm equilibrated with modern air, would liberate all of the previously dissolved gases into high vacuum in a matter of seconds. This single particle would initially contain and therefore release more than the 10^{-12} mole of gas detected in each of the gentle crush experiments of Berner and Landis. Only 90 of these microslivers would release 10^{-10} mole of air gases, which is the largest amount of gas detected by Berner and Landis in a single gentle crush. These 90 microfragments would weigh only 0.00004 g. These composite calculations strongly suggest that the experiments by Berner and Landis are significantly biased by gas that was originally dissolved. The bubbles therefore do not contain gases at superatmospheric pressures but, rather, most of the gas collected from the Dominican 2 sample was, more likely, initially dissolved in the amber matrix.

At equilibrium, the bubblelike inclusions should contain gas with a composition identical to that of the surrounding atmosphere. In marked contrast, the composition of the more abundant, dissolved matrix gas should be significantly different and should be determined by component partitioning between air and amber. The ratio of solubility coefficients describing the preferential absorption of O_2 relative to N_2 in polymers is typically on the order of 2.0 (*5*). If we assume a ratio of 2.0 for the O_2 to N_2 solubility coefficients in amber and that the amber had been in contact with air as we know it, the ratio of N_2 to O_2 concentrations, dissolved in the amber matrix and liberated upon crushing, would be 1.9, corresponding to an O_2 concentration of 35%.

The experiment with Cretaceous amber represented by sample III-A from table 2 of (*2*), not confounded by significant conversion of O_2 to CO_2, revealed an N_2 to O_2 ratio of 1.9 and an O_2 concentration of 32.6%, virtually identical to the respective values predicted by equilibrium partitioning of the air gases in the amber matrix. Interpretation of the experiments involving significant CO_2 concentrations require the rather arbitrary assumptions regarding complex chemistry, biochemistry, microbial activity, and specific stoichiometry that Berner and Landis adopt in their arguments. Corollary assumptions regarding the details of sample history and subsequent storage conditions become critically important as well to explain the experiments involving CO_2.

In summary, we conclude that the results reported to date regarding air in amber (*1–3*) are explained directly by the equilibrium, kinetic, and geometric factors controlling the transport and partitioning of atmospheric components in amber without changing previously held views of paleontolgy, geology, and atmospheric science. Although we have estimated and defended specific, quantitative values for the diffusion coefficients of the air gasses in amber, our fundamental conclusion that amber cannot trap ancient air would be valid even if our values are in error by many orders of magnitude.

HAROLD B. HOPFENBERG
LEONORE C. WITCHEY
Department of Chemical Engineering,
North Carolina State University,
Raleigh, NC 27695-7905
GEORGE O. POINAR, JR.
Department of Entomology and Parasitology,
University of California,
Berkeley, CA 94720

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Berner and Landis (*1*), in their study of gases in amber, write that "After discounting the possibility that the major gases N_2, O_2, and CO_2 underwent appreciable diffusion and diagenetic exchange with their surroundings or reaction with the amber, it has been concluded that in primary bubbles . . . these gases represent mainly original ancient air modified by the aerobic respiration of microorganisms." Their report shows that the authors discount two major sources of interference—diffusion and reaction with the matrix—solely by their interpretation of their own data.

On the topic of diffusion, Baltic amber that is rendered opaque by the presence of microscopic air bubbles (milky amber or bone amber) can be made transparent, as well as dyed, by heating it in a suitable medium. The ancient Romans used the fat of a suckling pig (*2*). The technique has been thoroughly investigated in modern times by Dahms (*3*) who recommends rapeseed oil. The efficacy of this "clarification" rests on filling the air bubbles with a liquid that has the same refractive index as the amber and thus depends on thorough penetration of the matrix by the oil or fat. Incidentally, the German amber researchers of the 19th and early 20th centuries were unanimous in their view that the bubbles originally contained water or "cellular fluid" derived from the source tree. When this water was lost by evaporation(!), it was *subsequently* replaced by air. In the first attempt to determine the contents of amber bubbles by crushing the matrix in a closed system, Plonait (*4*) found water rather than air. In brief, there is considerable evidence that at least some fossil resins, for example Baltic amber, are permeable to liquids and hence also to gases. It therefore seems inadvisable to assume the impermeability of amber axiomatically or to infer it from indirect evidence: it should be tested by direct measurements for *each* of the fossil resins under investigation.

Berner and Landis did consider that some of their "low values of O_2 and high values of CO_2 . . . represented reaction between original-air-entrapped O_2 and the amber," but "abandon[ed] this hypothesis" when they found "the highest O_2 contents" in "the oldest samples." However, the oxidizability of fossil resins by atmospheric O_2 is a firmly established fact. Every museum curator knows that the smooth surface of an amber object is disfigured by the attack of air in a matter of years. In archeological amber artifacts deposited in aerobic environments (such as Etruscan chamber tombs), this oxidation produces a progressive "weathering crust" that eventually destroys the find. These changes can be followed quantitatively by infrared spectroscopy (*5*). The oxidative effect of air on the interior surfaces of enclosed bubbles has been observed by microscopy (*6*). Some or all of the O_2 in contact with a terpenoid resin will be consumed in a relatively short time. In accordance with this expectation, Horibe and Craig have found (*7*) severe depletion of O_2 in the air contained in amber. They confirmed the oxidizability of amber by experiment and found that O_2 exposed to amber in the laboratory disappeared within a few days at 107°C, whereas at room temperature the half-life of O_2 was about 1 month.

One of the most significant measurements Berner and Landis made was that the gases released on crushing had ten times the calculated volume of the primary bubbles. They concluded that the average pressure in these bubbles was 10 atm, which resulted from compression of the amber during burial in the sediment. This conclusion is the least likely one that can be drawn from this severe discrepancy of volumes. It requires that fossil resins can contain gases at pressures of about 150 psi for millions of years. Moreover, the compression of a spherical bubble to one-tenth of its volume *while it retains its sphericity* would require the uniform application of pressure from all directions upon a perfectly isotropic matrix. Pressure caused by an overburden is largely unidirectional and flattens spherical bubbles into ellipsoids, a shape that is encountered in Baltic amber. Pressure is more commonly produced by the thermal expansion of the gaseous or liquid contents of a bubble, which leads to characteristic dendritic shapes. The most obvious interpretation of the volume of the bubbles coming to only 10% of the gases analyzed is that only 10% of the gases analyzed were derived from the bubbles.

What is the origin of the other 90% of the gases? The extensive, although widely scattered, earlier literature on amber research provides a clue. Berner and Landis assume that the gases exist (i) as such in "primary" air bubbles, (ii) as "irregular cavities in dessication [sic] cracks and secondary fractures," and (iii) as matrix gas, that is, "dissolved in the amber or dispersed as dense clusters of tiny submicroscopic bubbles (milky amber)." [There are two problems with their definition of milky amber: (i) opaque amber, known as bone amber rather than "milky amber," contains microscopic, not *sub*microscopic bubbles; they are readily seen under moderate magnification and measure from 0.8 to 4 μm in diameter (*3*). (ii) Berner and Landis did not analyze bone amber, so their "matrix gas" would have to have been derived entirely from dissolved gases.] An unstated but critical assumption is that the progressive crushing of the amber is a purely physical process that merely breaks an inert matrix to release previously existing gases. Berner and Landis do not acknowledge that the fracture of a polymeric organic substance is, in fact, a chemical reaction. As first shown by Lagercrantz and Yhland (*8*), by means of electron spin resonance (ESR), the breaking of a piece of amber (as well as irradiation with a xenon lamp) produces free radicals by the homolytic cleavage of carbon-carbon and carbon-hydrogen bonds. This work has been elaborated by Urbanski (*9*), who found that it also applied to cellulose, polyvinyl chloride, and charcoal. Predating these results were those of Staudinger's laboratory (*10*) that there is a reduction of the molecular weight when polystyrene, cellulose, or nitrocellulose is ground; nitrocellulose also suffers a loss of nitro groups. The ESR signal of freshly ground amber decays slowly, indicating that the free radicals are stabilized by secondary processes, which are likely to produce hydrogen, methane, and the "multitude of minor organic gases" that Berner and Landis mention but did not analyze. The principal reaction of a carboxylate radical is loss of CO_2 as in the Kolbe electrolysis (*11*). Thus the CO_2 observed may be derived from a *chemical* reaction of the matrix and cannot be simply added to the O_2 on the assumption that it must have been derived from matrix gas. Analogous decay of hydroperoxide radicals with release of O_2 is possible, but has not, to my knowledge, been established.

The chemical reactions brought about by crushing or grinding of a polymeric fossil resin must, of course, vary with the chemical composition of the resin, as must its oxidizability and its permeability. The term "amber" is applied to a wide range of materials with remarkably diverse botanical origins and dramatically different chemical structures. Some New Jersey "amber" is almost pure polystyrene, evidently derived from a *Liquidambar* species (*12*). Mexican and Dominican "amber" are products of the leguminous tree *Hymenaea courbaril* and have labdane carbon skeletons. Baltic amber or succinite is now known to be a copolymer of cummunic acid and communol, as is the kauri copal of Southeast Asia (*13*). Still other, nonpolymeric fossil resins are derived from pines. Any serious work on what is much too loosely called "amber" must take into consideration the nature of the particular resin studied. The variation of analytical data given by Berner and Landis for cedarite (chemawinite) from Canada, Dominican "amber," and Baltic succinite rather nicely illustrate this point: it is far more likely due to differences in the chemical composition of these resins than to differences in their ages. Any inferences about the composition of the earth's atmosphere during the Late Cretaceous and Early Tertiary must be considered premature.

CURT W. BECK
Amber Research Laboratory,
Department of Chemistry,
Vassar College, Poughkeepsie, NY 12601

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The report by Berner and Landis (*1*) on analyses of gases within fossil ambers presents results that are both interesting and enigmatic. When considered along with

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 O_2 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% O_2 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 O_2 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 O_2 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 (O_2 > 25%) to trigger a recurrence of the events that have been hypothesized to have caused the massive extinctions at the K-T boundary.

KEITH E. CHAVE
Department of Oceanography, and
Hawaii Institute of Geophysics,
University of Hawaii,
Honolulu, HI 96822
STEPHEN V. SMITH
Hawaii Institute of Marine Biology,
University of Hawaii

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Berner and Landis (*1*) believe that concentrations of the major gases N_2, O_2, and CO_2 have existed in amber since its formation and that the ratios of these components can be used to establish atmospheric O_2 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 O_2 contents in amber and pointed out that, because the N_2/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) O_2 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 CO_2, we report here only those experiments dealing directly with the question of the antiquity of O_2 and other gases. First, we measured O_2 consumption by reacting freshly ground ambers and copals with O_2 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 O_2 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 O_2 from air during a period of 31 days, with production of only 0.13 cc(STP) of CO_2. These experiments, and similar results at higher temperatures, showed that less than 10% of the O_2 consumed by amber appears as CO_2, that the activation energy for O_2 consumption is about 8.8 kcal/mole (much less than expected for simple oxidation), and that the mean-life for O_2 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 O_2 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 O_2 relative to N_2 and Ar that equilibrated with air by diffusion. Clearly, most of the O_2 that had diffused in to the amber fragments had been consumed within the matrix of the amber itself.

Second, measurements of N_2 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 $N_2/Ar \sim 39$, and in bubbles with the air ratio $N_2/Ar = 83.6$ (these results are derived from the relation of concentrations and ratios). The atmospheric equilibrium solubility of N_2 in amber was found to be $\sim 56 \times 10^{-3}$ cc(STP) (= 56 mcc) per gram, on the basis of diffusion experiments described below and on the maximum concentrations observed with the air solubility N_2/Ar ratio. The highest N_2/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 N_2 in these two samples, respectively, is dissolved in the matrix; the remainder is in bubbles that, however, contain essentially zero O_2 in crushed samples. Excluding bone and "misted" or "cloudy" ambers, all of our other ambers have an N_2/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 N_2 being present in bubbles. In all of these ambers and copals, including two different Canadian Cretaceous ambers and one Canadian Tertiary amber, the O_2/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 CO_2 concentrations after gas-chromatographic purification from hydrocarbons (such as ethane, propane, and acetylene); the mean CO_2/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 O_2 ratio to N_2 or Ar from the O_2 and CO_2 relations with N_2 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 vacuum 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 N_2/Ar ratio from the initial value of 39 to 1.30. Further, soaking our smallest 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.

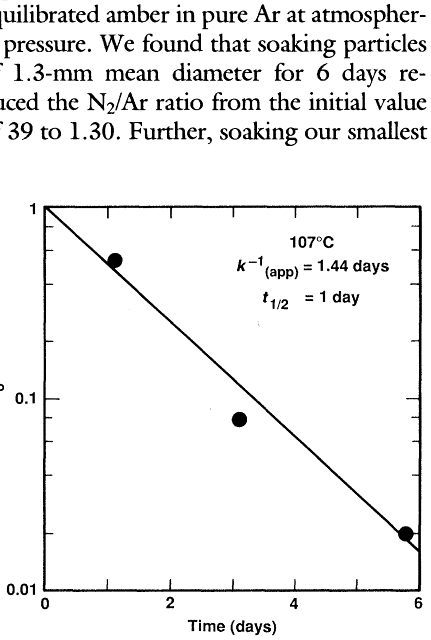

Fig. 1. O_2 consumption by freshly ground Baltic amber at 107°C in a closed system with air. The ordinate shows the concentration of O_2 in the tube versus that at the start, plotted versus time. The consumption rate is first order with a reaction (plus diffusion) "apparent" half-time of 1 day. The "apparent" 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.

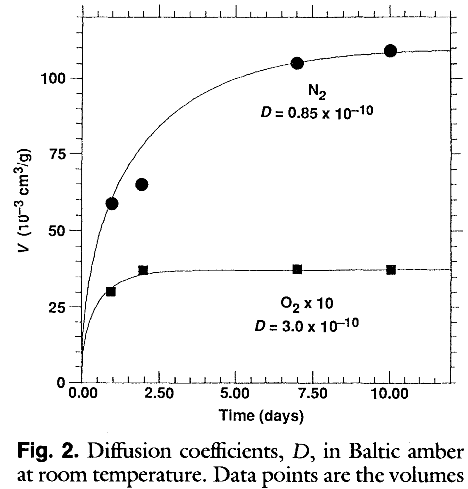

Fig. 2. Diffusion coefficients, D, in Baltic amber at room temperature. Data points are the volumes of gas (V) diffusing out of air-equilibrated crushed amber (40-80 mesh, mean diameter 0.276 mm) into an evacuated sealed glass tube, plotted as cumulative amounts versus time. The curves are calculated (*6*) for spherical fragments exsolving gases to vacuum. The total O_2 content [3.75×10^{-3} cc(STP)/g] is only 8.5% of that expected from the N_2 and Ar values (see text), indicating removal of O_2 within the amber by oxidation reactions. Argon data (not shown) gave a value of D equal to that for N_2: note that $D(O_2)$ is ~ 3.5 times larger than $D(N_2)$ in amber.

Figure 2 shows the results of one set of measurements on N_2 and O_2 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 N_2 concentration (110 mcc/g), approximately twice the atmospheric-equilibrium solubility, which, from the correlation with the measured N_2/Ar ratio of 52.4, corresponds to half the total N_2 being present in bubbles. Note that the O_2 content, 3.75 mcc/g, is much less than the concentration expected from the N_2 and Ar contents, 44 mcc/g. That is, even after soaking in air for several months, *less than 10%* of the O_2 that has diffused into the amber can be re-extracted by diffusion. We interpret this as indicating that O_2 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 that the value found for O_2 (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 O_2 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.

Y. HORIBE*
H. CRAIG
Scripps Institution of Oceanography,
University of California at San Diego,
La Jolla, CA 92093

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 N_2/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 N_2/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 N_2/Ar ratio showed that no bubbles were present gave D (N_2) = 2×10^{-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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*Present address: Department of Marine Science, Tokai University, Shizuoka, Japan.

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 O_2 and N_2, and the other end members being generally anoxic and enriched in CH_4, CO_2, H_2, and