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 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.

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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 $\mu$m 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 hydro-

peroxide 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.

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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

# Science

**In Reply: Is the Air in Amber Ancient?**

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