

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- μ m 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 condensable 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} cm²/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 μ m 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- μ m-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.

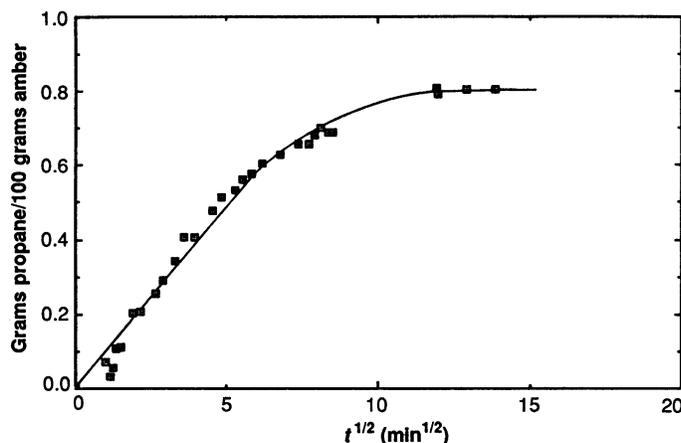
The results with the microflake sample confirmed the qualitative and quantitative

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} cm²/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 O₂ and N₂ are typically four orders of magnitude higher than the diffusivities characterizing propane transport (6). If we assume that the diffusion coefficients for O₂ and N₂ are on the order of 10^{-8} cm²/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 O₂ or N₂ 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 μ m, for example, would require less than 5 s to release half of the O₂ and N₂ dissolved in the amber matrix.

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

Fig. 1. The experimentally determined diffusion kinetics of propane sorbed in 1- μ m-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} cm²/s and an equilibrium absorption of 0.80% by weight.



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 noncondensable "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 O₂ and N₂ from air as we now know it, without taking into account the absorption of Ar and CO₂ that would, of course, complement the absorption of O₂ and N₂ from air. The predictions are made with the use of solubility coefficients for O₂ and N₂ in amorphous hydrocarbon polymers, which are on the order of 0.1 and 0.05 cc(STP)/cc atm for O₂ and N₂, 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 O₂ relative to N₂ in polymers is typically on the order of 2.0 (5). If we assume a ratio of 2.0 for the O₂ to N₂ solubility coefficients in amber and that the amber had been in contact with air as we know it, the ratio of N₂ to O₂ concentrations, dissolved in the amber matrix and liberated upon crushing, would be 1.9, corresponding to an O₂ concentration of 35%.

The experiment with Cretaceous amber represented by sample III-A from table 2 of (2), not confounded by significant conversion of O₂ to CO₂, revealed an N₂ to O₂ ratio of 1.9 and an O₂ 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 CO₂ 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 CO₂.

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 paleontology, 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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 9. We thank John Urquhart for calling to our attention the need to test the assumption that amber quantitatively entraps atmospheric gases.
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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 N₂, O₂, and CO₂ 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

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