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CHEMICAL ANALYSIS OF GASEOUS BUBBLE INCLUSIONS IN AMBER: THE COMPOSITION OF ANCIENT AIR?

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ABSTRACT. It has been suggested that gas bubbles enclosed in fossil amber may represent ancient air trapped at the time the original resin was exuded from its host tree. Through the use of quadrupole mass spectrometry, we have analyzed gaseous inclusions in two separate samples of amber from the Dominican Republic whose age is thought to be Oligocene or Miocene. The resulting data are compared with results for Baltic amber (Eocene) taken from the Russian literature, with published analyses of gases in shallowly-buried sediments, and with the composition of modern air. After consideration of a number of possible explanations, it is concluded that the gaseous inclusions represent ancient air modified by (1) the partial reaction of O_2 with amber to produce CO_2, (2) the addition of small amounts of hydrogen gas and hydrocarbons from amber decomposition, and, in the case of the Dominican amber, (3) the addition of excess argon during burial of the amber in sediments. The data suggest that the Eocene and Oligocene atmospheres, in terms of the principal gases N_2, O_2, and Ar, were not appreciably different in composition from that of today.

INTRODUCTION

It is well known that amber, or fossilized resin, is an excellent preservative of fossil insects and spores. Even its own chemical composition bears paleobotanical information (Langenheim, 1969; Beck, 1986). A common component of amber which has received much less attention, by contrast, is gaseous bubble inclusions. Roedder (1984), after considering several possible origins, suggested that these gas bubbles may represent ancient air trapped at the time the resin was originally exuded from its host tree, by analogy with present-day resinous secretions which are known to contain abundant gaseous inclusions. Roedder also suggested that the air might be mixed with volatile components of the amber. In the present paper, data are presented for the analysis of gaseous inclusion in two separate samples of amber from the Dominican Republic whose age is uncertain but thought to be either early Miocene-Oligocene or late Eocene (Wilson, 1985; Hueber and Langenheim, 1986). The data along with additional data from the literature on Eocene amber suggest that the Eocene and Oligocene atmospheres, in terms of the principal gases N_2, O_2, and Ar, were not appreciably different in composition from that of today.

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METHODS

The Dominican amber samples consisted of a number of centimeter-sized semi-transparent chunks provided by Dr. Jean Langenheim and a large (4–5 cm diam), round, transparent amber sample containing a few large millimeter-sized bubble inclusions and no included fossil material. The large transparent sample was purchased from the Amber Co. of Los Angeles. To isolate the gas bubbles for analysis, sections of each amber were cut into 1.5 to 2.0 cm chunks using a thin-blade diamond saw and water coolant. The amber was placed in stainless steel tubes fitted with a high vacuum valve at one end and welded shut at the other and then evacuated on the vacuum inlet to the mass spectrometer for 5 to 8 hrs until further outgassing stopped at the ultimate lowest value obtainable (approx 2×10^{-6} Torr pressure). This was done to remove all traces of modern air which could have entered cracks in the amber or been adsorbed on its surface. After evacuation and removal of modern air from the stainless steel crush tubes, the valves were closed, the tubes removed from the vacuum inlet, and the tubes containing the amber crushed while still under vacuum by using a 10-ton hydraulic press. The tubes were returned to the inlet and the gases, liberated from the amber bubbles, transferred to a quadruple mass spectrometer. The mass spectrometer was operated at approx 4×10^{-9} Torr during gas analysis. Better resolution of gases on the mass spectrometer and, thus, more accurate results were obtained when gas samples were separated cryogenically first at liquid nitrogen (−195°C) and then at solid carbon dioxide (−78°C) temperatures before analysis in the mass spectrometer. This resulted in N_2, O_2, H_2, and Ar in one fraction, CO_2 and light hydrocarbons in the second, and H_2O and heavy hydrocarbons in a third fraction. Analytical data for the various cryogenically separated gas fractions were later combined by knowing the pressure, temperature, and volume of the gas mixture in the inlet. Cryogenic separation was especially important so as to remove the diluting effect of H_2O which is a major component in all samples. (The water was seen under the microscope to be present as a separate liquid phase in several bubbles, but, from the analyses, far too little was present to supply appreciable amounts of dissolved gases.)

To convert ion intensity data from the mass spectrometer into gas data, the following parameters were applied to each gas in an M × N matrix solution: ionization fragmentation, gas sensitivity, and kinetic factors for adsorption/desorption of gas on vacuum surfaces. Detection limits by this method are about 10 ppm (molar) in a gas mixture (Landis and others, 1987), and analytical error was about ±2 percent of the amount present. Total gas masses were large and are given in the footnote to table 1; masses of background gases and those released from a blank stainless steel crush were negligible by comparison. The instrumental minimum detectable partial pressure (ion current) was 8×10^{-15} mbar, with a partial pressure sensitivity of 8×10^{-9} (8ppb).

Because of the inability completely to separate intensity contributions to the measured mass (AMU's) from more than one gas in the

TABLE 1

Chemical composition of gaseous inclusions in Dominican and Baltic amber compared to modern air and gases collected from shallowly-buried sediments. Values represent volume (mole) percent on a water-free basis.

Gas	Modern air	Dominican amber*		Baltic amber**			Glacial† drift	Marine†† sediment
		1	2	A	B	C		
N_2	78.1	79.0	84.3	92.1	88.1	86.5	12	14
O_2	20.9	3.5	0.8	0.5	0.5	0.6	0	0
Ar	0.9	1.4	1.9	1.2	1.2	1.1	0.2	0.4
CO_2	<0.1	12.5	12.1	3.6	10.2	5.1	2	<55
CH_4	$\ll 0.1$	0	0	0	0	0	86	>30
H_2	$\ll 0.1$	2.8	0.8	2.4	0	6.5	—	$\ll 0.1$
N_2/Ar	84	56	44	80	73	79	58 ± 10	35 ± 7

*Additional analyses: Dominican 1, 0.8% organic gases dominated by n-butane, 5.7×10^{-6} moles total gas; Dominican 2, 0.2% organic gases, 3.1×10^{-6} moles total gas.

**Data from Nesmelova and Khabakov (1967).

†Mean of 5 samples from Wasserburg, Mazor, and Zartman (1963).

††Mean of 32 samples of dissolved gases in organic-rich mud from Martens and Berner (1977) and Berner and others (1978). Inequality signs for CO_2 and CH_4 for depths below 1.5 m.

mixture, values for the rarer isotopes contained in N_2, O_2, Ar, and CO_2 (for example, ^{15}N, ^{18}O, ^{36}Ar, and ^{13}C) could not be determined with sufficient accuracy. It is hoped that in our future work this problem can be surmounted.

RESULTS

Results of our analyses are summarized in table 1. Also shown in the table are the gas analyses of Nesmelova and Khabakov (1967) for milky-white Baltic amber of Eocene age. (The milky-white color of the amber is due to inclusions of millions of microscopic gas bubbles which make the amber opaque.) Included in the table for reference are values for modern air and mean values for some shallowly buried sediments, summarizing five gas analyses for glacial drift (Wasserburg, Mazor, and Zartman, 1963) and 32 analyses for dissolved gases in modern organic-rich sediments (Martens and Berner, 1977; Berner and others, 1978). One can see, first of all, that gases trapped in amber differ considerably in composition from those found in shallowly-buried sediments especially with regard to methane content. This is important. It means that both the Dominican and the Baltic amber, which were buried in sediments for millions of years, have not readily exchanged gas with their surroundings and simply acquired the natural gas composition of the sediments. (More deeply buried sediment gases differ even more in composition from those in amber—for example, see Wasserburg, Mazor, and Zartman, 1963.)

On the other hand, there are some important differences between the amber gases and modern air. The main difference is much higher

CO_2 and much lower O_2 in the amber gases. This difference is most easily explained in terms of reaction of O_2 originally present in the amber bubbles with the amber itself (or with its breakdown products) with the production of CO_2. If one assumes that the originally included air contained CO_2 at levels less than 1 percent (which is necessary to preclude ridiculously high greenhouse temperatures for the Eocene-Oligocene Earth), then one can roughly back-calculate original O_2 percentages. Exact values depend upon O_2/CO_2 stoichiometry which depends, in turn, upon what organic compounds were oxidized. (Also, some of the CO_2 could have arisen by simple decarboxylation reactions but not with the production of gaseous hydrocarbons because concentrations of gaseous hydrocarbons were found to be far less than that of CO_2 in all samples. Furthermore, dehydrogenation to produce CO_2 plus H_2 cannot account for the CO_2 because of a relative lack of combined oxygen in the amber.)

The simplest approach in calculating original O_2 levels is to assume that amber, whose average elemental composition (Trofimov, 1974) can be represented as $C_9H_{13}O$, reacted with O_2 to produce CO_2 as follows:

$$4C_9H_{13}O + 47O_2 \rightarrow 36CO_2 + 26H_2O$$

(This reaction represents the sum of all intermediate reactions involving production of H_2, hydrocarbons, et cetera and subsequent oxidation.) Using $\Delta O_2/\Delta CO_2 = 1.31$ for this reaction, we can back-calculate, from measured CO_2 concentrations, original O_2 values for the amber gases:

Dominican	1	19.2 percent
Dominican	2	16.1 percent
Baltic	A	5.2 percent
Baltic	B	13.5 percent
Baltic	C	7.2 percent

These are only very crude values because of a lack of knowledge of the correct O_2/CO_2 stoichiometry: nevertheless, the Dominican results suggest the presence of appreciable O_2 in the atmosphere, approaching present day values, during Eocene-Oligocene time.

By visual inspection, the individual inclusions in our amber samples ranged from <0.01 to 2.0 mm in diameter, with typical gas contents of 85 to 100 volume percent (the remainder being liquid water). Considering the number and size of opened gaseous inclusions, a simple P–V–T calculation, using the total gas masses given in table 1, indicates that at least some of the opened gas bubbles were "overpressured"; that is, trapped gases were appreciably above atmospheric pressure. This is especially true of the large transparent sample which contained only a few large bubbles which, in aggregate, were calculated to be under 10 to 20 bars of pressure. Similar to fluid inclusions in salt (Roedder, 1984), the gaseous inclusions in amber apparently coalesced and equilibrated with the increased pressures of burial.

Since the composition of the amber gases is somewhat similar to present-day air, the possibility arises that what we are seeing in the amber is not ancient air at all but modern air that has diffused into the amber since erosion of the containing beds and exposure of the amber to the present atmosphere. This is unlikely for a number of reasons. First of all, the presence of excess pressure in the bubbles suggests maintenance of the high pressures generated during sediment burial and lack of exchange, and accompanying pressure drop, with present-day air. Secondly, diffusion of gases through the amber, so as to exchange with its environment, would be expected to be greater during the earlier history of the amber as the original resin hardened. This would be expected to result, if there were exchange, in an alteration of composition toward the gaseous composition of the early surrounding medium, or, in other words, the enclosing sediment. Later exchange with modern air would be expected to be less both because of a tighter amber and, more importantly, because of a much shorter period of exposure to modern air, after exhumation, than to sediment gas during millions of years of burial. Absence of methane in the amber indicates minimal exchange with sediment gas during burial and, because of hardening, even less exchange later during exposure to the modern atmosphere. Third, for the Dominican samples, all precautions were taken to remove modern air from the samples by pumping under vacuum for many hours prior to crushing and removal of the sealed-off bubbles. Fourth, similar results were found for Dominican amber sample 2 which consists of a few large (millimeter sized) bubbles separated from the outer surface of the amber by more than 1 cm of solid clear amber and for the milky Baltic amber which consists of millions of microscopic bubbles. One would expect greater exchange with, and similarity in composition to, the atmosphere for the Baltic amber because of its much more porous nature. But this was not found. Finally, appreciable (up to a few percent) H_2 gas was found in all but one amber sample and most likely represents some dehydrogenation of the amber. This H_2 would be expected to be the most easily exchanged gas with its environment because of its high diffusibility through solids. Yet it has (at least partly) been retained in the amber indicating a lack of total equilibration with modern air.

A puzzling observation remains, however. It is that the N_2/Ar ratio for the Dominican amber is considerably lower than that for modern air, whereas the ratio for the Baltic amber is close to that of air. Due to its origin from slow continual outgassing (Holland, 1984) the concentration of Ar in the atmosphere should not have varied appreciably during the past few tens of millions of years and certainly hasn't decreased with time. Thus, the lower N_2/Ar ratio for the Dominican amber cannot be due to higher atmospheric Ar at its time of formation. Also, the difference in N_2/Ar ratio between the Dominican and Baltic ambers cannot be ascribed to historical change in atmospheric N_2 as judged by the residence time of atmospheric N_2. The most reasonable explanation is that the Dominican amber during burial selectively picked up excess argon from sediment gases, which are similarly enriched in Ar relative to N_2 (see table 1). (Incidentally, Ar enrichment relative to N_2 in young sediments is due to the greater solubility of Ar in water and not to radioactive decay.) Since the amber didn't pick up methane, the question arises whether Ar can diffuse much faster through amber than CH_4. (Uptake of both CH_4 and Ar from sediment gas with subsequent total oxidation of the CH_4 is highly unlikely, because it requires unreasonably high original O_2 concentrations and doesn't agree with present CO_2 levels.) There is a problem, however. The milky Baltic amber, which is more porous and would be expected to have exchanged more readily with its surrounding sediment gases, shows no Ar enrichment. Also, simple calculations indicate that generation of ^{40}Ar, via radioactive decay of ^{40}K possibly in or near the amber, over 30 to 40 my would be far less than that required to account for the measured excess. Thus, the excess Ar in the Dominican amber remains to be explained.

In summary, these initial results indicate that the study of gases trapped in amber can provide interesting results, and we hope that this paper stimulates further research on the subject. What is especially needed is improved gas-handling techniques which will allow the measurements of isotopic composition and greater insight into the chemical composition of ancient atmospheres.

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