no correlation between summer CO and winter rain ($r = .07$). The absence of a precipitation effect on CO strengthens the biomass hypothesis and weakens the purely meteorological one. A multiple correlation coefficient of .92 was found for hydrocarbons with both CO and winter rain as independent variables, coefficients of the hydrocarbon-CO and hydrocarbon-rain simple correlations being .81 and .71, respectively. These values imply that at San Jose the biomass hydrocarbon emissions are not quite as important as the vehicular ones. However, the temperature-dependent biomass hydrocarbon emissions would vary more and therefore have a greater effect on ozone levels on hot days (as observed).

Further multiple correlations were used to examine the relative importance of hypotheses A and B. The best operating predictor of high ozone levels in the San Francisco air basin has been temperature. Thus, summer temperatures ≥ 32°C at San Jose and two-winter rain were compared with days of ozone levels > 8 pphm as a dependent variable. The multiple correlation coefficient was .870, with rain and O_3 correlated at $r = .869$ and temperature and O_3 at $r = .565$. The contribution of temperature to the multiple correlation was only .001. We infer from these values that temperature does not affect ozone independently, but through the biomass factor.

In the recent survey of ozone and photochemical oxidants by the National Academy of Sciences (*6*), ozone was taken as an acceptable surrogate for the complex mix of noxious substances developed photochemically from urban emissions, and it was suggested that this surrogate role be periodically reevaluated (*6*, p. 127). The relationship indicated in these data should be considered in such a reevaluation.

The apparent influence of biomass hydrocarbon emissions on ozone should justify a major research effort to measure and model the species and interactions involved. However, the first phase in evaluating the biomass hypothesis may be undertaken with no need for grant applications or ad hoc conferences. Nature has provided California with a very wet year after two drought years. Based on the relationships observed over the past decade, one may predict a 60 to 70 percent increase of ozone excesses (> 8 pphm) in the San Francisco air basin for 1978 compared to 1977, far outweighing the 5 to 6 percent annual decrease from control programs. Moreover, the increases should be most pronounced at outlying suburban stations and should also be reflected at the ≥ 20 pphm health advisory level. Since most of the western United States has had a similarly wet winter following a dry winter, the 1978 increases in ozone should be widespread. However, the quantitative aspects must be derived specifically for each air basin and watershed, possibly with guidance from locally knowledgeable dendrochronologists.

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Degraded Lignin Compounds Identified in Silicified Wood 200 Million Years Old

Abstract. *Degraded lignin compounds have been identified in Triassic age (about 200 million years) silicified wood from the Petrified Forest National Park in Arizona. The pyrolysis products from black carbonaceous samples include carbon dioxide, low-molecular-weight alkanes and alkenes, benzene, alkyl-substituted benzenes, phenol, cresol, xylenols, indenes, benzofurans, trimethylindanone, and naphthalenes. These compounds are also the primary pyrolyzates of modern lignin above 500°C.*

The Petrified Forest member of the Triassic Chinle Formation in Arizona contains a spectacular array of silicified wood embedded in friable clay-rich sandstones and shales. Analyses of the mineralized fossil wood indicate that organic material has been preserved in the black carbonaceous samples of silicified wood (up to 2.7 percent organic carbon), but that organic compounds are completely absent in the multicolored "woods" with no remaining biological structures. The well-preserved cell walls in the carbonaceous samples suggest that remnants of the original wood polymers have survived a 200-million-year history of silicification and diagenesis.

The principal components of wood cell walls are cellulose ($\sim$50 percent), hemicellulose (20 to 30 percent), and lignin (15 to 30 percent). Of these, lignin is the most resistant to decay (*1*) and was thus thought to be the most likely component to survive in the mineralized wood. Lignin is a complex three-dimensional polymer of phenylpropane derivatives (*2*), partially cross-linked by benzyl ether groups and connected to hemicellulose by covalent bonds (*3*). Lignin derivatives have been isolated from soils (*4*), unmineralized fossil wood, peat, and carbonaceous marine sediments (*5*). The results of these studies indicate that lignin degradation products are extremely stable with respect to time and that they can have long lifetimes in the geological record.

In this study, samples of the silicified (average 90 percent SiO_2) conifer *Araucarioxylon arizonicum* (the most abundant species of Chinle macrofossil) were analyzed by sequential high-vacuum (10^{-6} torr) pyrolysis and combined gas chromatography-mass spectrometry (GC-MS) as described in (*6*). Powdered samples were demineralized with concentrated HF at room temperature and washed first with cold distilled $6N$ HCl and then with triple glass-distilled water. A high-fired basalt was pretreated and analyzed in the same way as a check for organic contaminants in the extraction procedure. None were detected.

The samples were degassed at 150°C under high vacuum to remove adsorbed water and nonpolymeric organic fragments, and were pyrolyzed sequentially at 300°, 450°, and 600°C for 30 minutes at each step. An OS-138 (polyphenylether) support-coated tubular capillary column 45 m long and 0.05 cm in inside diameter was programmed from 40° to 190°C at 2.5°C per minute. The products were identified on the basis of their mass spectral fragment patterns and relative GC retention times. Brauns spruce lignin, a representative conifer lignin, was pretreated with HF, washed with $6N$ HCl and H_2O, pyrolyzed, and analyzed by GC-MS as a comparison for the fossil wood data.

The products released from interior sections of black silicified wood with preserved cell structures included a variety of alkyl-substituted phenolic and condensed aromatic compounds suggestive of lignin polymer degradation. At the 300°C pyrolysis step, the only products from the fossil were CO_2, H_2O, and low-molecular-weight alkanes and alkenes. At the same temperature, lignin decomposed and some decarboxylation and demethoxylation occurred, as indicated by the production of large quantities of CO_2, H_2O, acetic acid, ethanal (acetaldehyde), and propanol.

The 450°C pyrolyzates from the carbonaceous silicified wood also contained CO_2 and the low-molecular-weight alkanes and alkenes. The dominant aromatics consisted of phenol, cresol (methylphenol), xylenol and methylxylenol (di- and trimethylphenols), benzene, methyl-substituted benzenes, indenes, indanes, indanone, naphthalenes, and benzofurans. Although benzofurans are commonly reported as cellulose pyrolysis products (*7*), the lignin pyrolysis data reported here indicate that these compounds also form readily during thermally induced rearrangements of phenylpropane units. Alternatively, both the lignin standard and the fossil wood may have retained more cellulose and hemicellulose than anticipated.

The primary pyrolyzates for lignin at 450°C were guaiacol (*o*-methoxyphenol), methyl guaiacol (4-methyl-2-methoxyphenol), and ethyl guaiacol (4-ethyl-2-methoxyphenol). Substantial amounts of phenol, cresol, xylenols, and alkyl-substituted benzenes were also present (*8*). The last identifiable compounds to elute from both the fossil wood and the lignin polymers were trace quantities of syringaldehyde (2-methoxy-4-hydroxybenzaldehyde) and methylsyringaldehyde. Syringaldehyde is of particular interest since it is considered one of the key lignin indicator compounds in geological environments (*5*). The relatively low abundance of these compounds in vacuum pyrolyzates is expected since they are formed by oxidative degradation.

The 600°C pyrograms for lignin and carbonaceous silicified wood were very similar, both in major product composition (Table 1) and in relative product abundance (Fig. 1). The primary aromatic products at this temperature were benzene, alkyl-substituted benzenes, phenol, cresol, xylenols, benzofurans, and naphthalenes. The lignin methoxy compounds were present only in trace quantities. In both the fossil wood and the native lignin, there was a sharp increase in more condensed aromatic compounds at the higher temperature, an indication that rearrangement of the original polymers occurs during heating. This finding is significant in that it suggests the steps whereby the original wood was degraded. Consideration of the 300°C pyrolysis data indicates a prior heating and depletion of oxygen functional groups in fossil wood relative to the modern lignin. The 450° and 600°C steps suggest that demethoxylation was followed by extensive alkyl-substitution in the fossil wood polymer.

Table 1. Aromatic compounds from the 600°C pyrolysis of lignin and organic polymers in silicified wood. Compound numbers correspond to chromatogram peaks in Fig. 1.

Peak component	Peak component
1 Benzene	11 Indene
2 Toluene	12a 7-Methylbenzofuran
3 Ethylbenzene	12b 2-Methylbenzofuran
4 *p*-Xylene	13 Phenol
5 *m*-Xylene	14 Cresol
6 *o*-Xylene	15 Dimethylbenzofuran
7 Styrene	16 Naphthalene
8 Ethyltoluene	17 Xylenols
9 Trimethylbenzenes	18 Methyl xylenols
10 Benzofuran	19 1-Methylnaphthalene

This suggestion is in agreement with the results of studies of model lignin compounds in which methoxybenzene, veratrole, 4-methyl guaiacol, and 2,6-dimethoxyphenol mainly underwent demethoxylation when heated (*9*). Studies of diphenyl methyl ether and guaiacyl benzyl ether demonstrated that the benzyl ether bond begins to undergo free radical decomposition at 300°C (*10*). The free radicals can then participate in chain transfer processes or combine with methyl radicals to form cresol and xylenol (*11*). The pyrolysis of a guaiacol standard at 500°C showed a 30 percent conversion to *o*-cresol, xylenols, phenol, salicylaldehyde, and pyrocatechol (*12*).

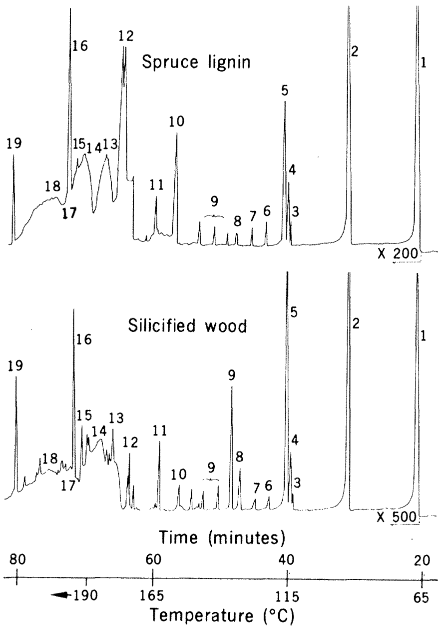

Fig. 1. Partial chromatograms of the 600°C pyrolyzates from modern lignin and demineralized fossil wood; 20 mg of sample were used for each. Peak numbers refer to compounds listed in Table 1.

A prior thermal history for the 200-million-year-old wood is probable since the Triassic sediments of the Colorado Plateau were covered by approximately 1500 to 4000 m of strata by the end of the Cretaceous (*13*). At an average geothermal gradient of 1°C per 30 m, the Petrified Forest sediments would have been exposed to temperature of at least 50° to 130°C over an extensive period of time. It is not unreasonable to conclude that these conditions were sufficient to disrupt the majority of the ether bonds, including those of the methoxy groups, without visibly destroying the appearance of many cell walls.

Analyses across a multicolored sample containing a black core, a red intermediate zone, and beige outer edge illustrate the range in the degree of organic polymer preservation within the strata of the Petrified Forest. Pyrolyses of the black core (1.9 percent carbon) produced the suite of phenolic compounds indicative of degraded lignin. The main pyrolyzates for the red and beige areas (< 0.05 percent carbon), however, were H_2O, CO_2, and SO_2. There were no aromatic monomers indicative of lignin derivatives. These results, along with photomicrographic data, provide additional evidence that the organic compounds in the carbonaceous samples represent in situ degraded wood tissue and not contaminants introduced at a later time.

Although the pyrolysis technique severely fragments the polymer under study, these fragments form a characteristic sequence of monomers representative of the parent polymer. Specifically, the high proportion of phenolic compounds are unique to the lignin derivative sequence (*4*); as a consequence, they may be differentiated from the products of other kerogenous polymers (*6*, *14*).

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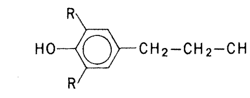
2. 
where R = H or OCH_3. See (*3*) for a more complete model lignin structure.
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Recovery and Maintenance of Live Amphipods at a Pressure of 580 Bars from an Ocean Depth of 5700 Meters

Abstract. *Amphipods were collected from an ocean depth of 5700 meters in a windowed pressure-retaining trap, kept alive in the trap for as long as 9 days aboard ship, and transported to a land laboratory. Observations suggest that the animals can easily tolerate decompressions of 29 percent and briefly of 70 percent of the value of 580 bars, the pressure of their natural habitat. The average pleopod beat frequency was 106 beats per minute. Evidence suggests that food (fish bait) can have at least a 4-day residence time in the gut of these animals.*

This is an account of the recovery of live amphipods four times in succession from a depth of about 5700 m in the central North Pacific Ocean. The pressure at this depth is about 578 bars, a pressure that disrupts the integrated functions of prokaryotic (*1*) and eukaryotic cells (*1, 2*) and of higher metazoa (*2*) found in shallow waters.

The unusual properties of the deep sea (*2, 3*) are a consequence of the considerable water column above it. The deep-sea habitat is characterized by a low temperature, a high hydrostatic pressure, the near absence of light, and a level of cosmic radiation substantially lower than that at the surface. The high pressure (*4*) renders this environment and its inhabitants refractory to study. Animals collected remotely with trawls, corers, and grabs are often torn or abraded, but even when intact they succumb as an apparent result of decompression.

Two approaches are used to circumvent these difficulties. One approach is to study animals and microbes in situ with submersibles [manned (*5, 6*) and unmanned (*7*)] and with free vehicle (a freely falling package) instruments (*8*). The other approach is to capture organisms in pressure-retaining devices and to maintain them in the laboratory for study within these devices or within high-pressure aquariums (*9*). The control over animals for experimentation should be greater in the laboratory than is possible in situ and should allow for otherwise infeasible studies. There have been only a few reports of the recovery of compressed samples from the ocean. Jannasch *et al.* (*10*) have described devices and used them (*6, 11*) to recover water samples from depths of about 3000 m. Macdonald and Gilchrist (*12*) designed a device for the study of animals and demonstrated its pressure-retaining feature by recovering a sample of water from a depth of 2000 m. Samples of plankton have been recovered with the device from depths of 600 m.

The size and behavior of the animals sought in the deep sea determine the design of the capture gear. Hessler *et al.* (*13*) suggested on the basis of photographs that amphipods might be the animals to pursue in the deep sea because of their attraction to baited traps. The successes (*14, 15*) with which amphipods have been trapped in the deep ocean over the past few years fully support their contention. Amphipods (Fig. 1) may indeed become important experimental animals in deep-sea biology.

The pressure-retaining characteristics of the device employed have been described elsewhere (*16*). With this device it has been possible to retrieve amphipods (*15*) from the Philippine Trench with a retention in the trap of 75 to 85 percent of the pressure (about 960 bars) at the trench floor. It was not possible to determine the viability of these amphipods because of the limitations in ancillary equipment. Three equipment improvements made possible the study reported here. (i) A gas-filled hydraulic accumulator (*17*) was attached to the pressure-retaining trap to diminish the pressure loss arising from metal expansion and seal movement encountered during the ascent of the trap to the sea surface. (ii) Thermal insulation was provided to prevent the animals from being exposed to the warm surface waters of the ocean. (iii) A pumping system (*18*) was designed so that seawater at a high pressure could be circulated through the trap after its retrieval and thus could provide oxygen to and remove waste products from the water bathing the animals.

The traps (Fig. 2) were deployed as free vehicles (*19*) that sink to the sea floor, rest there for a predetermined time, discard ballast, and rise to the sea surface where they are recovered onto the ship. The entrance to the pressure-retaining chamber of a trap is shut within a few seconds after the release of the ballast used to sink the free vehicle. The free vehicles were equipped with a radio transmitter and a flashing light to assist in locating them on the sea surface and were usually recovered within 1.6 km of the deployment site.

Seawater was circulated through the pressure-retaining amphipod traps (PRAT's) after recovery. The heart of the pumping system consisted of an air-driven high-pressure pump (*20*) that was compatible with seawater. A piece of 316 stainless steel tubing having an inside di-

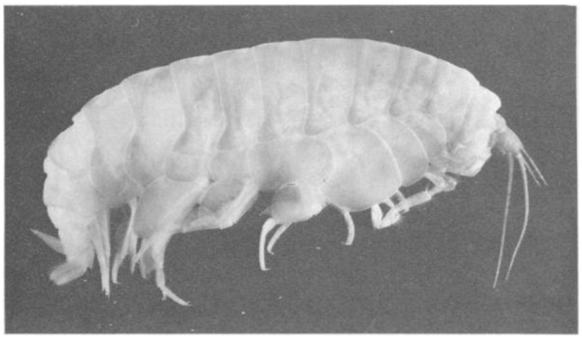

Fig. 1. Photograph of a preserved amphipod caught outside a PRAT in the central North Pacific Ocean and having an extended length of about 9 cm. Several genera occur in this locale (*14*).