# Reports

## Fossil Plants and Coal: Patterns of Change in Pennsylvanian Coal Swamps of the Illinois Basin

Abstract. *Coal palynology and studies of petrified peat indicate major changes in coal-swamp floras and the botanical constituents of coal throughout Pennsylvanian time. The changes are the result of broad climatic shifts and local environmental factors. The most striking is the change from a lycopod-dominated flora to one in which tree ferns were the major element. This change occurred at the Desmoinesian-Missourian (Westphalian-Stephanian) boundary and is probably multicontinental in scope.*

Strata in the Illinois Basin provide unique opportunities for tracing changes that occurred in composition of coal-forming swamp vegetation throughout the Pennsylvanian period. Vascular plants that contributed to coal accumulation are known from studies of petrified peat (coal balls) and from the study of spores and pollen (palynology) preserved in coal seams. Our data are from 17 coal-ball floras from published (*1, 2*) and recent studies of spore assemblages from 76 coals.

Coal-ball studies and coal palynology are in part complementary and generally corroborative. Plant materials in coal balls are direct evidence of swamp vegetation, and, through correlation of isolated spores and pollen with parent plants, coal palynology provides an extensive record of plant distribution. The most abundant spores and pollen are assignable to major plant groups, but plant sources of many others have not been definitely assigned.

Five major groups of plants lived in the peat-forming swamps—lycopods, ferns, pteridosperms, cordaites, and sphenopsids. Each is represented by tree forms that contributed the bulk of spores and pollen and account for most of the botanical constituents of Pennsylvanian coals. With the exception of *Psaronius*, swamp trees were woody. Unlike conifers and modern woody flowering plants, the lycopod trees developed massive bark layers thicker than their wood. Hollow-stemmed cordaites and calamites contained higher proportions of wood than the lycopods, and pteridosperms primarily contributed foliage and cortical tissues.

Lycopod trees of *Lepidophloios* and *Lepidodendron*, many of which were more than 30 m high, generally dominated Early and Middle Pennsylvanian coal swamp forests; *Lycospora* is correlative with the Pennsylvanian arborescent lycopods and was the principal dispersed spore (Fig. 1). The "Age of Ferns" in the Late Pennsylvanian was dominated by *Psaronius* tree ferns up to 7.5 m high. The principal plant constituents of coal derived from aboveground tissues and organs shifted from lycopod bark to support-roots of *Psaronius* at this time. The dominantly tree-fern coals are less extensive than the major lycopod-dominated coals.

The marked change from a lycopod-dominated flora to one of tree ferns as Desmoinesian (late Westphalian) gave way to Missourian (early Stephanian) time is probably multicontinental in scope and indicative of a broad climatic change. Of secondary magnitude is the development of lycopod, cordaitean, and sphenopsid floras in the Illinois Basin during Atokan time with concomitant cordaitean-dominated floras extending westward into Kansas and Iowa (*3*), probably as the result of local factors, such as proximity to marine influences. Evolutionary changes are interwoven with ecological changes.

Some comments about similarities of Pennsylvanian swamp floras in the Northern Hemisphere are appropriate because of the likelihood that major events marked by changes in swamp floras may be reflected in other Pennsylvanian floras of the United States and Europe. The largest change in coal-swamp floras, marked primarily by the abrupt disappearance of *Lycospora* and the dominant stem genera *Lepidodendron* and *Lepidophloios* and the expansion of tree ferns, coincides in general with the stratigraphically controversial Westphalian-Stephanian boundary and with a trend (*4*) toward development of floral provinces on a worldwide basis. Data from petrified floras, coal palynology, and compression floras indicate a major change that was multicontinental in scope.

In the United States the changes in coal-ball floras are generally consistent with the pattern from the Illinois Basin, but detailed comparative data on Upper Pennsylvanian petrified peat floras elsewhere are lacking. In the Stephanian of France petrified plants quite similar to those from the McLeansboro Group are found. Such similarities would be expected within a Euramerican floral province, but more comprehensive comparisons are needed to establish the degree of correlation between petrified Stephanian floras in the United States and France. The similarity of floras and the geographic relationship of Westphalian coals of Europe and coals of equivalent age in the midcontinental and eastern United States have been interpreted as evidence of a once continuous land mass. Most of the European coal-ball floras are from lower Westphalian coals and are older than the majority of coal-ball floras in the United States, which are largely Desmoinesian. The greatest potential for comparisons with coal-ball floras of the midcontinental United States exists in the Donetz Basin, where lycopods are abundant from Westphalian A to D. Detailed data are lacking for most of the 22 coals yielding coal balls, but plants described in detail from a lower Westphalian C coal of the Donetz Basin are identical to those known in the Western Interior Basin of the United States, particularly in Iowa, and to many in the Illinois Basin. The youngest coal balls in the Westphalian D are reported to contain plants with true growth rings (*5*), suggesting a greater climatic change than is evident in the Illinois Basin coal-ball

*Scoreboard for Reports*: In the past few weeks the editors have received an average of 68 Reports per week and have accepted 12 (17 percent). We plan to accept about 12 reports per week for the next several weeks. In the selection of papers to be published we must deal with several factors: the number of good papers submitted, the number of accepted papers that have not yet been published, the balance of subjects, and length of individual papers.

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floras and conditions that differ sharply from the supposed climatic conditions of the coal swamps (*6*).

Data on most coal palynology and coal balls in Europe and the Soviet Union terminate at or below the top of the Westphalian D (*7*). Palynological data reveal similarities between the Illinois Basin and Europe, but differences in spore ranges and abundances do exist. Major changes in spore assemblages have been reported from Europe at the middle Westphalian A and at the Westphalian B/C boundary (*8*). There is a need for more accurate comparisons of spore frequency data and recognition of the significance of the abundance of very small spores, such as *Punctatisporites minutus*, which have been correlated with marattiaceous ferns (*9*) in the Illinois Basin, and comparable spores (*Fabasporites*) reported from Monongahela and Dunkard coals in the Appalachian Basin (*10*).

Compression floras provide an additional and very significant parallel of changing patterns in the Northern Hemisphere. In the floral zonation of the United States, *Pecopteris* (many assignable to the Marattiaceae) foliage becomes abundant in Zone 10 of Read and Mamay (*11*) in the upper part of the Desmoinesian and continues through Zone 12 in the Missourian and Virgilian; seed ferns are considered the dominant forms. The changes in composition of floral zones noted in compressions in the United States and Europe also indicate the disappearance of *Lepidodendron* and *Lepidophloios* in the early Stephanian (*12*). Investigations carried out in Wales (*13*) and the Donetz Basin (*14*) reveal major changes in floras at the Westphalian-Stephanian boundary. In the Westphalian of Wales sphenopsids dominate 11 of 18 shale floras; in the Staffordian (in part Westphalian D), ferns and pteridosperms outnumber other groups in four of eight floras and dominate all three of the floras found in the Radstockian (Stephanian). In the Donetz Basin the shift at the Westphalian-Stephanian boundary was from lycopod-dominated floras to floras composed primarily of ferns and pteridosperms. Ferns and pteridosperms generally prove to be the two most important groups of plants in both coal and shale floras following changes at the Westphalian-Stephanian boundary.

To summarize, the Pennsylvanian coal swamp floras of the Illinois Basin changed in the following sequence: (i) During Early Pennsylvanian time, *Lycospora*-dispersing lycopod trees and herbaceous forms of lycopods yielding *Densosporites* (*Sporangiostrobus*) and *Cirratriradites* were dominant. (ii) In late Atokan and very early Desmoinesian times, *Lycospora* declined, tree ferns were abundant, and calamites attained their maximum peak. (iii) During the early portion of Desmoinesian time, lycopod trees again became dominant, with cordaites and ferns as secondary elements in many coals of the Spoon Formation and the lower

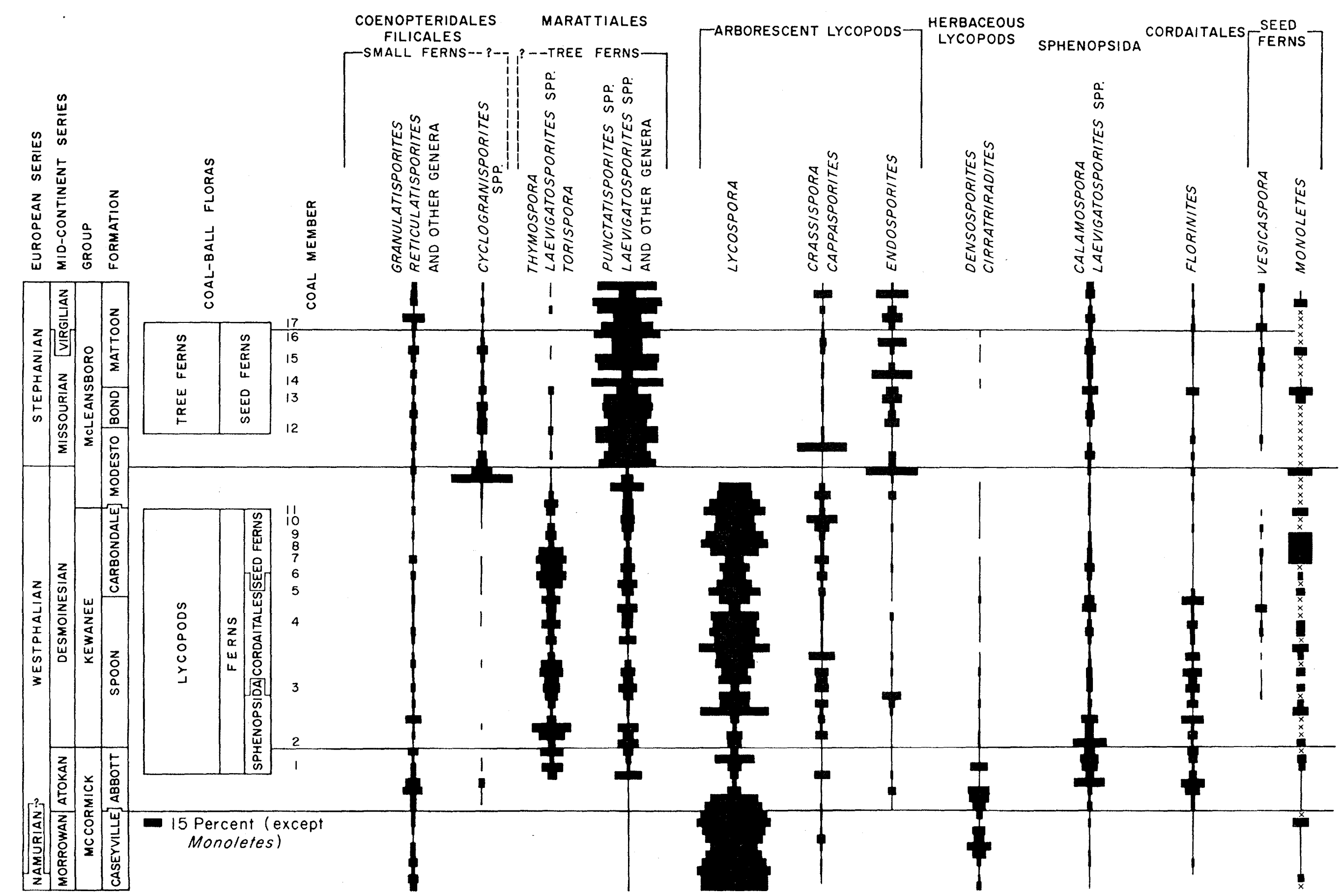


Fig. 1. Distribution (in percentages) of spores and pollen from coals, and relative abundance of major plant groups in coal-ball floras from Pennsylvanian coals of the Illinois Basin. Abundance of *Monoletes* is from Winslow [(*2*) (× indicates no data)]. Numbers given to coal-ball floras correspond to the following coals: (1) Lower Block Coal Member; (2) Buffaloville Coal Member; (3) Unnamed coal in Brazil Formation; (4) DeKoven Coal Member; (5) Colchester (No. 2) Coal Member; (6) Summum (No. 4) Coal Member; (7) Springfield Coal (V) Member; (8) Unnamed coal immediately above Springfield (V) Member; (9) Herrin (No. 6) Coal Member (No. 11 Coal Member of Kentucky); (10) "Baker" Coal Member; (11) Danville (No. 7) Coal Member; (12) Parker Coal Member; (13) Unnamed coal; (14) Friendsville Coal Member; (15) Opdyke Coal Member; (16) Calhoun Coal Member; and (17) Unnamed coal of Shumway Cyclothem.

part of the Carbondale Formation. (iv) During later Desmoinesian time lycopods still dominated younger floras, but ferns and pteridosperms were second and third in abundance. (v) At the Desmoinesian-Missourian boundary, *Lycospora*-producing lepidodendrids terminated abruptly. (vi) In Late Pennsylvanian time, tree ferns were dominant, except in several coal floras that contained abundant *Sigillaria* and *Polysporia*; seed ferns and calamites were subdominant.

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### References and Notes

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# Spectroscopy of Biological Compounds with Inelastic Electron Tunneling

Abstract. *Metal-insulator-metal electron tunnel junctions can be doped with a solution of an organic compound by placing a drop of the solution on the insulator and spinning off the excess. Electrical measurement of the second derivative of voltage with respect to current, as a function of applied voltage, then gives a spectrum of vibrational modes equivalent to an infrared or Raman spectrum, but with the use of only micrograms of sample.*

Inelastic electron tunneling can be used to detect vibrational modes of organic compounds that are active in both the infrared and Raman regions (*1, 2*). The method can be applied systematically to a wide range of organic compounds and can be used successfully as an analytical tool (*3, 4*). The compound to be investigated is placed on the insulator of a metal-insulator-metal electron tunnel junction. Inelastic electron tunneling events, in which an electron tunnels from one metal to the other with the excitation of a vibrational mode of the organic compound, then produce an abrupt change in the dynamic resistance, $dV/dI$, and a peak in the second derivative, $d^2V/dI^2$, at an applied voltage $V = \hbar\omega/e$, where $\hbar\omega$ is the characteristic energy of the mode excited, $e$ is electronic charge, and $I$ is current (*5*). The primary disadvantage of tunneling spectroscopy over infrared and Raman spectroscopy is that cryogenic temperatures are required. The primary advantage is that roughly 1/100 of the amount of sample is required: $< 10$ $\mu$g rather than $\gtrsim 1$ mg.

We report here preliminary results on a new method of doping junctions with organic compounds that is applicable to all organic compounds, including those of biological interest. The technique consists of placing a drop (2 to 10 $\mu$l) of a solution of the compound directly onto the insulating layer and then spinning the junction at approximately 3000 rev/min in order to remove the excess. Solvents such as water, alcohol, benzene, and chloroform have been used successfully. The concentration of the solution is only critical to within a factor of 2, and appropriate concentrations have been in the range 0.1 to 1.0 mg/ml.

Previous methods have used vacuum evaporation of the compound and were limited to compounds which evaporate before decomposing. The method discussed here also produces junctions with generally better resolution, which is probably connected with a more uniform doping of the junction since vacuum evaporation is difficult to control precisely.

The tunnel junctions were $Al-Al_2O_3-Pb$ sandwiches fabricated in the conventional (*6*) crossed film geometry on microscope slides (1 by 3 inches). The Al bottom electrodes were evaporated in a high-vacuum evaporator and then oxidized for roughly 5 minutes in a laminar flow bench. The oxidized Al strips were then doped as described in essence above and in detail elsewhere (*7*). Finally, the slides were returned to the vacuum evaporator for evaporation of the Pb top electrode.

The completed junctions were tested with a low-voltage ohmmeter (*8*). The undoped junctions had resistances in the range 15 to 40 ohms, while acceptable doped junctions had resistances in the range 1 to 100 kilohms. Connections were made to the electrodes with silver paint, and the junctions were then immersed in liquid helium. Curves of $d^2V/dI^2$ versus $V$ were plotted by applying an a-c modulation current at a frequency of approximately 1000 hertz and measuring the voltage at the second harmonic frequency with a lock-in amplifier.

Figure 1 shows spectra obtained from the amino acid L-phenylalanine in water and the pyrimidine base uracil in water. Tunneling spectra for these two compounds have been obtained by the vacuum evaporation technique (*4*), but the spectra in Fig. 1 show considerably improved resolution and generally resolve all modes that are resolved in the corresponding infrared spectra. The full width at half maximum of the sharper peaks in Fig. 1 is approximately 20 cm$^{-1}$, which is determined by the magnitude of the modulation, $(2\ \mathrm{mv})_{\mathrm{rms}}$ (rms = root mean square); the peak broadening due to a modulation voltage $V_m$ is $1.22 \times 8.065$ (cm$^{-1}$/mev) $\times\ eV_m$ (*2*). [Recent measurements with modulation voltages of $(0.6\ \mathrm{mv})_{\mathrm{rms}}$ have given full widths at half maximum as small as 7 cm$^{-1}$ (*7*).] At higher temperatures the line broadening is dominated by the thermal broadening of 5.4 $kT$