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Lignin biomarkers and pollen in postglacial sediments of an Alaskan lake

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Abstract—We analyzed a 12,000-yr sediment core from Wien Lake, central Alaska, for a suite of phenolic products from CuO oxidation of lignin polymers and compared their composition with pollen data from the same core to assess lignin phenols as sedimentary biomarkers. Inferences of the gross taxonomic origin of sediment organic matter from lignin-phenol composition agree with vegetational reconstructions based on pollen assemblages. In particular, the ratios of syringyl to vanillyl phenols are consistently higher before 6500 yr BP, when angiosperms dominated or codominated the regional vegetation, than after 6500 yr BP, when gymnosperms dominated. However, the ratios of cinnamyl (*p*-coumaric and ferulic acids) to total vanillyl phenols (C/V) do not show patterns expected from the abundance of woody plants. C/V ratios are particularly high (0.7–0.85) after 6500 yr BP when pollen spectra suggest closed boreal forests dominated by *Picea*, and the stratigraphic patterns are strikingly similar between C/V and *Picea* pollen concentrations. CuO oxidation of modern pollen of *P. glauca* and *P. mariana* yields exceptionally high amounts of cinnamyl phenols (8.90 and 6.41 mg/100 mg OC for *P. glauca* and *P. mariana*, respectively). In particular, *p*-coumaric acid is obtained in large amounts (8.87 and 6.41 mg/100 mg OC for *P. glauca* and *P. mariana*, respectively) versus vanillyl phenols (0.25 and 0.49 mg/100 mg OC for *P. glauca* and *P. mariana*, respectively) and ferulic acid (0.03 and 0.00 mg/100 mg OC for *P. glauca* and *P. mariana*, respectively). Thus lignin phenols derived from fossil *Picea* pollen preserved in sediments likely drive the C/V profile of the Wien Lake core. These data imply that if *Picea* pollen concentrations are sufficiently high, the amount of nonwoody tissue in sediments may be grossly overestimated when the lignin composition of gymnosperm needles is used as the end member of nonwoody tissues. Given that pollen grains are among the most resistant components of sedimentary organic matter and that *p*-coumaric acid is labile, it is important to consider pollen as a nonwoody tissue type when lignin biomarkers are used to determine the sources of vascular-plant material in sediments. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

Studies of biogeochemical processes in aquatic sediments, soils, and other geological deposits require tracers that are ubiquitous, source-indicative, and stable over long periods. Among the most useful tracers for the origin of terrestrial organic carbon are a suite of phenolic compounds derived from CuO oxidation of lignin polymers that are produced by all vascular plants (Sarkanen and Ludwig, 1971; Hedges and Mann, 1979). Extensive studies on fresh plant materials, forest floor litter, soils, and aquatic sediments have shown that these phenolic compounds are indicative of certain plant taxa and tissue types (e.g., Hedges and Mann, 1979; Hedges and Weliky, 1988). In particular, vascular plants can be distinguished from non-vascular plants since only vascular plants produce vanillyl phenols. Among vascular plants, angiosperms characteristically produce syringyl phenols, whereas gymnosperms do not. Nonwoody tissue of both gymnosperms and angiosperms can be distinguished from woody tissue by their lower yields of vanillyl and syringyl phenols and by the characteristic production of cinnamyl phenols. In addition, the acid-to-aldehyde ratio of vanillyl phenols may indicate the extent of microbial degradation of organic matter (Hedges et al., 1988; Goñi et al., 1993;

Opsahl and Brenner, 1995). These properties have been used to determine the amounts, types, and diagenetic histories of vascular-plant tissues in a number of biogeochemical analyses of sediments and soils (e.g., Hedges et al., 1982; Leopold et al., 1982).

Several uncertainties, however, may compromise the applications of lignin phenols as source indicators of sedimentary organic matter. For example, chemically based estimates of different types of vascular-plant tissue in natural environments are generally made by comparing them with the composition of fresh plant tissue. However, not all major types of vascular-plant tissue have been analyzed for lignin CuO oxidation products. The lignin-phenol composition of leaves and needles has been commonly used as the geochemical end member of nonwoody tissues (Hedges et al., 1982; Ertel et al., 1984). Although pollen grains are known to be among the sedimentary organic matter most resistant to microbial degradation and thus may also be important lignin contributors from sediments (Keil et al., 1998), this possibility has not yet been systematically explored for freshwater sediments. In addition, selective microbial degradation of lignin structures, such as syringyl relative to vanillyl groups, has been observed (Ertel et al., 1984; Hedges et al., 1985; Hedges and Weliky, 1989). Because our understanding remains inadequate concerning the diagenetic fates of various vascular plant components, the potential is great for diagenetically induced errors (Benner et al., 1984;

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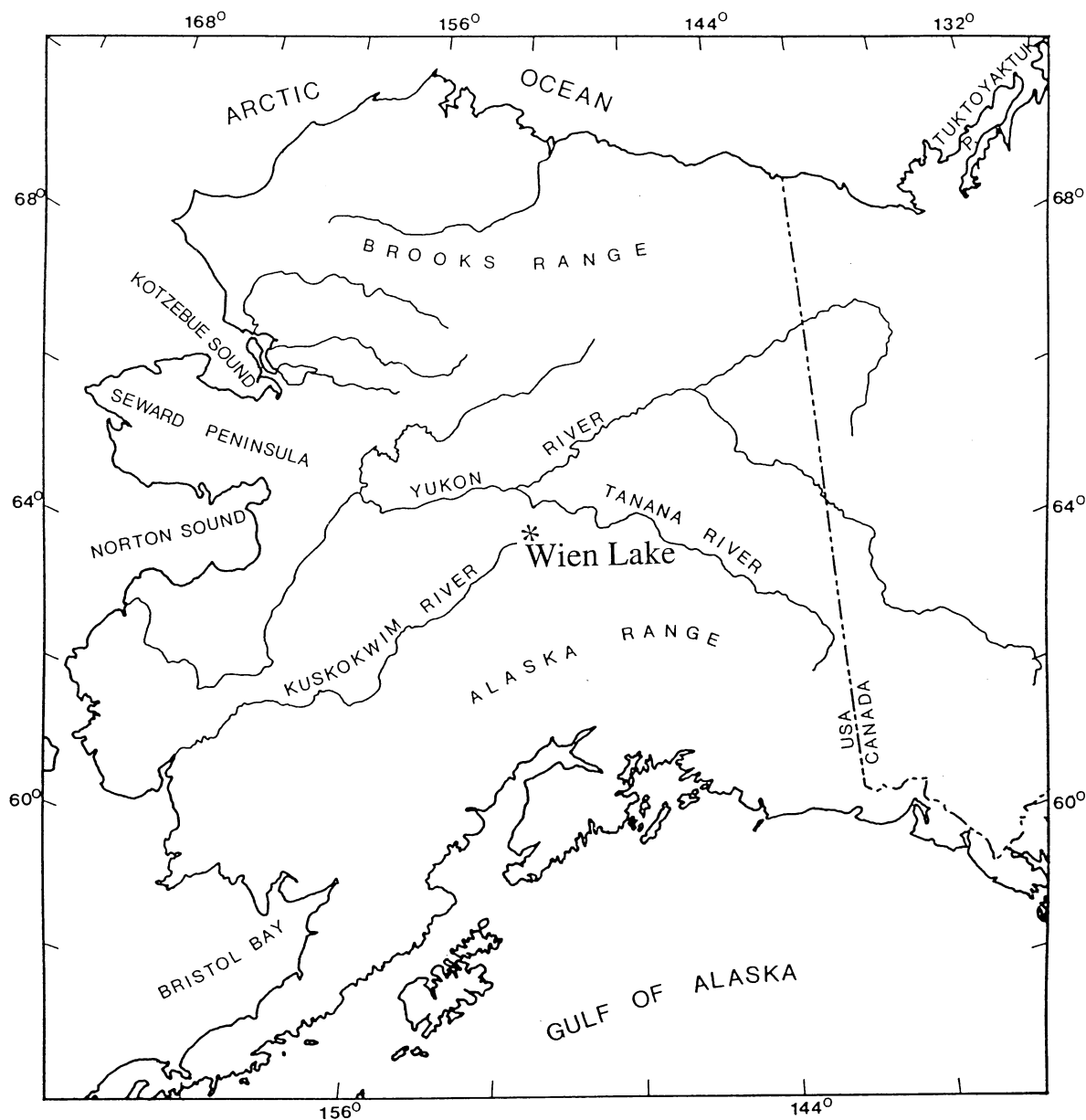


Fig. 1. Map of Alaska showing location of Wien Lake.

Hedges and Prah, 1989). Improving our knowledge about these issues is necessary to enhance the reliability of lignin phenols as sedimentary biomarkers.

We analyzed a sediment core from Wien Lake ($64^{\circ} 20' N$, $152^{\circ} 16' W$; Fig. 1) in central Alaska for lignin CuO oxidation products. Inferences of taxonomic (gymnosperm vs. angiosperm) and tissue origins (woody vs. nonwoody) from lignin-compound composition are compared with vegetation reconstructions based on a pollen record from the same core (Hu et al., 1993). Because pollen analysis is a well-established technique for paleovegetational studies (Faegri et al., 1992), such a comparison serves as a test of lignin compounds as tracers of taxonomic and tissue-type origins of vascular-plant material in sediments. Our results indicate that the composition of lignin

compounds in the sediments reflects gross differences in vegetation types defined by pollen assemblages, but the source-indicative signals of lignin biomarkers are obscured by selective diagenetic alterations on land and/or in surface sediments. In addition, our data provide evidence for fossil pollen as a major contributor of lignin compounds from freshwater sediments, which has important implications for the geochemical applications of lignin biomarkers.

2. STUDY AREA

Wien Lake (Fig. 1) is an oligotrophic lake with a surface area of 12 km^2 . The maximum and mean water depths are 30.1 m and 5.1 m, respectively. Secchi depth in the summer of 1990

was ~8 m. The lake at present has 3 small inlets and a single outlet draining to the Kantishna River.

Today, the regional climate is characterized by continental conditions, with a mean July temperature of near 15°C, mean January temperature of about -22°C, and annual average precipitation of 300 mm (Wahrhaftig, 1965). Most of central Alaska is underlain by discontinuous permafrost. The boreal forests that dominate the modern landscape of the region are characterized by mixed conifer-hardwood communities (Viereck et al., 1992). Forests dominated by *Picea glauca* (white spruce) occur on south-facing uplands, whereas *P. mariana* (black spruce)-moss communities characterize lowlands and poorly drained, north-facing slopes. Riparian forests are dominated by *Populus balsamifera* (balsam poplar) or *P. glauca*. Vegetation in the overall Wien Lake watershed is a closed boreal forest mosaic dominated by *P. mariana*, *P. glauca*, *Populus tremuloides* (aspen), *Betula papyrifera* (paper birch), various ericaceous species and bryophytes. Communities dominated by hardwood species are primarily found in the western portion of the watershed where forest fires have recently occurred.

3. MATERIAL AND METHODS

A sediment core of 2.55 m was recovered from an extensive, 14 m deep shelf on the west side of Wien Lake with a modified Livingstone corer (Wright et al., 1984). Subsamples were taken for pollen analysis and ¹⁴C dating, the methods and results of which have been described in detail elsewhere (Hu et al., 1993). Three samples representing each of the 4 pollen zones (see below) were taken from the core for CHN and lignin analyses. Modern samples of *P. glauca* and *P. mariana* pollen for lignin analysis were provided by Dr. E. Cushing's pollen laboratory at the University of Minnesota.

Samples of lake sediments and modern pollen were prepared according to the CuO oxidation procedure of Hedges and Ertel (1982) as modified by Goñi and Hedges (1990). About 300 mg of dry sediment was oxidized at 155°C for 3 hours with CuO under basic (8% NaOH) conditions. The reaction solution was acidified and extracted with ethyl ether. Acidic reaction products were converted to trimethylsilyl derivatives and analyzed with a Hewlett Packard 5730A gas chromatography fitted with 2 fused silica capillary columns coated individually with DB-1 and DB-1701 liquid phases. Identities of all phenols were confirmed with commercial standards by co-injection on both columns. An example of the gas chromatographic trace of the CuO oxidation product mixture from the *P. mariana* pollen is provided in Fig. 2. The average analytical precision is ±10% for lignin CuO oxidation products.

Samples of dry carbonate-free sediment were processed in duplicate with a Carbo Erba Model 1106 CHN analyzer by the method of Hedges and Stern (1984). The average reproducibilities for this sample set were ±2% and ±3%, respectively, for weight percentages of organic carbon (%OC) and atomic carbon/nitrogen ratios (C/N).

4. RESULTS AND DISCUSSION

4.1. Pollen Assemblages and Elemental Composition

Pollen data (presented as percentages of total pollen grain counts) from the Wien Lake core and their vegetation implica-

tions are described in detail in Hu et al. (1993). Here we provide a brief description of the pollen record to facilitate comparison of pollen and geochemical results. The pollen stratigraphy is divided into four zones based on characteristic assemblages. In Zone I (12,500–10,500 yr BP; represented by samples 250 cm, 239 cm, and 219 cm), pollen spectra are dominated by *Betula* (65–75%), Cyperaceae (10–20%), and *Salix* (~10%). The landscape surrounding Wien Lake was dominated by shrub *Betula* tundra. Shrubs and herbs present were all angiosperm taxa, and trees were absent. In Zone II (10,500–9,500 yr BP; represented by samples 195 cm, 192 cm, and 188 cm), pollen spectra are characterized by the abundance of *Populus* (20–25%), *Salix* (~25%), and *Betula* (40–50%). *Populus* forests were likely prominent within the Wien Lake watershed during this period. In addition to the shrubs and herbs in Zone I, angiosperm trees were common within the watershed, but gymnosperms were absent. In Zone III (9,500–6,500 yr BP; represented by samples 159 cm, 138 cm, and 110 cm), *Populus* and *Salix* pollen decrease dramatically, *Picea* pollen increases to reach ~20%, and *Betula* pollen remains abundant (45–85%). The dominant vegetation in the Wien Lake region was mixed gymnosperm-angiosperm forests codominated by *Picea* and *Betula* trees. In Zone IV (6500–0 yr BP; represented by samples 70 cm, 40 cm, and 20 cm), pollen spectra are characterized by the abundance of *Picea* (~40%), *Betula* (~40%), and *Alnus* (~20%). The regional vegetation was closed boreal forests dominated by two gymnosperm species (*P. glauca* and *P. mariana*), similar to those in interior Alaska today.

The Wien Lake sediments are silty-clayey with allochthonous silicates as the dominant component in Zone I (Hu et al., 1993). The sediments of Zones II–IV are gyttja containing much greater amounts of autochthonous iron oxyhydroxide and biogenic silica than those in Zone I. On the basis of 8 conventional ¹⁴C dates of bulk sediments and 1 AMS ¹⁴C date of plant macrofossils, sedimentation rates are generally greater in Zone I than in Zones II–IV, but variations in sedimentation rate are relatively small throughout the core (Hu et al., 1993). Organic-carbon concentrations (%OC) are low (1.5–2.5%) in Zone I and increase markedly at the transition from Zone I to Zone II (Fig. 3). This %OC increase probably resulted from enhanced vegetational cover and soil stability as *Betula* shrub tundra in Zone I was replaced by various types of forest in Zones II–IV (Hu et al., 1993). No stratigraphic trend of %OC exists in the samples of the upper 3 zones, despite major vegetational changes inferred from pollen data.

The atomic ratio of organic carbon to nitrogen (C/N) has a relatively wide range of 6.5–17.0 for the Wien Lake core (Fig. 3). In general, C/N is highest in Zone I (16.3–19.8), lowest in Zone II (7.6–12.5), and intermediate in Zones III and IV (12.8–17.5). The ratio exhibits an overall upward decrease from ~19.0 to 7.6 in Zones I and II, followed by an increase from 13.7 to 17.5 with a reversal at 40 cm. These C/N values suggest that organic matter in the Wien Lake sediments is a mixture of planktonic organisms (C/N = ~6–8, Redfield et al., 1963; Meybeck, 1982) and terrestrial plant tissue and peat (C/N = ~20–100) (Brenner et al., 1978; Hedges and Oades, 1997) in various proportions. The decrease in Zones I and II suggests increasing importance of aquatic organic matter at the expense of terrestrial organic matter, which is supported by the increas-

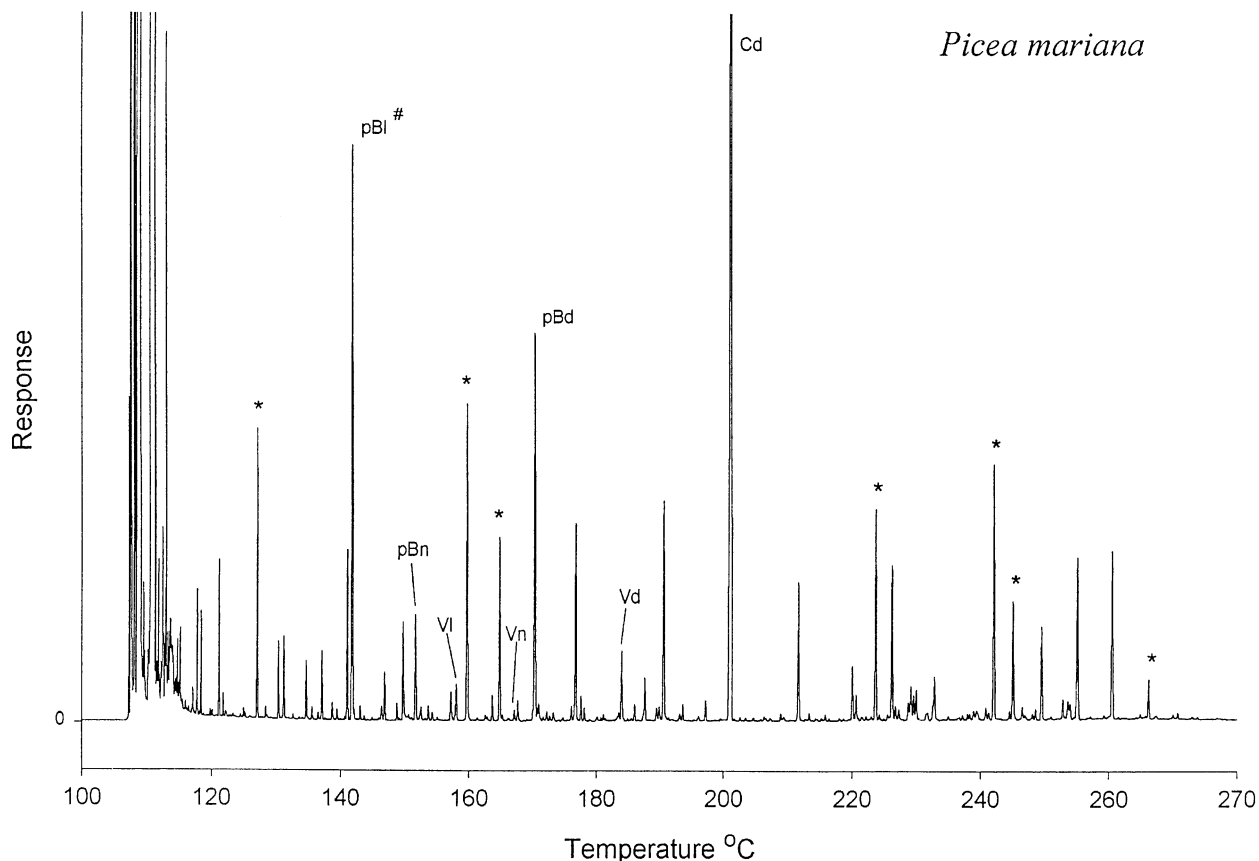


Fig. 2. Gas chromatographic trace of the trimethylsilyl derivatives of the CuO oxidation product mixture from fresh pollen of *Picea mariana* (black spruce). The sample was analyzed with He carrier gas on a J&W 30 m \times 0.25 mm o.d. fused silica column coated with DB-1 (methylsilicone) liquid phase. Oven temperature was programmed from 100°C to 270°C at 4°C/min with no initial delay. Peak identities (in elution order): pBI, *p*-hydroxybenzaldehyde (# indicates coelution of another reaction product); pBn, *p*-hydroxyacetophenone; VI, vanillin; Vn, acetovanillone; pBd, *p*-hydroxybenzoic acid; Vd, vanillic acid; Cd, *p*-coumaric acid. Internal standard peaks are indicated by asterisks. Of the commonly quantified "monomeric" lignin phenols, syringaldehyde, acotsyringone, syringic acid and ferulic acid were not detected.

ing abundance of diatoms as measured by biogenic silica (Hu et al., 1993). The subsequent increase reflects a general increase in sedimentary organic matter of terrestrial origin. However, the low C/N values in Zone II compared to Zones III and IV are not caused by increased aquatic productivity, as biogenic silica does not show peak values in this Zone (Hu et al., 1993). Instead increasing C/N ratios from Zone II to Zones III and IV probably reflect changes in terrestrial vegetation from *Populus* woodland to *Picea* forest at the end of Zone II (Hu et al., 1993), since deciduous litterfall typically is more enriched in nitrogen than coniferous litterfall (Flanagan and van Cleve, 1983). Alternatively, the lower C/N ratios in Zone II than in Zones III and IV could be due to a higher fraction of soil organic matter (C/N = ~12) versus plant debris in Zone II, as extensive soil erosion probably occurred during this period (Hu et al., 1993).

4.2. Lignin CuO-Oxidation Products as Source Indicators of Sedimentary Organic Matter

The total weight of all 8 vanillyl, syringyl, and cinnamyl phenols in mg per 100 mg of organic carbon (Λ , Hedges et al., 1982) has been used as an indicator of the relative concentra-

tion of vascular-plant material in a sedimentary organic mixture. However, Λ does not have a strictly direct relationship to the abundance of vascular plant material in sediments, because of a number of factors including variations in lignin composition related to vegetational changes and diagenetic loss of any vascular plant component. A Λ range of 0.66 to 2.09 is observed for the Wien Lake samples (Fig. 3). These values are comparable to those of sediments from Lake Washington (0.9–1.91) (Leopold et al., 1982; Hedges et al., 1982) and coastal marine sediments of the Pacific Northwest (1.4–3.25) (e.g., Ertel and Hedges, 1984). No corresponding patterns exist between Λ and pollen-inferred vegetation type. However, Λ shows an upward decrease in the uppermost 3 samples. This Λ decrease, along with no change or a slight increase in %OC, suggest dilution by an increased input of non-vascular plant tissue, probably resulting from the establishment of an extensive understory moss cover in the *Picea mariana* forests of Zone IV (Hu et al., 1993). However, this interpretation is inconsistent with the lack of corresponding changes in C/N ratio, which should become elevated with increased moss-derived organic matter. Alternatively, the upward decrease in Λ

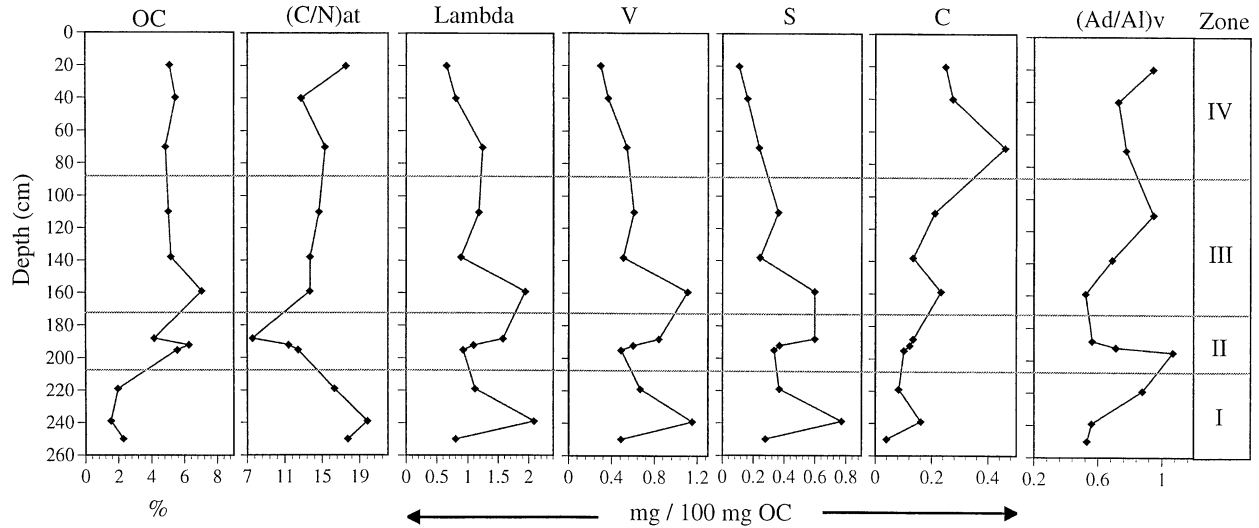


Fig. 3. Stratigraphies of elemental composition and various lignin parameters, Wien Lake. OC: organic carbon. (C/N)_{at}: atomic ratio of carbon to nitrogen. Lambda (Λ): see definition in text. V: total vanillyl phenols. S: total syringyl phenols. C: total cinnamyl phenols. (Ad/Al)_v: weight ratio of acid to aldehyde in the vanillyl group.

probably resulted from an increasing proportion of lignin-poor soil organic matter at the expense of lignin-rich plant debris in the sedimentary matrix.

Vanillyl and syringyl phenols both exhibit stratigraphic patterns similar to those of Λ , and all 3 parameters are significantly correlated ($R^2 > 0.88$, $p < 0.001$, $n = 12$). The strong correlation between vanillyl and syringyl phenols suggests that angiosperm tissues are an important component of sedimentary lignin throughout the Wien Lake record. Cinnamyl phenols show stratigraphic patterns different from those of vanillyl phenols, syringyl phenols, and Λ . The concentrations of cinnamyl phenols are low in Zones I and II (0.04–0.16 mg/100 mg OC) and increase greatly in Zones III and IV (0.14–0.46 mg/100 mg OC). The elevated cinnamyl-phenol concentrations from Zones I and II to Zones III and IV, however, do correspond to the establishment of *Picea*.

Weight ratios of total syringyl and cinnamyl phenols to total vanillyl phenols (S/V and C/V ratios) in the lignin CuO oxidation products have been used in previous studies to trace the taxonomic and tissue type sources of terrestrial plant tissues in sediments and soils (e.g., Hedges et al., 1979, 1982; Ertel et al., 1984). In the S/V versus C/V plot of the Wien Lake samples (Fig. 4a), Zone IV is clearly separated from the other 3 zones. C/V is substantially higher than in other zones, likely because the abundance of *Picea* pollen yields an extremely high amount of *p*-coumaric acid, as discussed in the next section. S/V is consistently lower in Zone IV (0.36–0.44) than in the other 3 zones (0.48–0.70), suggesting that gymnosperms became more abundant at the expense of angiosperms. Pollen data also suggest that angiosperms dominated or codominated the vegetation of Zones I–III, despite major differences in species composition among these 3 vegetation zones, and that gymnosperms, namely *P. glauca* and *P. mariana*, predominated in Zone IV (Hu et al., 1993). Thus this comparison of lignin biomarkers and fossil pollen indicates that the S/V ratios of these sediments reflect the broad taxonomic origin of terrestrial organic matter.

This conclusion is remarkable, as various factors could have caused major discrepancies in vegetation signals from lignin phenols and from pollen. For example, lignin in the Wien Lake sediments appears to have been subjected to substantial diagenetic alterations, as discussed below. In addition, pollen may have arrived at the lake from plants far away from the lake watershed, whereas the source of lignin from non-pollen tissues is likely within the lake watershed, particularly along the shoreline.

Neither S/V nor C/V clearly separates Zones I, II, and III. However, among these 3 zones, the average S/V is highest in Zone II and lowest in Zone III, whereas the average C/V is highest in Zone III and lowest in Zone I. Although the S/V values are lower in Zone III, as expected from the presence in this zone and absence in other zones of gymnosperm trees, the separation of these zones by S/V is ambiguous compared to the differences in pollen-inferred vegetation. Two possible factors are responsible for this lack of distinction. First, the watershed of Wien Lake was probably dominated by deciduous plants in Zone III despite the presence of conifers. This interpretation is plausible, as pollen and plant macrofossils suggest that *Betula* and other angiosperm species were common and that *Picea* trees were probably scattered in the Wien Lake region (Hu et al., 1993). Second, diagenetic changes of the lignin parameters may have obscured the lignin signals of organic carbon sources in the Wien Lake sediments. Preferential degradation of syringyl over vanillyl phenols is indicated by comparing the S/V and C/V ratios of the Wien Lake samples with those of fresh tissues of a number of vascular plant species (Hedges and Mann, 1979) (Fig. 4b). The S/V ratios of Zones I–II samples should all fall within the space defined by the S/V ranges of woody and nonwoody tissues of angiosperms, because these samples represent vegetation types (birch shrub tundra and poplar woodland) without conifers and because organic matter in the sediments likely derives from the mixture of woody and nonwoody tissues. However, all 12 samples from Wien Lake

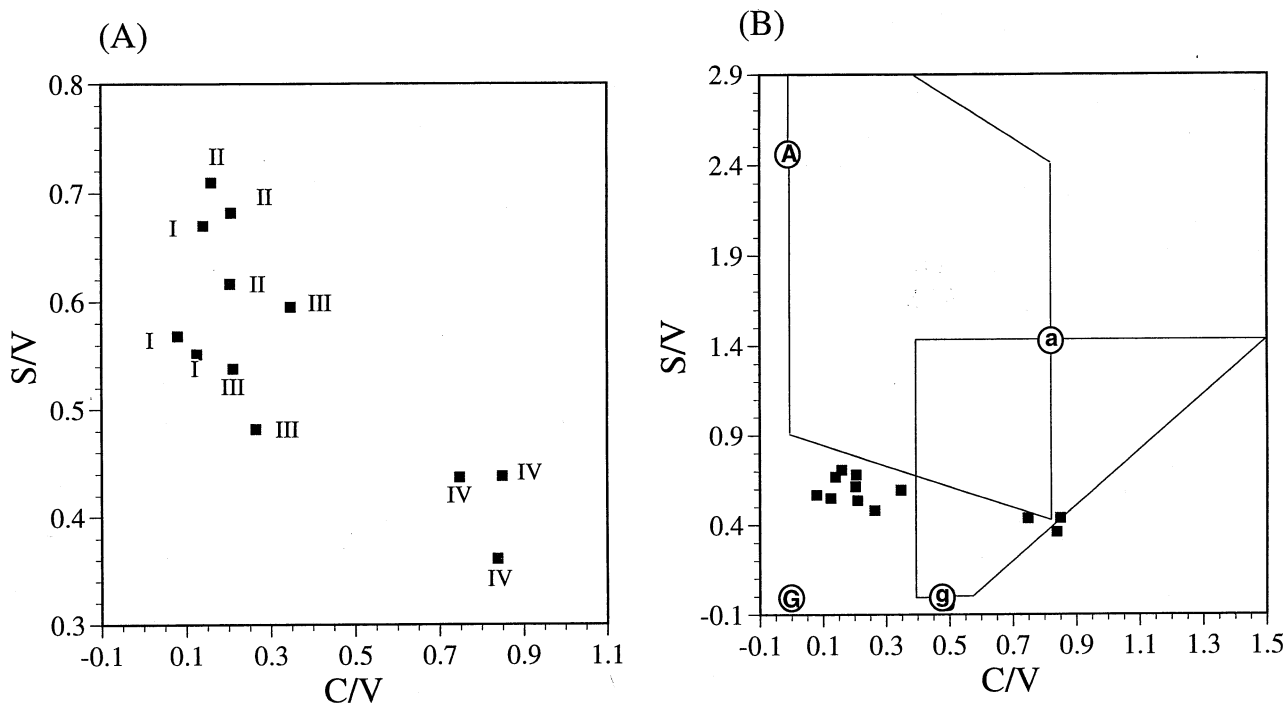


Fig. 4. Plot of S/V and C/V values. (A) Wien Lake sediment samples. I–IV are vegetation zones defined by pollen assemblages (Hu et al., 1993). (B) Comparison of sediment samples from Wien Lake with the averages of fresh plant tissues of various taxonomic origins based on Hedges and Mann (1979) (A: angiosperm woody tissue. a: angiosperm non-woody tissue. G: gymnosperm woody tissue. g: gymnosperm non-woody tissue).

plot below this region, suggesting that syringyl phenols has been preferentially degraded compared to vanillyl phenols. This conclusion is consistent with the results of a controlled laboratory study indicating that syringyl phenols are more labile to fungal degradation than vanillyl phenols (Hedges et al., 1988). Preferential degradation of syringyl over vanillyl phenols would have resulted in reduced S/V ratios in Zones I and II, making them more similar to those in Zone III than otherwise.

Within the vanillyl family the acid/aldehyde ratio [(Ad/Al)v] has been demonstrated to increase with the degree of oxidative alteration of vascular plant tissues by white-rot and soft-rot fungi (Hedges et al., 1988; Goñi et al., 1993; Nelson et al., 1995) and during subaqueous degradation by mixed microbial communities (Opsahl and Brenner, 1995). Fresh plant tissues yield (Ad/Al)v ratios in the range of 0.1–0.3, with substantially elevated ratios corresponding to increased microbial degradation (Hedges et al., 1988). The (Ad/Al)v ratios of the Wien Lake samples range from 0.52 to 1.07 (Fig. 3). These (Ad/Al)v values are high and comparable with those of humic substances from soils, sediments, and natural waters (0.6–2.0) (Ertel and Hedges, 1984; Ertel et al., 1984), suggesting that the vascular plant material in the Wien Lake sediments is highly degraded. The high (Ad/Al)v values of sediments in Zones III and IV probably resulted in part from the abundance of *Picea* pollen (Fig. 5), since fresh *Picea* pollen samples yield much higher (Ad/Al)v values (Table 1) than other fresh plant tissues. (Ad/Al)v fluctuates greatly throughout the core, and these fluctuations are not significantly correlated with stratigraphic changes in either C/N or Δ . No systematic differences exist among the

4 vegetation zones, but (Ad/Al)v increases upward in Zones I and III and decreases upward in Zone II. Although the causes of these stratigraphic changes are unclear, they are likely related to the degree of oxidative degradation as well as other factors, such as the relative proportions of soil-derived organic matter versus plant debris. The lack of a downward increasing trend in (Ad/Al)v indicates that oxidative degradation likely occurred on land or in the surface sediments and that in situ degradation is minimal below the surface sediments. This conclusion is further supported by the facts that anoxic degradation of polymeric lignin is slow (Kirk, 1984), that total lignin phenol yields do not show a downcore trend toward lower values, and that the samples from the core bottom retain high yields of potentially reactive syringyl phenols.

4.3. Pollen-Derived Lignins and Geochemical Implications

The low S/V ratios in Zone IV compared with those of other zones are expected from the pollen-inferred paleovegetation. In contrast, the strikingly high C/V ratios (0.7–0.85) of the Zone IV samples are surprising, because pollen data indicate that closed boreal forests became established at the onset of this zone around 6500 yr BP (Hu et al., 1993). This vegetational change likely resulted in an increased proportion of woody plants on the landscape, which should lead to decreased C/V ratios, since cinnamyl phenols are produced only by nonwoody tissues whereas vanillyl phenols derive from both woody and nonwoody tissues. A possible interpretation for the elevated C/V ratios is that the ratio is higher for gymnosperm needles

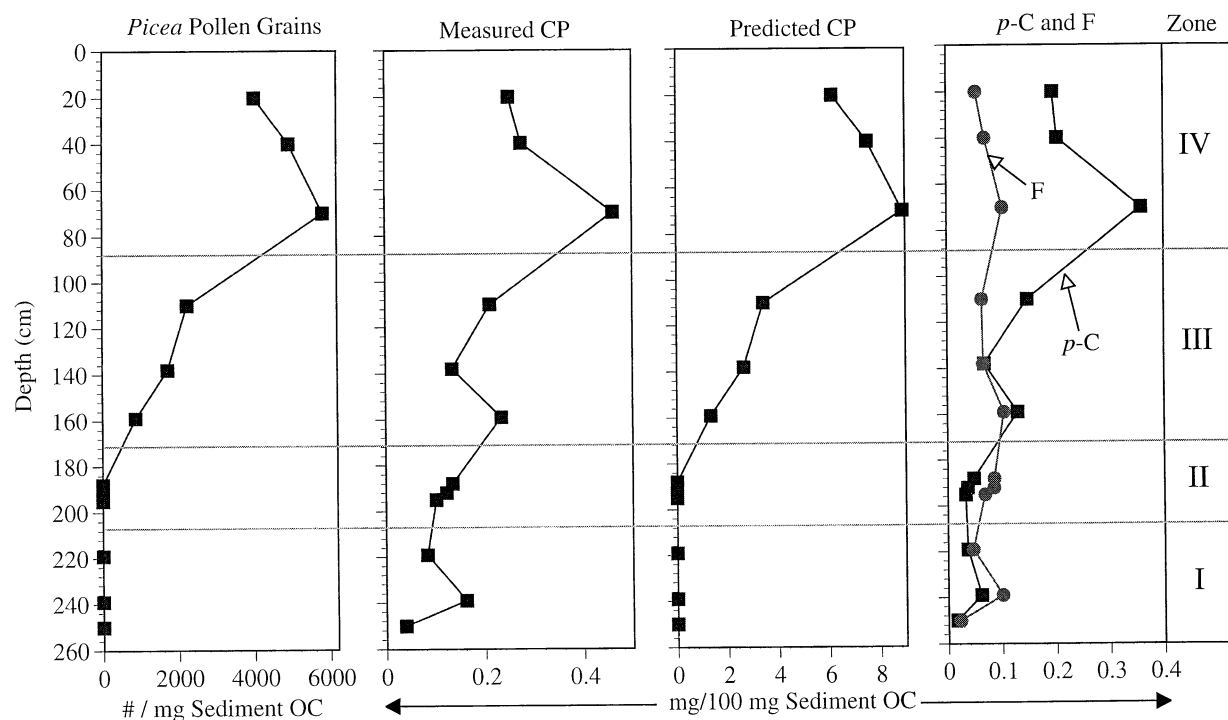


Fig. 5. Stratigraphies of *Picea* pollen concentration, measured yield of CP (cinnamyl phenols), predicted yield of CP, measured yield of *p*-coumaric acid (*p*-C), and measured yield of ferulic acid (F) in the Wien Lake sediments.

than for angiosperm leaves. However, this interpretation contradicts results from studies of modern leaves/needles of various plants, which indicate that the average C/V ratio is 0.49 (0.38–0.57) and 0.85 (0.36–1.5) for gymnosperms and angiosperms, respectively (Hedges and Mann, 1979). The elevated C/V ratios in Zone IV cannot be explained by diagenetic changes either. Recent studies have found precursors of cinnamyl phenols to be highly labile compared to syringyl and vanillyl precursors in conifer needles (Hedges and Weliky, 1989), cypress needles, mangrove leaves and cordgrass (Opsahl and Benner, 1995). Given that the (Ad/Al)_v values of the Zone IV samples are consistently >0.5, the bulk lignin would appear at face value to be degraded and thus should carry little remnant cinnamyl phenol of needle/leaf origin.

The unusually high C/V ratios in Zone IV are probably related to the abundance of *Picea* pollen, as suggested by the striking similarity in the stratigraphic patterns of *Picea* pollen concentrations and cinnamyl phenols (Fig. 5). To test this possibility, we analyzed modern pollen of the 2 *Picea* species found in the Wien Lake sediments for lignin CuO-oxidation products. Our results (Table 1, Fig. 6) show that, as with gymnosperm needles (Hedges and Mann, 1979), no appreciable amount of syringyl phenols is produced from the pollen of these two *Picea* species. Nevertheless, the yields of cinnamyl phenols are much higher from the pollen of *P. glauca* (8.90 mg/100 mg OC) and *P. mariana* (6.41 mg/100 mg OC) than from needles (1.00 mg/100 mg OC). The elevated yields of cinnamyl phenols from the pollen of both species are caused almost exclusively by high *p*-coumaric acid, as the yields of ferulic acid of these pollen samples (0.026 and 0.000 mg/100 mg OC for *P. glauca* and *P. mariana*) are lower than those of

Table 1. Lignin-phenol yields (mg/100 mg OC) and inter-class ratios of modern *Picea glauca* and *P. mariana* pollen.

Lignin Phenols	<i>Picea glauca</i> Pollen	<i>P. mariana</i> Pollen
Individual Phenols (mg/100 mg OC)		
vanillic acid	0.08	0.28
vanillin	0.14	0.16
acetovanillone	0.03	0.05
syringic acid	0.00	0.00
syringaldehyde	0.00	0.00
acetosyringone	0.00	0.00
<i>p</i> -hydroxybenzoic acid	1.33	1.11
<i>p</i> -hydroxybenzaldehyde	2.53	1.99
<i>p</i> -hydroxyacetophenone	0.34	0.34
<i>p</i> -coumaric acid	8.87	6.41
ferulic acid	0.03	0.00
Extensive Lignin Parameters (mg/100 mg OC)		
V	0.25	0.48
S	0.00	0.00
C	8.90	6.41
P	4.20	3.45
Lambda	9.15	6.90
Σ8 (mg/10 g dry mass)	453.27	333.22
Interclass Ratios		
C/V	35.17	13.20
S/V	0.00	0.00
C/F	342.39	
P/V	16.58	7.09
Acid/Aldehyde Ratios		
V	0.56	1.73
S		
P	0.53	0.56

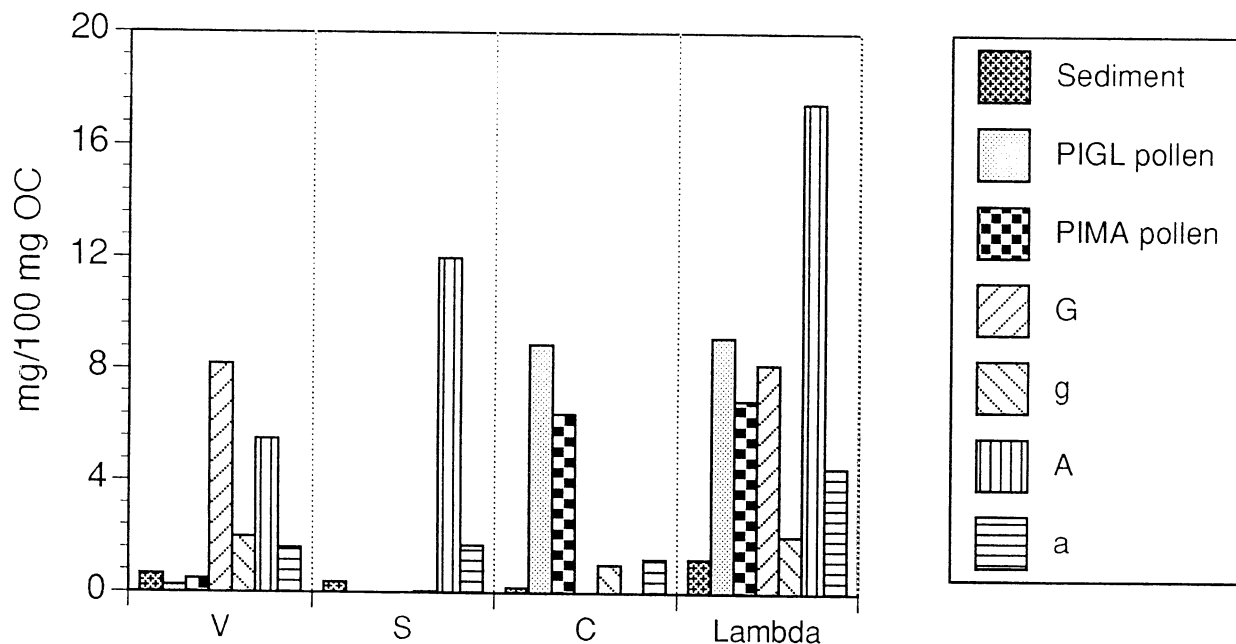


Fig. 6. Comparison of lambda (see text for definition) and yields of vanillyl, syringyl, and cinnamyl phenols in the Wien Lake sediments, modern *Picea glauca* pollen (PIGL), modern *P. mariana* pollen (PIMA), and fresh gymnosperms woody (G), gymnosperm non-woody (g), angiosperm woody (A), and angiosperm non-woody (a) tissues of various species (Hedges and Mann 1979).

needles (~ 0.21 mg/100 mg OC). In contrast to cinnamyl phenols, the yields of vanillyl phenols are much lower from the pollen of *P. glauca* (0.25 mg/100 mg OC) and *P. mariana* (0.49 mg/100 mg OC) than from needles (2.00 mg/100 mg OC). The higher yields of cinnamyl versus vanillyl phenols result in extremely high C/V ratios of *Picea* pollen (35.2 for *P. glauca* and 13.2 for *P. mariana*) compared to those of gymnosperm needles (0.36–1.1, Hedges and Mann, 1979) and essentially any other measured type of nonwoody vascular-plant tissue. Because of the high yields of cinnamyl phenols, the Λ values of *Picea* pollen are also strongly elevated (9.15 mg/100 mg OC for *P. glauca* and 6.90 mg/100 mg OC for *P. mariana*). The pollen Λ values are similar to those of gymnosperm woody tissues (8.2 mg/100 mg OC), but much higher than those of gymnosperm needles (2.04 mg/100 mg OC). Thus, pollen produces sufficient cinnamyl phenol per unit organic carbon to strongly express their characteristically high yields of *p*-coumaric acid in C/V ratios obtained from mixtures of sedimentary vascular-plant tissues.

Using the average cinnamyl-phenol yield of the fresh pollen of the 2 *Picea* species reported above and the *Picea* pollen concentrations in the Wien Lake sediment samples (Hu et al., 1993), we can estimate the amount of cinnamyl phenols produced by *Picea* pollen in these samples (Fig. 5). The estimates are based on several assumptions:

1. pollen grains contain 50% organic carbon;
2. the average mass of a fresh pollen grain of *P. glauca* or *P. mariana* is 3.983×10^{-4} mg, similar to that of *P. rubens* (red spruce) (Heathcote, 1978; S. Sugita, personal communication);

3. the lignin-phenol composition of a fossil *Picea* pollen grain is similar to that of a fresh one; and
4. the mass of a fossil *Picea* pollen grain is similar to that of a fresh one.

Although some of these assumptions may be invalid, which would affect the accuracy of our estimates, our estimates serve to illustrate the importance of pollen in determining sedimentary lignin composition. Based on these estimates, cinnamyl phenols are absent in Zones I and II because of the absence of *Picea* pollen in these 2 zones; the measured cinnamyl phenols are likely produced by the non-woody angiosperm tissues. In Zones III and IV, the estimated abundances of cinnamyl phenols ranges from 1.33 to 8.89 mg/100 mg OC, which are much higher than the measured values. This discrepancy is probably due to the fact that the third and fourth assumptions are unreasonable. Lignin-phenol composition differs between fresh and experimentally degraded pollen grains (M. A. Goñi, personal communication), implying that pollen degradation may alter the relative abundances of various phenolic compounds. Furthermore, in a fossil pollen grain, much of the original mass has been lost during various processes leading to its incorporation in sediments, and the major remnant structure is the exine, which is extremely resistant to microbial degradation (Faegri et al., 1992). Because we do not know the mass percentage of the exine in a *Picea* pollen grain and the amount of cinnamyl phenols lost through pollen degradation, we cannot calculate how much of the cinnamyl-phenol yield from a bulk sediment comes from *Picea* pollen exines. Nevertheless, the exine of *Picea* pollen is robust, and it likely forms a substantial proportion of the total mass of a fresh grain. If the exine mass of a

Picea pollen grain is 7.0% of that of an entire fresh grain and if the abundance of cinnamyl phenols in a fossil grain is 50% of that of a fresh one, *Picea* pollen in the Wien Lake sediments could be solely responsible for the observed stratigraphic changes in cinnamyl phenols and C/V ratio.

The stratigraphic profiles of the 2 cinnamyl phenols, *p*-coumaric acid and ferulic acid, in the Zone IV samples (Fig. 5) further suggest that *p*-coumaric acid from *Picea* pollen is responsible for the high C/V ratios in this uppermost interval. This observation is consistent with our conclusion that the elevated C/V ratios in Zones III and IV were induced by fossil *Picea* pollen preserved in sediments. The high abundance of *p*-coumaric acid has also been documented in the sporopollenin skeleton of pollen from another pine family species (*Pinus mugo*) by pyrolysis mass spectrometry (Wehling et al., 1989). However, despite the high Λ values of *Picea* pollen and the high concentrations of *Picea* pollen in Zone IV, the Λ values of the Zone IV samples are relatively low and show an upward stratigraphic decrease. This trend probably reflects the dilution effect of lignin-poor organic matter from soils, as discussed in the previous section.

As an alternative interpretation, post-depositional diagenesis could have resulted in the loss of potentially labile cinnamyl phenols, leading to higher C/V ratios in Zones III and IV than in Zones I and II. This interpretation is unlikely because of anoxic sedimentary conditions ~10 cm below the sediment-water interface, under which polymeric-lignin degradation is slow (Kirk, 1984). In addition, no major changes in the physical and chemical characteristics of the Wien Lake sediments (Hu et al., 1993) exist that would indicate changes in the extent of post-depositional degradation from Zone I through Zone IV. The increasing trend in C/V in Zones III and IV could also result from other major pollen types in the Wien Lake sediments, which include *Betula* and *Alnus* (Hu et al., 1993). We have not analyzed the lignin-phenol composition of pollen grains from these 2 taxa to assess this possibility. However, the pollen grains of *Betula* and *Alnus* are much smaller than those of *Picea* (Faegri et al., 1992), and thus their effects on sedimentary lignin composition is likely much less prominent. Lignin analysis of pollen grains of several other taxa (Keil et al., 1998; M. A. Goñi, personal communication) also suggests that only pine family pollen yields exceptionally abundant *p*-coumaric acid.

Our results provide strong evidence for a direct linkage between lignin biomarkers and fossil pollen in sediment records. Previous studies have used the lignin composition of fresh leaves/needles as a geochemical end member of non-woody vascular-plant tissue to estimate the amount of non-woody tissue in marine and lacustrine sediments without taking pollen into consideration (e.g., Hedges et al., 1982; Leopold et al., 1982; Ertel and Hedges, 1984). Such estimates may be reasonable if pollen concentrations are low in sediments, but could be strongly biased if pollen concentrations are high. The pollen concentrations of sediments from Alaskan and other high latitude lakes are generally low compared with those from lower latitude lakes. Nevertheless, as we demonstrate here, the pollen concentrations of Wien Lake sediments are high enough to exert a significant influence on lignin-phenol compositions. Similar situations may occur in the sediments of coastal regions. For example, pollen-derived lignins probably drive the

offshore increases in C/V typical of the Washington coast (Keil et al., 1998). Because of the extremely high yields of cinnamyl phenols and resultant high Λ values of *P. glauca* and *P. mariana* pollen, substantial concentrations of these pollen types in sediments would likely result in overestimates of non-woody tissue and bulk vascular-plant material, if the lignin compositions of gymnosperm needles are routinely used as the end member for nonwoody tissue. The magnitude of such overestimates of non-woody tissue may be reinforced by the high resistance of pollen grains to degradation (Faegri et al., 1992; Keil et al., 1994) versus cinnamyl phenols in leaves and needles (Hedges and Weliky, 1989). A recent lignin study of several other pollen types suggest that the striking differences in the lignin composition between pollen and needles may also apply to other species of the pine family (e.g., *Pinus ponderosa*; Keil et al., 1998), which produce abundant, widespread pollen that is commonly found in aquatic sediments from many regions (Faegri et al., 1992). These new findings together underscore the importance of characterizing the composition of modern pollen from different species to improve the biogeochemical interpretations of sediment lignin records.

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