Diagenesis of Vascular Plant Organic Matter Components during Burial in Lake Sediments

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Abstract. Diagenetic changes are difficult to distinguish from variations in sources of organic matter to sediments. Organic geochemical comparisons of samples of wood, bark, and needles from a white spruce (*Picea glauca*) living today and one buried for 10,000 years in lake sediments have been used to identify the effects of diagenesis on vascular plant matter. Important biogeochemical changes are evident in the aged spruce components, even though the cellular structures of the samples are well preserved. Concentrations of total fatty acids dramatically diminish; unsaturated and shorter chainlength components are preferentially lost from the molecular distributions. Concentrations of total alcohols are similar in the modern and 10,000-year-old wood and bark but markedly lowered in the aged needles. Hydrocarbon concentrations and distributions show little diagenetic change in the 10,000-year-old plant materials. Cellulose components in the wood decrease relative to lignin components, although both types of materials remain in high concentration in comparison to other organic components. Aromatization of abietic acid proceeds more rapidly in buried spruce wood than in bark; retene is the dominant polyaromatic hydrocarbon in the aged wood. In contrast to the variety of changes evident in molecular compositions, neither δ^{13}C values nor C/N ratios differ significantly in the bulk organic matter of modern and aged spruce components.

Key words: Alkanols, C/N ratios, δ^{13}C, fatty acids, lignin hydrolysates, *n*-alkanes, organic matter, sterols.

1. Introduction

Organic matter dispersed in subaqueous sediments has the potential to provide evidence of its original biotic sources on the basis of its elemental, isotopic, and molecular compositions, but these source identifiers may be modified by diagenesis. Postdepositional alterations of organic biomarkers, for example, are well documented in marine and freshwater sediments (cf. Matsuda and Koyama, 1977; Nishimura and Koyama, 1977; Cranwell, 1981; Meyers *et al.*, 1984; Haddad *et al.*, 1992; Canuel and Martens, 1993; Ho and Meyers, 1994). Diagenetic changes in bulk organic matter parameters, particularly organic carbon δ^{13}C values and atomic C/N ratios, have been postulated to occur in modern and ancient sedimentary settings (Spiker and Hatcher, 1987). A mixture of sources contribute organic substances to sediments, moreover, and the relative importance of different sources

often varies over time at a given location (cf. Gaskell *et al.*, 1975; Reed, 1977; Canuel and Martens, 1993). The variability in source composition complicates and even obscures identification of diagenetic effects.

A special opportunity to distinguish between postburial changes in the character and variations in the sources of organic matter was provided by the discovery in 1976 of a spruce forest buried 9850 = B1300 years ago in northern Michigan (Hughes and Merry, 1978; Traver, 1980). Because these buried spruce samples are structurally intact, the problem of a mixture of organic matter sources is eliminated. In this report, we examine the consequences of diagenesis on the molecular, isotopic, and elemental compositions of the buried spruce samples.

2. Samples and Methods

2.1. SAMPLES

Samples of wood, needles and bark were obtained from a white spruce (*Picea glauca*) which was part of a forest which had been rapidly buried in sediment 10,000 years ago. The trees were first drowned in their upright, growth positions as a consequence of glacial damming of a stream near present day Marquette, Michigan (Traver, 1980). The periglacial lake was subsequently filled with sand and fine gravel washed in by the stream, burying the trees. Needles and seed cones from the drowned trees sank and accumulated around the base of the trunks, where they were recovered after exhumation of the forest in 1977. Good preservation of cellular structure in the wood enabled identification of the trees to the species level and provided countable tree rings that showed that the samples are from a tree between 130 and 150 years old (Hughes and Merry, 1978). Samples of wood, needles, and bark were also collected from a white spruce living in the Matthaei Botanical Gardens of The University of Michigan, Ann Arbor, Michigan. The ancient and the modern samples were similarly frozen, freeze-dried, and finely ground prior to analysis.

2.2. EXTRACTION AND ANALYSIS OF LIPID COMPONENTS

Both the extractable and bound fractions of lipid components of the spruce samples were isolated using the extraction and analysis scheme of Leenheer *et al.* (1984). The dried samples were first Soxhlet-extracted for 48 hours with a 2/1 mixture of toluene/methanol to yield the unbound lipid materials. The extracted samples were then saponified with 0.5N KOH in 95% methanol:toluene to release the lipids that were bound in the tissue matrices. Both fractions were treated with methanolic-BF_3 to convert their fatty acids to methyl esters. The lipid fractions were partitioned into several subfractions using silica gel column chromatography. Elution with petroleum ether, 85:15 petroleum ether:benzene, benzene and 1:1 ethyl acetate:benzene gave subfractions containing hydrocarbons, aromatics, fatty acid methyl esters and sterols + alcohols, respectively. Components of the sterol +

alcohol subfraction were converted to silyl ethers using BSFTA (*bis* trimethlysi-lyltrifluoroacetamide).

2.3. HYDROLYSIS OF CELLULOSE AND LIGNIN COMPONENTS OF WOOD

Alkaline hydrolysis was used to degrade the cellulose and lignin biopolymer contents of aged and modern wood samples into analyzable monomeric molecules (cf. Bourbonniere and Meyers, 1983). Samples were hydrolyzed in stainless steel reaction tubes using nitrogen-purged 5N aqueous NaOH and heating for 12 hr at 170°C. The basic solution in the tubes was acidified with 6N HCl, and the hydrolysis products were extracted from the acidic solution with ethyl acetate. The whole hydrolysis extract was silylated with BSFTA prior to analysis to convert alcoholic groups to silyl ethers and carboxylic acid groups to silyl esters.

2.4. GAS CHROMATOGRAPHY

The extractable and bound lipid subfractions and the hydrolysis products were analyzed using a Hewlett-Packard Model 5830 gas chromatograph equipped with a flame ionization detector. Columns used for the lipid subfractions were 10 m fused silica capillary columns coated with either SP2100 or SE52. They were programmed from 70°C to 150°C at 30°/min and then from 150°C to 270°C at 4°/min. The column used for the alkaline hydrolysis products was 3 m × 1/8 in. (3.1 mm) stainless steel packed with 10% SP2250 on 100/120 mesh Supelcoport (Supelco Inc.). It was temperature-programmed from 110°C to 300°C at 4°/min.

Preliminary identifications of compounds were done by comparing gas chromatographic retention times of samples with those of standards. Identifications of components were confirmed using computerized GC-MS of selected samples using a Finnigan 1015 Quadrupole system equipped with a 21 m SE52 glass capillary column.

2.5. ORGANIC CARBON ANALYSIS AND C/N RATIOS

Organic carbon contents of the freeze-dried spruce samples were determined by combustion at 1050°C in a Carlo Erba 1108 CHNS analyzer. Organic matter atomic C/N ratios were calculated from the results of the CHN analysis.

2.6. ORGANIC CARBON ISOTOPIC ANALYSIS

Organic carbon stable isotope ratios of the wood samples were measured using a Finnigan Delta S mass spectrometer calibrated with NBS-20 (carbonate) and NBS-21 (graphite) standards. Combustion of the carbonate-free organic matter was done at 800°C in sealed Vycor tubes in the presence of CuO and Cu. Data are corrected for ^{17}O and are expressed in conventional $\delta^{13}C$ notation relative to the PDB standard.

TABLE I. Geochemical comparisons of wood, needles, and bark from modern and 10,000-year-old white spruce (*Picea glauca*). Concentrations of solvent-extractable and non-solvent-extractable lipid fractions (bound) are given in mg/g dry weight. Organic carbon concentrations are expressed as percent dry weight of each component. Differences between modern and aged samples are indicated by Δ values.

Fraction	Spruce Wood			Spruce Needles			Spruce Bark		
	Modern	Aged	Δ	Modern	Aged	Δ	Modern	Aged	Δ
Fatty Acids									
extractable	1414	77	−1337	7588	1088	−6500	119338	3816	−115522
bound	27	20	−7	504	380	−124	3204	86	−3118
Total	1441	97	−1344	8192	1468	−6724	122542	3902	−118640
Alcohols and Sterols									
extractable	930	731	−199	2400	50	−2350	5943	3770	−2173
bound	38	24	−14	276	58	−218	3669	156	−3513
Total	968	755	−213	2676	108	−2568	9612	3926	−5686
Hydrocarbons									
extractable	27	36	+9	147	197	+50	1608	680	−928
bound	1	1	0	289	10	−279	70	59	−11
Total	28	37	+9	436	207	−229	1678	729	−939
Organic carbon	49	53	+4	50	28	−22	49	41	−8

3. Results and Discussion

The Wisconsin ice sheet retreated from northern Michigan shortly after burial of the spruce forest, and the trees remained covered by sand and gravel. Isostatic rebound elevated the region well above the level of nearby Lake Superior. Gentle hills cover the area, and groundwater easily percolates through the porous sediments of this former lake bottom. The depositional setting has consequently been one of dysaerobic, as opposed to aerobic or anaerobic, conditions.

3.1. ORGANIC CARBON CONCENTRATIONS

The organic carbon concentrations of wood, needles, and bark from the living white spruce are virtually the same (50%), but not in the aged spruce components. The concentration is 41% in the bark recovered from the 10,000-year-old tree, and it is only 28% in the aged needles (Table I). The decreases in the carbon content of these forms of plant-derived organic materials require degradation of carbon-rich fractions such as lipids, dilution of the carbon contents by incorporation of oxygen into the original organic components, or some combination of these two processes. In contrast to the concentration decreases in the needles and bark, the carbon content of the aged wood increases slightly from 49 to 53%. This small

increase suggests preferential losses of organic matter fractions relatively low in carbon, such as carbohydrates and proteins, from the wood. Comparisons of the lipid compositions and of the products of alkaline hydrolysis of modern and aged spruce materials reveals some of the geochemical changes that have occurred.

3.2. EXTRACTABLE AND BOUND LIPIDS

The results of preliminary lipid analyses from modern and aged spruce components were presented by Meyers *et al.* (1980). We have repeated most of these earlier analyses to take advantage of improvements in our analytical procedures, yet some of our earlier data remain unchanged.

The lipid contents of the modern white spruce samples are dominated by fatty acids, whereas hydrocarbons constitute their smallest fraction (Table I). The highest concentrations of all lipid components are found in the bark, where lipid-rich resin is abundant. The needles also have relatively high lipid contents due to their waxy coatings. Wood, which is composed mostly of cellulose and lignin, has the lowest proportion of lipid materials.

Comparison of modern and 10,000-year-old spruce samples reveals dramatic differences in their lipid contents. Concentrations of nearly all of the extractable and bound fractions of the wood, needle, and bark samples are lower for the aged spruce than for the modern spruce (Table I). Total fatty acid concentrations decrease by over 80% in all of the spruce components. Alcohol and hydrocarbon concentrations are similar in the modern and 10,000-year-old wood, but the concentration of alcohols is much lower in the aged needles than the modern ones. Hydrocarbon concentrations increase in the aged, as opposed to modern, wood and in the extractable needle subfraction. Losses of all types of extractable and bound aliphatic lipid components are particularly great in the bark. On the assumption that the biosynthetic processes of this species of spruce have not changed over the past 10,000 years, these differences must arise from diagenesis of the aged material during burial in the water-logged sediment.

Fatty acid concentrations generally show the greatest differences, and these decreases reflect loss and degradation of carboxylic acids originally present in the wood, needles, and bark of the tree. In particular, the extractable fractions of the fatty acids comprise the majority of the total fatty acids and they have greater proportional decreases than found in the bound fractions (Table I). Because the extractable acids are readily released from the tree tissues by simple solvent extraction, it is probable that they exist in forms that are either susceptible to dissolution in sediment pore waters or are vulnerable to microbial attack when buried in sediments.

Our earlier analyses of the fatty acid compositions of wood and needles from the buried spruce revealed preferential losses of unsaturated acid components (Meyers *et al.*, 1980). Present results confirm this finding. The dominant constituent of the extractable acid fraction of modern needles is *n*-octadecenoic acid (n-$C_{18:1}$), which
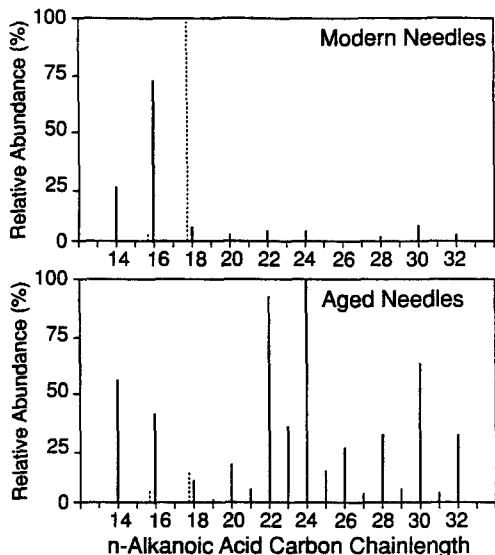
Fig. 1.   Compositions of extractable *n*-alkanoic acids in modern and 10,000-year-old white spruce needles. Contributions of each component are shown in proportion to the major component in each extract. Dotted lines represent total unsaturated C_{16} or C_{18} *n*-acids.

becomes a minor contributor to the total acids extracted from the aged needles (Figure 1). Furthermore, the contributions of all of the shorter chainlength acids are diminished in the aged needles relative to the modern sample. For example, *n*-hexadecanoic acid (n-$C_{16:0}$) changes from being the dominant saturated acid in the modern sample to a minor one in the aged needles. Preferential preservation of the longer constituents magnifies their relative contributions as the concentration of total fatty acids decreases, so that n-$C_{24:0}$ becomes the major component in the fatty acid distribution of the 10,000-year-old needles. The decreases of unsaturated and shorter-chain acids that have been observed in sediment trap studies in Lake Michigan (Meyers and Eadie, 1993) and in sediments of Cape Lookout Bight (Haddad *et al.*, 1992) have been interpreted to indicate preferential degradation of these components. The similar losses found in the spruce needles support the concept of faster diagenetic alteration of unsaturated and lower molecular weight aliphatic acids relative to saturated and longer chain analogs.

The loss in fatty acid concentration is greatest for the spruce bark (Table I), presumably because the modern bark is rich in resinous matter containing relatively low molecular weight lipids. The fatty acid distributions of the modern bark confirm this hypothesis. Neither the extractable nor the bound distributions contain significant contributions of n-C_{26+} components (Figure 2). Both have large amounts of n-$C_{18:1}$, and they differ from the distribution of extractable fatty acids of the needles in having n-$C_{22:0}$ and n-$C_{24:0}$ as major alkanoic acids. The fatty acid distributions of the aged bark are similar for the extractable and bound fractions (Figure 2). Unsaturated components are diminished, and n-$C_{22:0}$ is the dominant
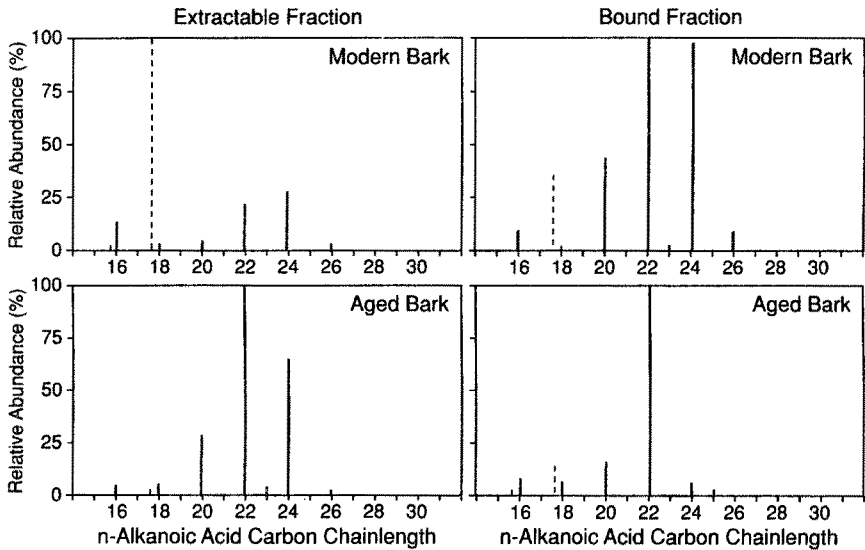
Fig. 2. Compositions of extractable and bound *n*-alkanoic acids in samples of modern and 10,000-year-old white spruce bark. Contributions of each component are shown in proportion to the major component in each subfraction. Dotted lines represent total unsaturated C_{16} or C_{18} *n*-acids.

component. These diagenetic changes resemble those identified in the extractable fatty acids from the needles and earlier reported for spruce wood (Meyers *et al.*, 1980).

Results of a comparison of the fatty acid compositions of preserved and fresh components of the marine macroalga *Sargassum* bear many similarities to our results. Concentrations of total fatty acids in 380-year-old *Sargassum* recovered from the seabottom in the Orca Basin, northern Gulf of Mexico, were half those of a living plant (Kennicutt *et al.*, 1992). The proportions of unsaturated acids decreased markedly in the fronds and bladders of the aged plant, but remained fairly well preserved in the woody stipes (Harvey and Kennicutt, 1992). Although *Sargassum* and *Picea glauca* are very different kinds of plants, the results of the two studies show that the original compositions of their different plant components impact the susceptibilities of biomarkers to diagenesis in sediments. A particularly important difference between the two studies is that the Orca Basin is an anoxic marine setting, whereas the former lake basin is a dysaerobic freshwater setting. Some of the losses of unsaturated acids observed in the aged *Sargassum* may be from conversion to saturated forms by hydrogenation of carbon-carbon double bonds under the anoxic conditions and from incorporation of sulfur across the double bonds (Harvey and Kennicutt, 1992). These types of diagenetic changes are unlikely to have participated in diminishing the proportion of unsaturated acids in the spruce components. Instead, these fatty acid components were either dissolved
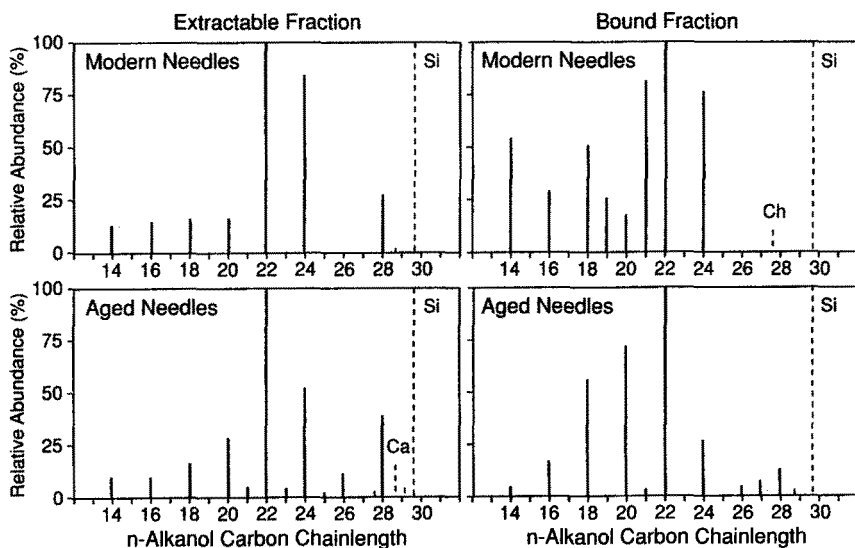
Fig. 3.   Compositions of extractable and bound n-alkanols and sterols in samples of modern and 10,000-year-old white spruce needles. Contributions of each component are shown in proportion to the major component in each subfraction. Dashed lines represent sterols: cholesterol (Ch), Campesterol (Ca), Stigmasterol (St), and -Sitosterol (Si).

and washed away as a consequence of their greater solubility than saturated acids, or preferentially degraded by microbes.

The greatest overall decrease found in the various lipid subfractions of the spruce components is in the concentration of the extractable alcohol plus sterol fraction, which has a 98% decrease between the modern and aged needles (Table I). Unlike the fatty acids, distributions of individual n-alkanol and sterol components of the modern and aged needle samples are similar and therefore indicate no selective losses (Figure 3). The major components are $C_{22:0}$ in the n-alkanol distributions and β-sitosterol in the sterol distributions. The dramatic decreases in concentration have no effect on these compositions. Similar preservation of the original relative proportion of sterols has also been reported in the sediments of Rostherne Mere, England (Gaskell and Eglinton, 1977), indicating that this class of lipids retains a record of its original biological source in freshwater sediments.

Concentrations of fatty alcohols plus sterols in the *Sargassum* components also had the greatest differences between fresh and aged material, decreasing an average of 54% in the stipes, fronds, and bladders (Harvey and Kennicutt, 1992). Unlike found in the spruce components, however, major changes occurred in the compositions of the fatty alcohol and in the sterol fractions of the algal samples. n-Alkanols were selectively degraded, with the result that contributions of the isoprenoid alcohol phytol became magnified. Among the sterols, fucosterol was preferentially preserved in all three *Sargassum* components, while contributions of other sterols became depleted. Reduction of originally unsaturated stenols to
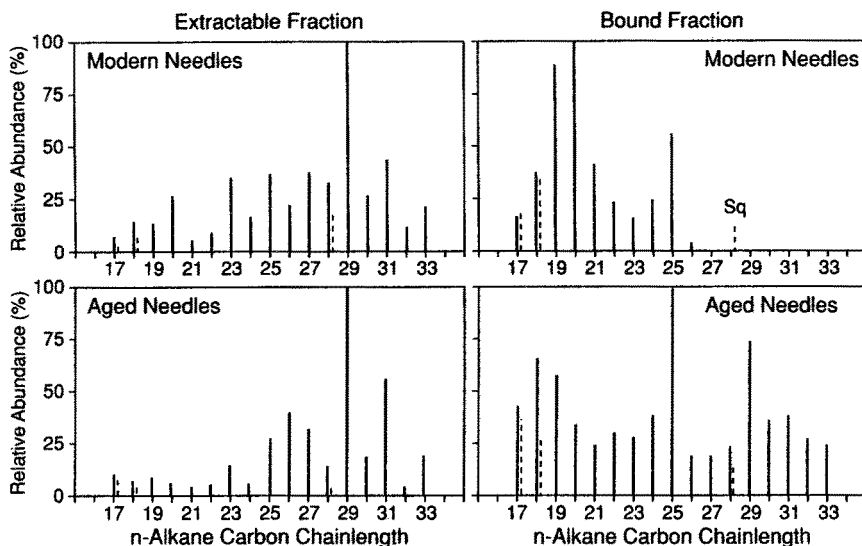
Fig. 4.   Compositions of extractable and bound n-alkanes in samples of modern and 10,000-year-old white spruce needles. Contributions of each component are shown in proportion to the major component in each subfraction. Dotted lines represent the isoprenoid hydrocarbons pristane (Pr), phytane (Ph), and squalene (Sq).

their saturated analogs, stanols, has been postulated to improve preservation of sterols in sediments (Gaskell and Eglinton, 1975). Cholestanol was curiously at lower amounts in the aged *Sargassum* than in fresh material. This finding is quite unexpected in an anoxic setting and suggests that sterols experience complicated diagenetic alterations in marine sediments.

Hydrocarbons are generally considered to be less sensitive to diagenetic alteration and destruction in lake sediments than other types of lipids (cf. Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993). The increase in their concentration in the aged wood probably reflects greater proportional losses of non-hydrocarbon components and mirrors the observed increase in carbon content (Table I). If the hydrocarbons are assumed to be relatively resistant to diagenetic changes, then their composition should not be greatly affected by burial in sediments for 10,000 years. This assumption is borne out by the evidence of little difference in the distributions of the hydrocarbons extracted from the modern and aged needle samples (Figure 4).

The bound hydrocarbon fraction of the needles differs from the extractable fraction in displaying several important and curious differences between the modern and aged samples. First, a large (96%) decrease in the concentration of bound hydrocarbons occurs (Table I). Second, significant differences in the distributions of individual n-alkanes are evident (Figure 4). Third, relatively large contributions of the isoprenoid hydrocarbons pristane and phytane are present in these distributions. These compounds are believed to originate either from thermal alterations of the
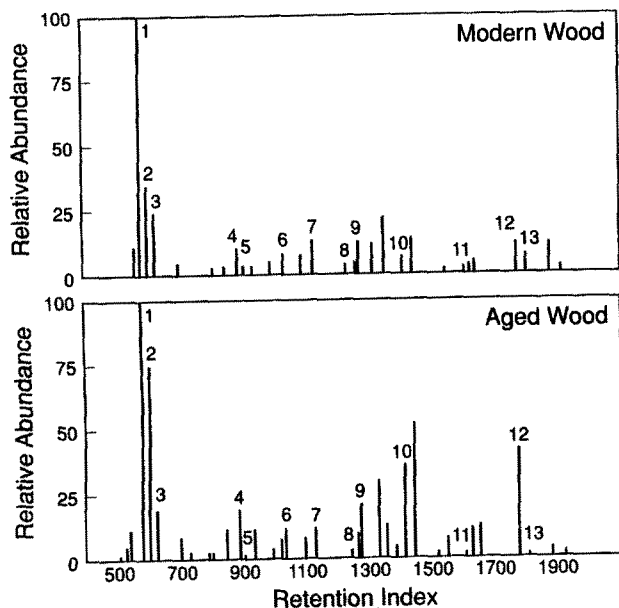
Fig. 5.   Products of alkaline hydrolysis of modern and 10,000-year-old white spruce wood reported by Bourbonniere and Meyers (1983). Identifications of numbered individual components are provided in Table II.

chlorophyll sidechain phytol or from methanogenic bacteria (cf. ten Haven *et al.*, 1987), and neither possibility is likely in this case. Finally, it is not clear in what form hydrocarbons, which possess no functional groups, come to be bound at such a high proportion in the modern needles (Table I). These differences remain unexplained.

3.3. ALKALINE HYDROLYSATES

Important differences appear between the alkaline hydrolysis products of the 10,000-year-old and modern spruce wood (Figure 5; Bourbonniere and Meyers, 1983). Lactic acid is the dominant product for both samples and is possibly derived from cellulose (Table II; Samuelson and Stolpe, 1973). Oxalic, vanillic, and ferrulic acids are proportionally more abundant in the old sample than in the modern one. The vanillic and ferullic acids are derived from lignin. Their proportional increase in the older wood indicates selective preservation of lignin relative to polysaccharides such as cellulose, which agrees with other studies of aged wood (Leo and Barghoorn, 1970; Hatcher *et al.*, 1981; Hedges *et al.*, 1985; Spiker and Hatcher, 1987). As noted by Meyers *et al.* (1980), the ratio of cellulose-derived components to lignin-derived components decreases from 2.2 in the modern wood to 1.2 in the aged wood. Cellulose nonetheless remains the major biogeochemical component in the 10,000-year-old wood on the basis of the dominance of the lactic acid peak.

TABLE II. Selected components obtained from alkaline hydrolysis of modern and aged wood. Numbers refer to relative concentration peaks in Figure 5.

Peak Number	Tentative Identification	Possible Source	Reference
1	Lactic acid	cellulose	Samuelson and Stolpe (1973)
2	Oxalic acid	fungi	Stevenson (1967)
3	2-Hydroxybutanoic acid	cellulose	Lowendahl et al. (1976)
4	Succinic acid	all plants	Stevenson (1967)
5	Maleic & fumaric acids	all plants	Stanier et al. (1970)
6	3,4-Dihydroxybutanoic acid	cellulose	Lowendahl et al. (1976)
7	2-Hydroxybenzoic acid	fungi	Martin et al. (1972)
8	4-Hydroxybenzoic acid	lignin	Flaig et al. (1975)
9	2,5-Dihydroxy-3-pentenoic acid	cellulose(?)	Sowden (1957)
10	Vanillic acid	lignin	Hedges and Parker (1976)
11	n-C_{16} acids	ubiquitous	
12	Ferulic acid	lignin	Robinson (1963)
13	n-C_{18} acids	ubiquitous	

The proportions of n-alkanoic acids produced by alkaline hydrolysis are less in the old wood than in the modern sample. Both n-$C_{16:0}$ and n-$C_{18:0}$ diminish in relative contribution to the hydrolysis products of the 10,000-year-old sample, indicating their selective diagenetic degradation. This decline in abundance is similar to those of the extractable fatty acids in the wood, needles, and bark of the buried tree (Table I), but it is not as extensive. The fatty acids released by extraction of the spruce components are probably more available to diagenetic attack than those released by alkaline hydrolysis of the wood.

3.4. CYCLIC HYDROCARBONS

LaFlamme (1979) examined samples of the aged wood and bark for polycyclic aromatic hydrocarbons and found diagenetic products derived from abietic acid. Retene was the major cyclic hydrocarbon present in the extract of the aged wood and was accompanied by a small amount of fichtelite (see Figure 6). These components were present in the ratio 6/1. In contrast, the retene/fichtelite ratio in the bark extract was 1/5. Neither retene nor fichtelite was present in the extracts of modern wood or bark, although abietic acid methyl ester was present in the wood extract.

Disproportionation is a process that converts some precursor organic compound into equal portions of an oxidized, aromatic product and a reduced, hydrogenated product (Figure 6). Disproportionation of abietic acid into fichtelite and retene (Simoneit, 1977; Barnes and Barnes, 1983) may have occurred in the spruce materials while buried in the waterlogged sediments for 10,000 years, but the predicted 1/1 ratio of products is not found. The difference in the ratios of retene and fichtelite between the wood and the bark shows that aromatization, an oxidative
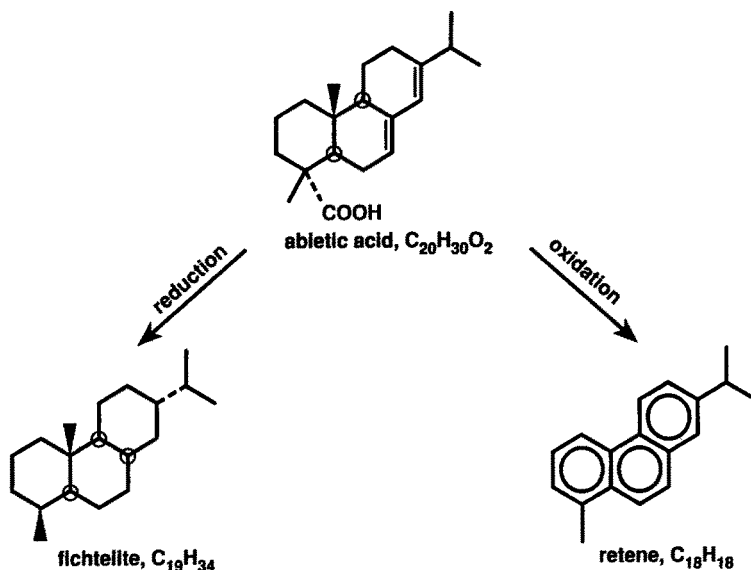
Fig. 6. Disproportionation of abietic acid to yield fichtelite and retene (after Skragin, 1964). The disproportionation products were found in samples of 10,000-year-old white spruce wood and bark by LaFlamme (1979), but not in the equal proportions expected from this process.

process, proceeds faster in the wood than in the bark. Spruce bark evidently contains biochemical components that retard microbial oxidation of organic matter in a subaqueous setting.

3.5. CARBON ISOTOPIC COMPOSITIONS

The changes evident in the lipid, cellulose, and lignin compositions indicate that early diagenetic alterations have occurred to the spruce samples. Preferential degradation of more reactive fractions of the total organic matter has the potential to modify the bulk carbon isotopic compositions of the spruce materials. Organic matter is a mixture of different types of compounds which have different carbon isotopic compositions. The amino acid fraction of marine plankton, for example, has an average $\delta^{13}C$ value of $-17‰$, whereas the lipid fraction has an average value of $-28‰$ (Degens, 1969). Field data suggest that alterations of carbon isotopic compositions may in fact occur in sediments. For example, a downcore change to lighter carbon isotope values has been noted in organic-carbon-rich sapropelic sediments from Mangrove Lake, a seawater-dominated system on Bermuda (Hatcher et al., 1982). The total difference in the carbon isotope values is $\cong -2‰$ over the past several thousands of years during which these sediments have accumulated. This shift is postulated to result at least partly from selective loss of the isotopically heavy carbohydrate fraction of total organic matter (Spiker and Hatcher, 1984), but changes in the mix of land-derived and marine-derived organic matter in the sediments of Mangrove Lake may also contribute (Meyers, 1994).

TABLE III. Comparisons of elemental and isotopic compositions of samples of fresh plant matter to those of plant matter buried in sediments. Organic C/N values are atom/atom ratios. $\delta^{13}C_{organic}$ values are given relative to the PDB standard. Differences between modern and ancient samples are indicated by Δ values.

Sample	Δ Age	Atomic C/N			$\delta^{13}C$ (‰)			Reference
		modern	aged	Δ	modern	aged	Δ	
White spruce wood	3 months	191	161	−30	nd	nd	−	Goñi et al. (1993)
Spartina roots	18 months	113	49	−64	−13.1	−14.1	−1.0	Benner et al. (1992)
Cedar needles	~100 years	51	29	−22	nd	nd	−	Hedges and Weliky (1989)
Fir/hemlock needles	~100 years	58	49	−9	nd	nd	−	Hedges and Weliky (1989)
White oak wood	~180 years	218	128	−90	nd	nd	−	Wilson et al. (1993)
White oak wood	~340 years	218	60	−158	nd	nd	−	Wilson et al. (1993)
Sargassum	~380 years	nd	nd	−	−16.1	−16.5	−0.4	Harvey and Kennicutt (1992)
Sphagnum	~1000 years	9	10	+1	−27.5	−27.1	+0.4	Macko et al. (1991)
Red alder wood	~2500 years	264	106	−158	nd	nd	−	Hedges et al. (1985)
Spruce wood	~2500 years	546	541	−5	nd	nd	−	Hedges et al. (1985)
White spruce wood	~10,000 years	163	240	+77	−23.1	−23.6	−0.5	this study
White spruce needles	~10,000 years	42	39	−3	−25.1	−27.5	−2.4	this study
White spruce bark	~10,000 years	57	93	+36	−23.5	−24.7	−1.2	this study
White oak wood	~25,000 years	276	111	−165	nd	nd	−	Hedges et al. (1985)

Comparison of the bulk organic $\delta^{13}C$ values of modern plant components to those that have been aged in sediments for various times shows that shifts to more negative values are common. The increased $\delta^{13}C$ depletion in the aged components varies between -0.4 to $-2.4\%o$ (Table III). The largest shifts are found in the 10,000-year-old spruce needles and bark. In similar studies, laboratory decomposition of the marsh grass, *Spartina alterniflora*, selectively removed isotopically heavy organic material and created a bulk organic carbon $\delta^{13}C$ shift of $-1\%o$ (Table III; Benner *et al.*, 1987). Also, small shifts to a lighter $\delta^{13}C$ values have been reported in the 380-year-old *Sargassum* preserved in the Orca Basin ($-0.4\%o$: Harvey and Kennicutt, 1992) and in *Spartina* buried for 18 months in a salt marsh ($-1.0\%o$: Benner *et al.*, 1992). As concluded by Spiker and Hatcher (1987), shifts of this type can be expected from diagenetic losses of cellulosic components relative to lignin, which is consistent with the changes found in the spruce wood hydrolysates (Figure 5). Preferential degradation of the relatively reactive and isotopically heavy proteinaceous fraction would contribute to the observed shift to lighter isotopic compositions.

In contrast to the general pattern of shifts to more negative compositions, one study of diagenetic carbon isotope change, that of *Sphagnum*, found that a small positive shift of $0.4\%o$ occurred (Table III; Macko *et al.*, 1991). This isotopic change was accompanied by a decrease in the carbon content of the *Sphagnum* from 60% to 43% (Macko *et al.*, 1991). The combination of the isotopic and elemental changes suggests that selective losses of isotopically light lipid-rich material may have occurred in this plant material and that cellulosic material became concentrated by this type of diagenetic change.

None of the isotopic alterations listed in Table III are adequate to erase the differences (cf. Meyers, 1994) that exist between the general sources of organic matter to sediments. They are large enough, however, to mask isotopic evidence for changes in productivity (e.g., Schelske and Hodell, 1991). Important diagenetic $\delta^{13}C$ shifts with depth are generally absent in lake sediments. In a core from Lake Michigan, for example, $\delta^{13}C$ values remained at $-26\%o$ from modern to 3500-year-old sediments in which organic carbon concentrations varied between 1 to 3% (Rea *et al.*, 1980). Similarly, Jasper and Gagosian (1989) report that the source of organic matter controls the $\delta^{13}C$ values of a 100 Ky sediment core from the Pygmy Basin in the Gulf of Mexico. Fluctuations from $-22.5\%o$ to $-26.5\%o$ are caused by shifts in relative proportions of terrigenous and marine inputs to this coastal marine setting.

3.6. ORGANIC C/N RATIOS

Origin of organic matter from aquatic as opposed to land sources can be distinguished from the C/N ratios of organic matter in sediments. The presence or absence of cellulose in the plant sources of organic matter influences the sedimentary C/N ratios. Nonvascular aquatic plants have low C/N ratios, typically between 4 and

10, whereas vascular land plants, which contain cellulose, have C/N ratios of 20 and greater.

Selective degradation of organic matter components during early diagenesis can modify elemental compositions and hence C/N ratios of organic matter in sediments. C/N ratios of modern plant samples are typically higher than those of plant matter that has been buried in sediments (Table III). A similar change, although much more subtle, accompanies deposition of disseminated organic matter. Settling particles in Lake Michigan have a C/N value of 9; the ratio in resuspended bottom sediments is 8 (Meyers and Ishiwatari, 1993). A decrease in C/N ratios has also been observed in soils (e.g., Sollins *et al.*, 1984), where it involves the microbial immobilization of nitrogenous material accompanied by the remineralization of carbon. These changes in the elemental composition of sedimentary organic matter are not commonly large enough, however, to erase the original C/N difference between vascular and non-vascular plants.

Atomic C/N ratios both increase and decrease in the aged spruce components that we have studied. The C/N ratio in fresh wood is 163 whereas that in the aged wood is 240, and the ratios of the respective samples of needles are 42 and 39 (Table III). In comparison, Benner *et al.* (1992) report a decrease from 113 to 48 in the C/N ratio of *Spartina* tissues, mostly rhizomes, during decomposition while buried in a salt marsh. These changes imply selective loss of carbon-rich fractions of organic matter and selective retention of nitrogen-rich components during early diagenesis. Polysaccharides, in particular, appear to be especially prone to diagenetic removal (Benner *et al.*, 1992).

Burial in sediments appears to stabilize organic matter C/N ratios to major diagenetic alteration. Preservation of the C/N source signal is found by Ertel and Hedges (1985), who demonstrate that vascular plant debris isolated from a coastal marine sediment sample having a bulk C/N of 15 retains the elevated C/N values characteristic of cellulosic plants. The sediment ratio indicates mixing of vascular and nonvascular plant debris rather than diagenetic alteration. Talbot and Johannessen (1992) similarly conclude that selective diagenesis has had no discernible effect on organic matter C/N ratios in sediments as old as 27,500 years in Lake Bosumtwi, Ghana. The C/N ratios of the aged spruce components retain the elevated values indicative of their original, vascular plant origins.

4. Summary and Conclusions

This comparison of the organic geochemical characteristics of spruce components buried in lake sediments for 10,000 years with those of a living white spruce has shown that important compositional changes occur at the molecular level. Despite these changes, the elemental and carbon isotopic source characters of the three types of plant material studied do not undergo substantial alteration. Furthermore, many of the biomarker molecules that are considered diagnostic of land-derived plants

remain well preserved in the buried tree material. The findings of the comparisons can be summarized as:

1. Fatty acids, alkanols, and sterols experience significant diagenetic alterations. Concentrations of these oxygen-containing lipids decrease up to 97% between the modern and the aged components. Unsaturated and short-chain fatty acids are particularly subject to diagenetic loss.

2. Molecular distributions of alkanols, sterols, and hydrocarbons reveal little compositional change between the modern and 10,000-year-old samples despite substantial decreases in concentrations of the alkanol and sterol fractions. The vascular plant biomarkers, β-sitosterol and n-C_{29} alkane, are the dominant components in their respective lipid subfractions.

3. Cellulose components are diminished relative to lignin components in hydrolysates of the aged wood, as compared to modern wood. Cellulose remains the dominant wood content, yet it is evidently more susceptible to diagenesis than is lignin.

4. Carbon isotopic compositions of the buried plant material change very little in comparison to the magnitudes of the molecular alterations. $\delta^{13}C$ values remain close to their initial values and preserve their source character.

5. Large changes occur in the C/N ratios of vascular plant matter during burial in sediments, but these changes are not adequate to erase the characteristically high C/N values of land-derived cellulose-rich organic matter.

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References

Barnes, M. A. and Barnes, W. C. (1983) Oxic and anoxic diagenesis of diterpenes in lacustrine sediments. In *Advances in Organic Geochemistry 1981* (ed. M. Bjorøy), John Wiley, Chichester, pp. 289–298.

Benner, R., Fogel, M. L., and Sprague, E. K. (1992) Diagenesis of belowground biomass of *Spartina alterniflora* in salt-marsh sediment. *Limnol. Oceanogr.* **36**, 1358–1374.

Benner, R., Fogel, M. L., Sprague, E. K., and Hudson, R. E. (1987) Depletion of $\delta^{13}C$ in lignin and its implications for stable carbon isotope studies. *Nature* **329**, 708–710.

Bourbonniere, R. A. (1979) *Geochemistry of Humic Matter in Great Lakes Sediments*, PhD Dissertation, University of Michigan, Ann Arbor, 373 pages.

Bourbonniere, R. A. and Meyers, P. A. (1983) Characterization of sedimentary humic matter by alkaline hydrolysis. *Org. Geochem.* **5**, 131–142.

Canuel, E. A. and Martens, C. S. (1993) Seasonal variations in the sources and alteration of organic matter associated with recently-deposited sediments. *Org. Geochem.* **20**, 563–577.

Cranwell, P. A. (1981) Diagenesis of free and bound lipid components in terrestrial detritus deposited in a lacustrine sediment. *Org. Geochem.* **3**, 79–89.

Degens, E. T. (1969) Biogeochemistry of stable carbon isotopes. In *Organic Geochemistry – Methods and Results* (eds. G. Eglinton and M. T. J. Murphy), Springer, New York, pp. 304–329.

Ertel, J. R. and Hedges, J. I. (1985) Sources of sedimentary humic substances: vascular plant debris. *Geochim. Cosmochim. Acta* **49**, 2097–2107.

Flaig, W., Beutelspacher, H., and Rietz, E. (1975) Chemical composition and physical properties of humic substances. In *Soil Components* (ed. J. B. Giesking), Springer, New York, Vol. 1, pp. 1–211.

Gaskell, S. J. and Eglinton, G. (1976) Sterols of a contemporary lacustrine sediment. *Geochim. Cosmochim. Acta* **40**, 1221–1228.

Gaskell, S. J., Morris, R. J., Eglinton, G., and Calvert, S. E. (1975) The geochemistry of a recent marine sediment off northwest Africa. An assessment of source of input and early diagenesis. *Deep-Sea Res.* **22**, 777–789.

Goñi, M. A., Nelson, B., Blanchette, R. A., and Hedges, J. I. (1993) Fungal degradation of wood lignins: Geochemical perspectives from CuO-derived phenolic dimers and monomers. *Geochim. Cosmochim. Acta* **57**, 3985–4002.

Haddad, R. I., Martens, C. S., and Farrington, J. W. (1992) Quantifying early diagenesis of fatty acids in a rapidly accumulating marine sediment. *Org. Geochem.* **19**, 205–216.

Harvey, H. R. and Kennicutt II, M. C. (1992) Selective alteration of *Sargassum* lipids in anoxic sediments of the Orca Basin. *Org. Geochem.* **18**, 181–187.

Hatcher, P. G., Breger, I. A., and Earl, W. L. (1981) Nuclear magnetic resonance studies of ancient buried wood – I. Observations on the origin of coal to the brown coal stage. *Org. Geochem.* **3**, 49–55.

Hedges, J. I. and Parker, P. L. (1976) Land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochim. Cosmochim. Acta* **40**, 1019–1029.

Hedges, J. I. and Weliky, K. (1989) Diagenesis of conifer needles in a coastal marine environment. *Geochim. Cosmochim. Acta* **53**, 2659–2673.

Hedges, J. I., Cowie, G. L., Ertel, J. R., Barbour, R. J., and Hatcher, P. L. (1985) Degradation of carbohydrates and lignins in buried wood. *Geochim. Cosmochim. Acta* **46**, 701–711.

Ho, E. S. and Meyers, P. A. (1994) Variability of early diagenesis in lake sediments: Evidence from the sedimentary record in an isolated tarn. *Chem. Geol.* **112**, 309–324.

Hughes, J. D. and Merry, W. J. (1978) Marquette buried forest 9,850 years old (abs). Abstracts of Papers of the 144th National AAAS Meeting, 115.

Jasper, J. P. and Gagosian, R. B. (1989) Glacial-interglacial climatically-forced sources of sedimentary organic matter to the late Quaternary northern Gulf of Mexico. *Nature* **342**, 60–62.

Kennicutt, M. C., Macko, S. A., Harvey, H. R., and Bidigare, R. R. (1992) Preservation of *Sargassum* under anoxic conditions: Molecular and isotopic evidence. In *Organic Matter: Productivity, Accumulation, and Preservation in Recent and Ancient Sediments* (eds. J. Whelan and J. W. Farrington), Columbia University Press, New York, pp. 123–141.

LaFlamme, R. (1979) *Polycyclic Aromatic Hydrocarbons in the Sedimentary Environment*, PhD Dissertation, Tufts University, Boston, 208 pages.

Leenheer, M. J., Flessland, K. D., and Meyers, P. A. (1984) Comparison of lipid character of sediments from the Great Lakes and the Northwestern Atlantic. *Org. Geochem.* **7**, 141–150.

Leo, R. F. and Barghoorn, E. S. (1970) Phenolic aldehydes: Generation from fossil woods and carbonaceous sediments by oxidative degradation. *Science* **168**, 582–584.

Lowendahl, L., Petersson, G., and Samuelson, O. (1976) Formation of carboxylic acids by degradation of carbohydrates during kraft cooking of pine. *Tappi* **50**, 118–121.

Macko, S. A., Engel, M. H., Hartley, G., Hatcher, P., Helleyr, R., Jackman, P., and Silfer, J. A. (1991) Isotopic compositions of individual carbohydrates as indicators of early diagenesis of organic matter in peat. *Chem. Geol.* **93**, 147–161.

Martin, J. P., Haider, K., and Wolf, D. (1972) Synthesis of phenols and phenolic polymers by *Hendersonula toruloidea* in relation to humic acid formation. *Soil Sci. Soc. Am. Proc.* **36**, 311–315.

Matsuda, H. and Koyama, T. (1977) Early diagenesis of fatty acids in lacustrine sediments – I. Identification and distribution of fatty acids in recent sediment from a freshwater lake. *Geochim. Cosmochim. Acta* **41**, 777–783.

Meyers, P. A. (1994) Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* **114**, 289–302.

Meyers, P. A. and Eadie, B. J. (1993) Sources, degradation and recycling of organic matter associated with sinking particles in Lake Michigan. *Org. Geochem.* **20**, 47–56.

Meyers, P. A. and Ishiwatari, R. (1993) Lacustrine organic geochemistry – an overview of indicators of organic matter sources and diagenesis in lake sediments. *Org. Geochem.* **20**, 867–900.

Meyers, P. A., Kawka, O. E., and Whitehead, D. R. (1984) Geolipid, pollen, and diatom stratigraphy in postglacial lacustrine sediments. *Org. Geochem.* **6**, 727–732.

Meyers, P. A., Leenheer, M. J., Erstfeld, K. M., and Bourbonniere, R. A. (1980) Changes in spruce composition following burial in lake sediments for 10,000 yr. *Nature* **287**, 534–536.

Neyroud, J. A. and Schnitzer, M. (1975) The alkaline hydrolysis of humic substances. *Geoderma.* **13**, 171–188.

Nishimura, M. and Koyama, T. (1977) The occurrence of stanols in various living organisms and the behavior of sterols in contemporary sediments. *Geochim. Cosmochim. Acta* **41**, 379–385.

Rea, D. K., Bourbonniere, R. A., and Meyers, P. A. (1980) Southern Lake Michigan sediments: Changes in accumulation rate, mineralogy, and organic content. *J. Great Lakes Res.* **6**, 321–330.

Reed, W. E. (1977) Biogeochemistry of Mono Lake, California. *Geochim. Cosmochim. Acta* **41**, 1231–1245.

Robinson, T. (1963) *The Organic Constituents of Higher Plants.* Burgess.

Samuelson, O. and Stolpe, L. (1973) Degradation of cellulose and glucose by oxygen-alkali treatment. *Acta Chem. Scand.* **27**, 3061–3068.

Schelske, C. L. and Hodell, D. A. (1991) Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments. *Limnol. Oceanogr.* **36**, 961–975.

Simoneit, B. R. T. (1977) Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. *Geochim. Cosmochim. Acta* **41**, 463–476.

Skragin, A. I. (1964) Preparation and utilization of fichtelite and retene. *Tr. Vses. Nauchn.-Tekhn. Soveshch. Gorki 1963*, 108–115.

Sollins, P., Spycher, G., and Glassman, C. A. (1984) Net nitrogen mineralization from light-fraction and heavy fraction forest soil organic matter. *Soil Biol. Biochem.* **16**, 31–37.

Sowden, J. C. (1957) The saccharinic acids. In *Advances in Carbohydrate Chemistry* (eds. M. L. Wolfram and R. S. Tipson), Academic Press, New York, Vol. 12, pp. 35–79.

Spiker, E. C. and Hatcher, P. G. (1987) The effects of early diagenesis on the chemical and stable isotopic composition of wood. *Geochim. Cosmochim. Acta* **51**, 1385–1391.

Stanier, R. Y., Doudoroff, M., and Adelberg, E. A. (1970) *The Microbial World*, 3rd edn. Prentice Hall.

Stevenson, F. J. (1967) Organic acids in soil. In *Soil Biochemistry* (ed. A. D. McClaren and G. H. Peterson), Marcel Dekker, Vol. 1, pp. 119–146.

Talbot, M. R. and Johannessen, T. (1992) A high resolution palaeoclimatic record for the last 27,500 years in tropical West Africa from the carbon and nitrogen isotopic composition of lacustrine organic matter. *Earth Planet. Sci. Lett.* **110**, 23–37.

Ten Haven, H. L., de Leeuw, J. W., Rullkötter, J., and Sinninge Damsté, J. S. (1987) Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. *Nature* **330**, 641–643.

Traver, R. (1980) Riddles of a buried forest. *Am. Forests* **86**, 32–35, 51–54.

Wilson, M. A., Godfrey, I. M., Hanna, J. V., Quezada, R. A., and Finnie, K. S. (1993) The degradation of wood in old Indian Ocean shipwrecks. *Org. Geochem.* **20**, 599–610.