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Composition of Lignin-Degradation Products, Lipids, and Opal Phytoliths in a Peat Profile Accumulated since 32,000 Years B.P. in Central Japan

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The compositions of lignin degradation products, fatty acids as well as opal phytoliths of peaty sediments were correlated with the environmental and climatic changes of a wetland which has been formed continuously since 32,000 yBP in Central Japan. Determination of phenolic and lipid compounds provided information on the aerobic and anaerobic conditions of the wetland as well as the types of vegetation. Palmitic and stearic acids were more decomposable and their contents reflected well the changes in the state of the wetland. These trends agreed well with the field-observation of the characteristics of the profile and with the results of opal phytolith analysis. The combination of organic chemical analysis and plant phytolith analysis was found to be effective for elucidating the paleo-environment surrounding the wetland.

Key Words: **fatty acid composition, lipids, opal phytoliths, phenolic acids, radiocarbon dating.**

The formation of the Ohnohara wetland at Tsukude-village in central Japan started ca. 32,000 years ago (Tsutsuki and Kuwatsuka 1992). It is considered that this wetland provides information on the environmental and climatic changes which occurred during the Holocene and the late Pleistocene periods by the analysis of its sediments. Peaty sediments of this wetland have been subjected to geological, palynological, mineralogical, and biological studies by several researchers belonging to the Ohnohara wetland research group (Ohnohara Wetland Research Group 1989, 1991). In this study, we analyzed the soil organic constituents to define the past environmental changes, because some plant constituents such as lignin and lipids are resistant to decay under the anaerobic conditions prevailing in wetlands (Stevenson 1982). We analyzed the contents of the phenolic and lipid compounds in the peat samples collected from different layers of the profile to correlate their changes with paleoenvironments. Opal phytolith analysis was also carried out to identify the plant species predominating in the wetland in each period. Time scales of peat soil development were determined based on ^{14}C dating and tephrochronology data.

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SOIL PROFILE AND SAMPLES EXAMINED

A series of peat samples was collected from two soil profiles in the Ohnohara wetland area, Tsukude-Village, Minami-Shidara, Aichi Prefecture (36°53′55″N, 138°27′28″E). The Ohnohara wetland and several other wetlands are located within a small basin developed on a highland plain at an altitude of 530–535 m surrounded by hills of an elevation of 700–800 m. The major part of the wetland which previously occupied ca. 20 ha has been utilized as paddy fields since 1964–1966. In some parts of this wetland area peaty material is being excavated for processing as a soil conditioner by a company. By courtesy of the company, samples were collected at the open cut site of the peat profile. The Hosoda profile was excavated at the Hosoda site on Feb. 15, 1987, and the Shirasu profile was excavated at the Shirasu site on Jan. 17, 1988. Samples were collected from these profiles at intervals of ca. 10 cm. Diagrams of the investigated profiles are presented in Fig. 1.

ANALYTICAL METHODS

1. Radio-carbon dating of sediments. Radio-carbon dating of sediments was carried out according to the method of Nakamura et al. (1992) using the Tandetron accelerator mass-spectrometer of Nagoya University.

2. Determination of C and N contents. Determination of C and N contents was carried out using the carbon and nitrogen analyzer (CN corder MT-500, Yanaco) with cobalt oxide as oxidizing agent.

3. Opal phytolith analysis. According to Kondo and Sase (1986), the peat sample was digested with a mixed acid solution of $HClO_4$, HNO_3, and H_2SO_4 (4 : 10 : 1), and treated with ultrasonics (150 W, 10 kc s^{-1}, 5–10 min). Particles smaller than 10^{-6} m were removed by the sedimentation method, and opal phytoliths were separated by floating on a heavy liquid with a specific gravity of 2.3. After the amounts of the opal phytoliths was determined, they were identified and counted under an optical microscope.

4. Phenolic degradation products. Degradation of peat samples with CuO-NaOH and subsequent extraction of phenolic compounds were carried out according to the method of Hedges and Ertel (1982). The contents of the phenolic compounds in the degradation products were determined after silylation with *N,O*-bis-trimethylsilyl-acetamide by gas-liquid chromatography according to the method of Tsutsuki and Kuwatsuka (1979) with slight modifications, where phenoxyacetic acid was used as the internal standard while SE-30 on Chromosorb WAW DMCS packed in a glass column with 2 m length, 3 mm I.D., and 5 mm O.D. was used as a GC column. The column temperature was programmed from 100 to 250°C at a rate of 5°C min^{-1}. The temperature of the injection port was 280°C. The total content of the phenolic substances was also determined by colorimetry as follows. A 0.1 mL aliquot of the sample solution in methanol was dried under N_2, to which 1 mL of the Folin-Ciocalteu's phenol reagent was added, and after allowing the solution to stand for 20 min, 5 mL of 200 g L^{-1} $NaCO_3$ was added. The absorbance at 700 nm was determined. The calibration curve was made by using *p*-hydroxybenzoic acid ($0–40 \times 10^{-6}$ g).

5. Total lipids. Total lipids were extracted with a mixed solvent of benzene and methanol (6 : 4). Five grams of the sample were extracted 4 times with 40 mL of the mixed solvent by ultrasonic treatment and the extracts were combined together. A portion of this material was dried up to determine the content by weight. The remaining portion was concentrated and stored in a freezer. The glyco-lipid content was calculated from the monosaccharide content in the lipid fraction by the anthrone method using the factor of 4.4 based on the structure of monogalactosyl-distearyl-glyceride. The content of the phospholipids was determined by colorimetry (Bartlet 1959), after they were separately eluted on a Sep-pak silica column (Waters Assoc. Co.). The conversion factor (phospholipid/phosphorus) was 25 based the structure of lecithin.

6. Fatty acid composition. A portion of the lipid extract was dried up and mixed with 1 mL of 100 g kg^{-1} anhydrous HCl-methanol in a test tube with a Teflon coated screw cap. It was heated at 100°C in a water bath for 3 h, then extracted 3 times with 5 mL of hexane, washed once with 4 mL of 20 g L^{-1} $NaHCO_3$ and dried with Na_2SO_4. After the solvent was removed under a flow of nitrogen, the extract was dissolved in 200 μL of hexane containing squalane as an internal standard and analyzed by capillary gas-liquid chromatography. The contents of fatty acids with carbon numbers from 16 to 30 were determined. The column used was Durabond DB1 (15 m×0.25 mm I.D.) and the oven temperature was programmed from 180 to 250°C at the rate of 5°C min^{-1}. The instrument used was Hitachi 263 type GC equipped with a solvent-cut injector from Gasukuro Kogyo Co. Ltd. The injection temperature was 280°C.

RESULTS AND DISCUSSION

1. Radio-carbon ages of sediment samples

1) Shirasu profile. As shown in Fig. 1, the ^{14}C ages determined at 5 depths of the Shirasu profile were: A: 48-52 cm, 3,097±133 yBP; B: 68-72 cm, 3,608±49 yBP; C: 96-100

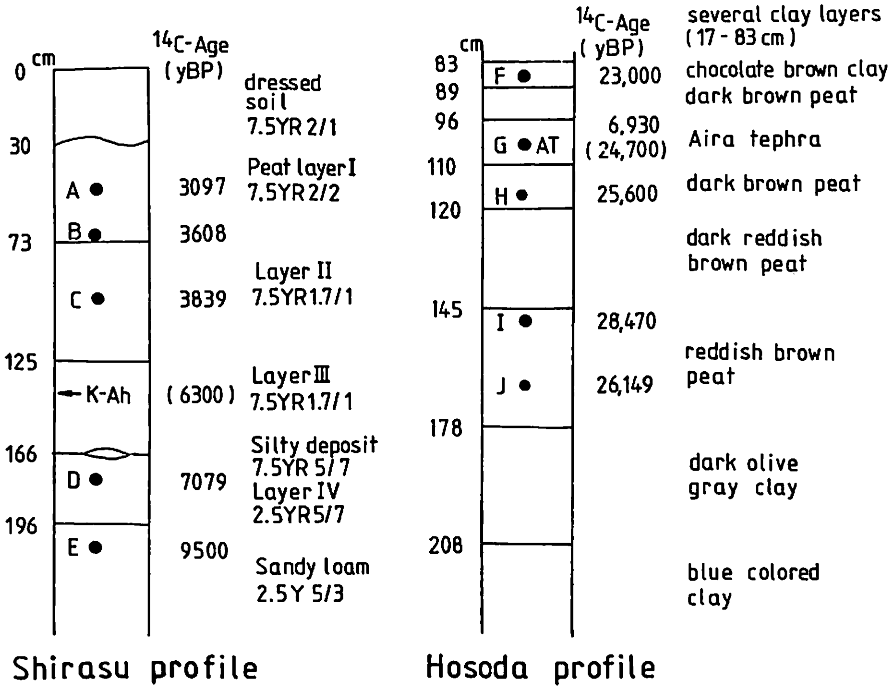

Fig. 1. Diagrams of investigated peat profiles.

cm, 3,839±435 yBP; D: 174-178 cm, 7,079±273 yBP, and E: 206-210 cm, 9,500±409 yBP. Information on the soil age was also obtained from the volcanic ash layer at the depth of 140-144 cm. This volcanic ash was identified as Akahoya tephra (Tsukude Research Group et al. 1989), which fell in ca. 6,300 yBP (Machida and Arai 1978).

2) Hosoda profile. As shown in Fig. 1, the ^{14}C ages determined at 5 depths of this profile were: F: 80-88 cm, 23,000±400 yBP; G: 98-105 cm, 6,930±10 yBP; H: 115-120 cm, 25,600±400 yBP; I: 150-155 cm, 28,470±70 yBP; J: 165-170 cm, 26,149±233 yBP. Based on the oldest ^{14}C-age of the peaty sediment excavated near this site (Tsutsuki and Kuwatsuka 1992), the formation of the peaty sediment in this wetland is considered to have started in ca. 32,000 yBP. Regardless of the younger age of sample J, the rate of accumulation was very slow throughout the peaty layer (0.12-0.13 mm year^{-1}). The Aira tephra was found at the depth of 96-110 cm in this profile. Based on the ^{14}C-dating data obtained here, the age of the Aira tephra is considered to fall between 23,000 and 25,000 yBP, which agreed well with the recent results of ^{14}C dating of the Aira tephra; 24,720±290 yBP (Matsumoto et al. 1987). The age of the plant debris found at the depth of 98-105 cm (point G) was unexpectedly young, presumably due to the contamination by a younger carbon which occurred in spite of the most careful treatment of the sample for dating. It is assumed that since this volcanic ash layer was very permeable and fertile, some younger plant roots may have reached this layer. The ^{14}C-dating data of the Hosoda profile indicated that this profile was formed during the coldest period of the last glacial maximum era.

2. Humus content and C/N ratio of peat layers

The carbon content in the Shirasu profile (Fig. 2) was about 100 g kg^{-1} in the deepest layers and the values increased gradually in the upper layers. The low humus contents in the lower layers may be ascribed to the following factors: (1) enhancement of organic matter decomposition under relatively aerobic conditions, and (2) transportation of soil from the surrounding hills. The carbon content reached a maximum value of 380 g kg^{-1} in the 50-60 cm layer, which suggests the development of wetland conditions at this depth. The decrease in the carbon content in the 0-30 cm layer may be due to soil dressing and the use of the wet land as a paddy field.

The carbon content of the Hosoda profile was constantly around 400 g kg^{-1} in the layers between 110-160 cm (Fig. 2). In the layer where the Aira tephra was interposed, it decreased to 330 g kg^{-1}. In the layers upper than the tephra, the content decreased to around 100 g kg^{-1}. These findings imply that before the fall of the Aira tephra, wetland conditions were stable and peat formation proceeded continuously in this area. The fall of the Aira tephra seriously affected the environment of this wetland as well as that in south-west and central Japan as suggested from the decrease in the soil carbon content.

The ratio of C/N ranged between 26 and 39 and was relatively stable in the Hosoda profile. In the Shirasu profile, the C/N ratio reached an extremely high value of 70 at the depth of 150-160 cm, where the humus content was very low (Fig. 2). The high C/N ratio, may be due to the exhaustive decomposition of nitrogenous compounds in peat when the layer was exposed to dry conditions. Inflow of silty materials near this depth may have also enhanced the organic matter decomposition. In the layers between 30-70 cm, where the humus contents were high, the C/N ratios showed low values (19-27), suggesting that the relatively eutrophic conditions prevailed in this profile.

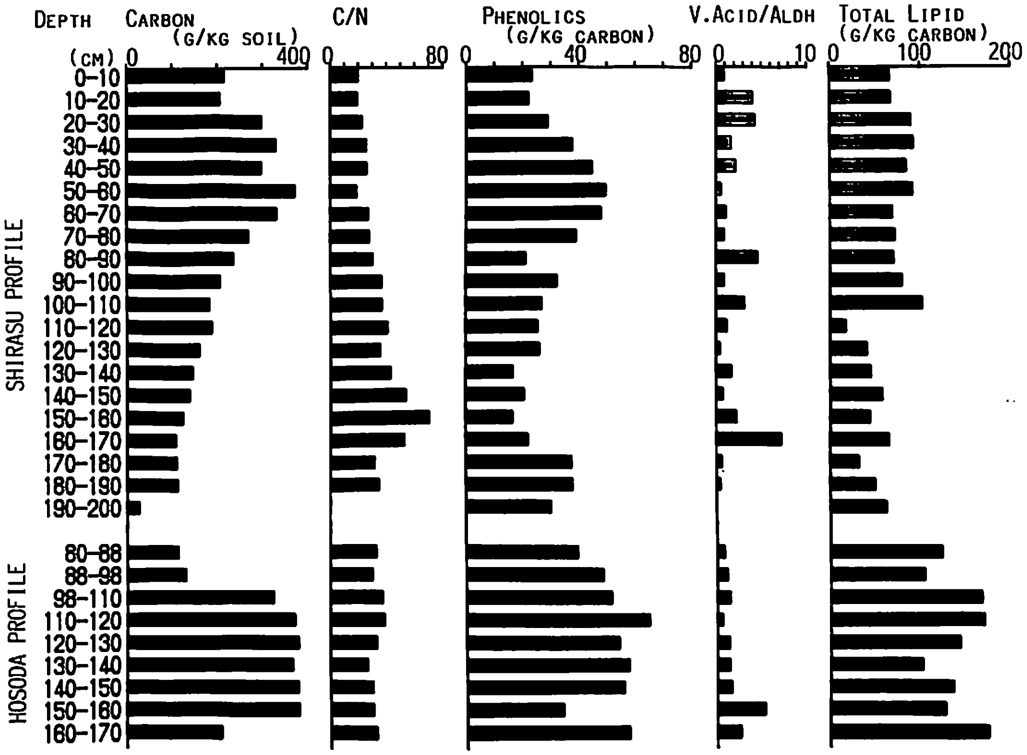

Fig. 2. Carbon contents, C/N, phenolics, and lipid contents in the two peat profiles. "Phenolics" denotes total phenolic substances liberated by CuO-NaOH degradation and determined colorimetrically. "V. Acid/Aldh" denotes the ratio of vanillic acid/vanillin.

3. Opal phytolith analysis

The percentages of opal phytoliths found in the Shirasu profile samples are shown in Table 1. Among several classes of grass phytoliths, the short-cell phytoliths reflected very well the succession of the vegetation in the wetland as shown in Fig. 3.

In layer IV (170-200 cm, ca. 7,000-9,500 yBP), panicoid phytoliths from *Zizania* spp. (wild rice) and *Moliniopsis japonica* were observed in large amounts along with bambusoid phytoliths from *Pleioblastus* spp. (Table 1, Fig. 3).

In the lower part of layer III (130-170 cm, ca. 5,000-7,000 yBP), chloridoid phytoliths from *Phragmites* spp. were dominant, while panicoid phytoliths from *Moliniopsis japonica* became dominant in the upper layer, suggesting the change from fen to transition peatland.

In layer II (80-130 cm, 3,600-5,000 yBP), the percentages of the phytoliths from *Phragmites* spp. and *Moliniopsis japonica* decreased and that of bambusoid phytoliths from *Pleioblastus* spp. increased remarkably and peaked at 100 cm (ca. 3,800 yBP). Assuming that this *Pleioblastus* spp. was growing in the wetland, the wetland should have been relatively dry during this period because *Pleioblastus* spp. is a grass inhabiting dry areas in nature. It is also possible that the phytoliths of *Pleioblastus* spp. may have been transported from the surrounding hills. Arai (1989) and Arai et al. (1988) suggested that humic volcanic ash soil had been transported into this wetland from the surrounding hills. Arai (1989) indicated that the peak of the transportation of humic volcanic ash soil occurred at around 120-130 cm, which is different from the peak of the *Pleioblastus* spp. phytoliths.

Table 1. Percentages of opal phytoliths found in the Shirasu profile.

Class	Short-cell phytoliths					Large-cell phytoliths					Unk.	Total counts
	Bambu.	Pani.	Festu.	Chlo.	Oth.	Fan.	Point.	Elong.	Ptero.	Tree.		
Depth (cm)												
Layer I												
30-40	4.1	11.9	1.9	11.9	21.9	9.1	1.3	7.6	0.1	0.0	30.3	538
40-50	8.6	8.0	0.2	10.1	23.9	4.5	3.3	6.2	2.3	0.0	32.9	514
50-60	10.8	8.2	1.2	12.0	19.3	9.3	7.0	8.2	2.5	0.0	21.5	600
60-70	6.5	13.8	1.5	13.7	31.9	5.8	2.7	6.4	1.2	0.0	16.5	520
70-80	10.4	6.4	0.7	14.8	24.0	7.4	5.1	6.4	1.4	0.0	23.3	566
Layer II												
80-90	14.6	3.6	0.7	6.3	25.3	3.7	7.0	8.0	0.8	0.0	30.0	616
90-100	17.9	2.6	0.0	4.9	24.7	5.5	7.7	6.3	1.4	0.0	22.0	507
100-110	26.1	4.9	0.4	3.8	22.8	7.8	4.9	7.3	0.0	0.0	22.1	552
110-120	24.3	4.9	1.2	2.7	25.9	6.0	4.4	7.4	0.4	0.3	23.8	753
120-130	16.4	10.5	0.8	6.0	23.0	6.7	3.0	7.7	1.7	0.2	24.0	847
Layer III												
130-140	11.7	18.8	1.6	5.1	23.8	7.1	3.8	5.8	0.8	0.0	21.1	759
140-150	12.6	9.5	0.0	3.6	31.9	6.2	5.6	3.0	0.0	0.0	27.5	772
150-160	10.6	9.5	2.0	10.4	21.7	9.5	5.0	4.5	0.3	0.0	26.2	442
160-170	7.5	10.2	0.5	4.6	26.6	4.6	6.8	2.5	1.1	0.0	35.6	736
Layer IV												
170-180	8.5	9.8	0.0	5.4	26.4	5.8	7.3	4.2	1.5	0.5	30.8	672
180-190	5.9	8.4	1.3	1.8	17.6	6.6	4.6	7.7	2.1	0.2	44.3	562
190-200	11.6	13.3	0.9	3.6	19.0	8.3	3.1	10.9	0.7	0.7	27.8	542

Bambu., bambusoid class (mainly *Pleioblastus* spp.); Pani., panicoid class (mainly *Moliniopsis japonica*); Festu., festucoid class (mainly Pooideae); Chlo., chloridoid class (mainly *Phragmites* spp.); Oth., phytoliths from other short cells (not included: bambusoid, panicoid, festucoid, and chloridoid); Fan., fan-shaped class (mainly pleioblastus, moliniopsis, and phragmites); Point., point-shaped class; Elong., elongate-class; Ptero., pteropsida class; Tree., opal phytoliths originating from trees; Unk., opal phytoliths of unknown origin and weathered and broken fragments.

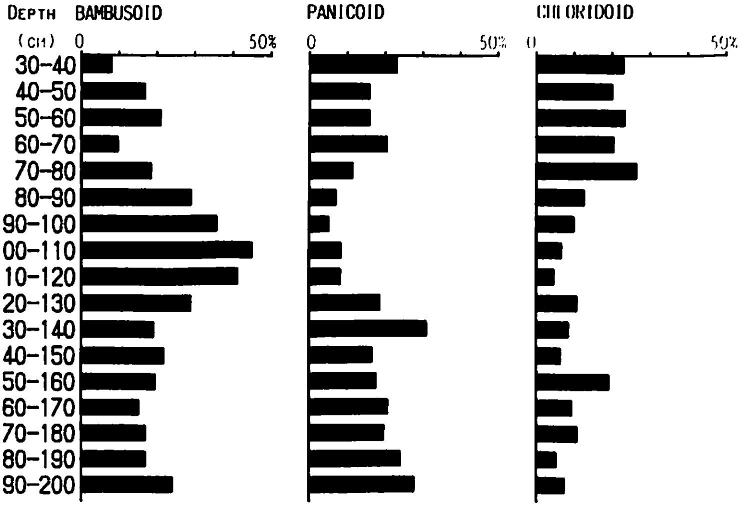

Fig. 3. Phytolith diagram in the Shirasu profile expressed as the percentages among short cell phytoliths. Bambu., bambusoid class; Chlo., chloridoid class; Pani., panicoid class.

After peaking, the percentages of the *Pleioblastus* phytoliths decreased and *Phragmites* spp. were thriving at the start of layer I (30-80 cm, ca. 2,000-3,600 yBP), indicating the resumption of the wetland conditions. Following the peak of *Phragmites* spp., the percentage of the phytoliths of *Moliniopsis japonica* also increased (60-70 cm, between 3,000-3,600 yBP), which suggested the change to transition peatland. The second but smaller peak of *Pleioblastus* was observed at 50-60 cm (ca. 3,000 yBP).

4. Phenolic compounds released by CuO-NaOH degradation

The degradation of plant materials with CuO-NaOH results in the formation of phenolic compounds with characteristics varying with the types of plants (Hedges and Mann 1979; Hedges and Ertel 1982).

In the Shirasu profile, the total yields of the phenolic compounds obtained by CuO-NaOH degradation were relatively low in the layers between 80-170 cm (3,600-7,000 yBP) as well as in the dressed soil layer above 30 cm, which suggested the decomposition of lignin components under the prevalence of a more aerobic environment caused by the lowering of the water table in the corresponding period (Table 2, Fig. 2). In contrast, the yields of the phenolic compounds were high at the depth between 30-80 cm (ca. 2,000-3,600 yBP), which implied that the lignin structure was well preserved here due to the anaerobic conditions of the wetland.

In the Hosoda profile (23,000-32,000 yBP), the total yields of phenolic compounds were constantly high in layers below the Aira tephra, but they decreased drastically after the fall of the tephra.

Each phenolic compound showed also a very characteristic variation with depth. For example, vanillin and vanillic acid differed in their behavior, though they belonged to the same vanillyl compound. Consequently, the ratio of vanillic acid to vanillin varied according to the depth (Fig. 2). In the Hosoda profile, the ratio was considerably lower than in the Shirasu profile. In the Shirasu profile, the ratio peaked at four distinct depths in layers II and III, which also suggested that these layers were formed under a relatively aerobic environment. This ratio was very low in layer I where the yields of the phenolic compounds were very high.

A reverse trend was observed in the yield of the phenolic compounds and the ratio of phenolic acid/aldehyde in both profiles as a rule. Therefore, the low value of this ratio suggests that the oxidative alteration of the lignin structure was the least pronounced.

When the phenolic compounds were grouped into *p*-hydroxyl, vanillyl, syringyl, and cinnamyl compounds, the yields of these compounds peaked at similar depths but not always at the same depth (Table 2), which may reflect the difference in the vegetation as well as the decomposability of the lignin structure.

Also based on the relatively high ratios of the syringyl/vanillyl compounds and cinnamyl/vanillyl compounds (Table 2), the contribution of the non-woody tissues of Angiosperm plants to the wetland vegetation was inferred (Hedges and Mann 1979). Especially in the recent 4,000 years, the yield of cinnamyl compounds had increased remarkably, which suggested the contribution of the Gramineae plants (Higuchi et al. 1967).

5. Lipid content and fatty acid composition

The yield of the lipids was very high and ranged between 100-180 g kg^{-1} of total carbon in the sediment in the Hosoda profile (Fig. 2, Table 3). In the Shirasu profile, the yield of the total lipids ranged from 70 to 100 g kg^{-1} of total carbon in the layers above 110 cm (ca.

Table 2. Yields (g kg^{-1} soil) of phenolic compounds after CuO-NaOH degradation.

Depth (cm)	Total phenolics	Group of phenolic compounds				S/V ratio	C/V ratio
		Van.	Syr.	Cin.	pHB		
Shirasu profile							
Dressed soil							
0-10	5.00	0.71	0.53	0.00	0.49	0.74	0.00
10-20	4.57	0.73	0.44	0.68	0.23	0.61	0.94
20-30	8.61	0.96	0.65	1.07	0.14	0.67	1.11
Layer I							
30-40	12.41	2.43	1.87	2.09	0.70	0.77	0.86
40-50	13.29	2.03	1.67	1.93	0.66	0.82	0.95
50-60	18.42	3.16	3.10	2.25	1.92	0.98	0.71
60-70	15.87	2.57	2.89	1.56	1.14	1.12	0.61
70-80	10.50	1.39	1.31	1.44	0.57	0.94	1.04
Layer II							
80-90	5.00	0.70	0.50	0.74	0.24	0.73	1.06
90-100	6.67	1.41	1.15	0.85	0.88	0.82	0.60
100-110	4.92	0.55	0.46	0.66	0.10	0.84	1.21
110-120	4.77	0.50	0.70	0.62	0.19	1.39	1.22
120-130	4.20	0.51	0.56	0.29	0.37	1.11	0.58
Layer III							
130-140	2.43	0.20	0.15	0.34	0.06	0.76	1.75
140-150	2.86	0.47	0.35	0.29	0.30	0.76	0.62
150-160	2.03	0.28	0.17	0.24	0.12	0.61	0.86
160-170	2.36	0.46	0.34	0.33	0.13	0.74	0.72
Layer IV							
170-180	4.09	0.47	0.44	0.33	0.33	0.94	0.69
180-190	4.20	0.55	0.53	0.28	0.38	0.96	0.50
190-200	0.79	0.06	0.10	0.05	0.02	1.57	0.75
Hosoda profile							
Chocolate brown clay							
80-88	4.46	1.64	0.84	0.20	0.35	0.51	0.12
Dark brown peat							
88-98	6.30	1.43	0.97	0.16	0.40	0.68	0.11
Layer with interposition of the Aira tephra							
98-110	16.70	3.56	2.77	0.76	0.45	0.78	0.21
Dark brown peat							
110-120	24.10	4.80	5.81	1.39	0.82	1.21	0.29
Dark reddish brown peat							
120-130	20.51	3.77	3.18	1.51	1.78	0.84	0.40
130-140	21.10	4.36	3.29	2.68	0.38	0.76	0.62
140-150	21.10	4.63	3.64	2.12	0.64	0.79	0.46
Reddish brown peat							
150-160	13.02	2.10	1.74	1.67	0.37	0.83	0.80
160-170	12.10	2.97	2.62	1.96	0.12	0.88	0.66

Van., vanillyl compounds = vanillic acid + vanillin + acetovanillon; Syr., syringil compounds = syringic acid + syringaldehyde + acetosyringon; Cin., cinnamyl compounds = *p*-coumaric acid + ferulic acid, pHB., *p*-hydroxyphenyl compounds = *p*-OH benzoic acid + *p*-OH benzaldehyde + *p*-OH acetophenon.

3,800 yBP), while it was as low as 20-60 g kg^{-1} in the layers below 110 cm. The relatively high lipid yield may be due to the cold climate and to the stable wetland conditions as shown in the Hosoda profile. The sudden increase in the lipid content at 110 cm may be correlated with the peak of the occurrence of *Pleioblastus* spp., because the change from a dry environment to a wet environment may be considered to have started already at this depth.

The proportion of the glyco-lipids to the total lipids was ca. 10% in the Shirasu profile and ca. 20% in the Hosoda profile (Table 3). This proportion did not vary appreciably with depth.

Table 3. Yields (g kg^{-1} soil) of lipid compounds.

Depth (cm)	Total lipid	Glycolipid	Phospholipid	Stearic acid (C_{18})	Montanic acid (C_{28})	Total nFA (C_{16}-C_{30})
Shirasu profile						
Dressed soil						
0-10	14.2	1.28	0.044	0.315	0.464	2.24
10-20	13.8	2.68	0.316	0.288	0.360	1.96
20-30	26.8	3.35	0.108	0.211	1.02	3.11
Layer I						
30-40	30.4	3.80	0.097	0.228	1.39	5.59
40-50	25.0	3.28	0.036	0.164	1.33	5.59
50-60	34.0	6.02	0.090	0.199	1.32	4.83
60-70	22.8	2.60	0.126	0.394	1.73	6.72
70-80	19.2	2.73	0.083	0.137	0.847	3.93
Layer II						
80-90	16.4	2.15	0.065	0.046	0.533	2.28
90-100	16.2	1.77	0.078	0.017	0.537	2.14
100-110	18.4	2.45	0.747	0.092	1.32	5.46
110-120	3.2	0.89	0.097	0.030	0.567	2.07
120-130	6.4	0.76	0.041	0.000	0.238	0.92
Layer III						
130-140	6.4	0.47	0.075	0.145	0.235	1.08
140-150	7.8	0.93	0.114	0.140	0.263	1.52
150-160	5.3	0.56	0.074	0.142	0.291	1.67
160-170	6.8	0.78	0.031	0.016	0.455	1.54
Layer IV						
170-180	3.4	0.67	0.017	0.000	0.380	1.19
180-190	5.4	0.82	0.107	0.088	0.413	1.75
190-200	1.6	0.19	0.004	0.023	0.116	0.54
Hosoda profile						
Chocolate brown clay						
80-88	13.8	2.61	0.032	0.584	0.797	3.42
Dark brown peat						
88-98	13.4	2.53	0.065	0.700	0.724	3.12
Layer with interposition of the Aira tephra						
98-110	54.0	10.3	0.078	2.20	1.07	7.22
Dark brown peat						
110-120	62.8	13.2	0.146	2.04	2.99	11.3
Dark reddish brown peat						
120-130	54.0	10.9	0.354	2.13	2.81	9.44
130-140	37.0	7.77	0.292	1.96	1.51	8.17
140-150	51.0	10.1	0.195	2.32	2.04	10.6
Reddish brown peat						
150-160	48.0	8.11	0.170	1.45	1.85	9.89
160-170	36.5	4.74	0.097	0.423	1.18	6.61

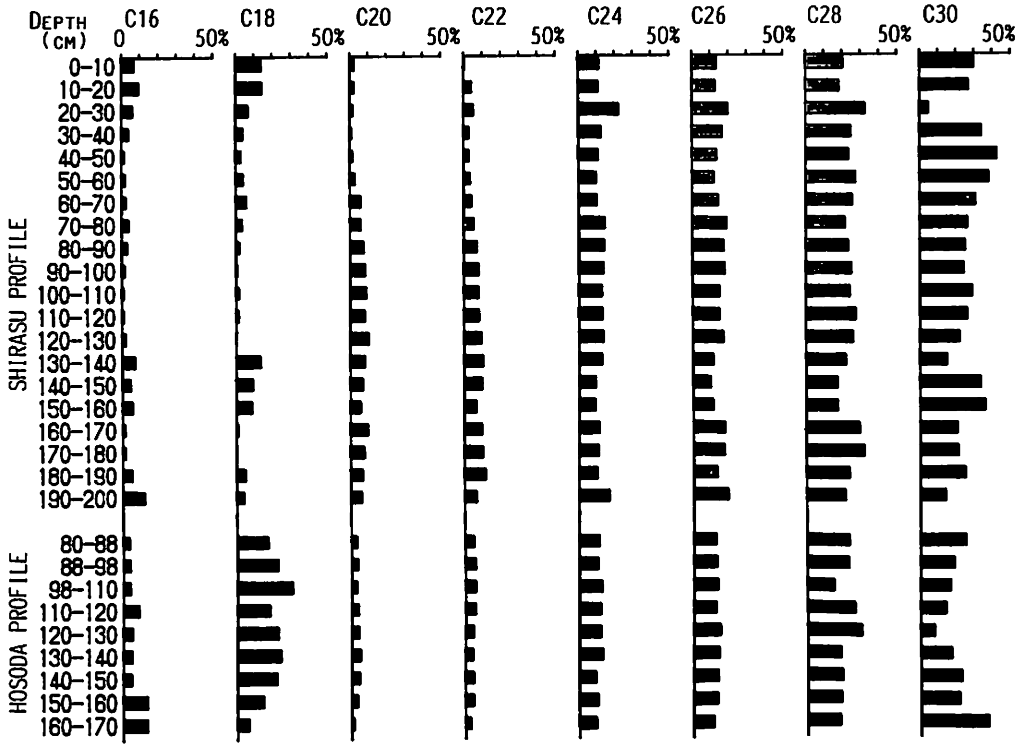

Fig. 4. Relative percentages of *n*-fatty acids (C_{16}-C_{30}) in the lipid fraction obtained from different layers of the two peat profiles.

The proportion of the phospho-lipids to the total lipids was lower than 0.5% in the layers above 100 cm but it increased to values as high as 4.2% in the layers below 100 cm (ca. 3,800 yBP) in the Shirasu profile. In the Hosoda profile, this proportion was as low as 0.3-1.3%. The proportion of the phospho-lipids tended to increase with the decrease in the yield of the total lipids. This observation suggests that the phospholipids originated mainly from microbial metabolites of peat.

Each fatty acid showed more characteristic variations with depth in each profile (Table 3, Fig. 4). Montanic acid (C28) and mellisic acid (C30) were the most abundant fatty acids. These long-chain fatty acids are considered to originate from wax components which are resistant to decomposition. The yields of palmitic (C_{16}) and stearic (C_{18}) acids were considerably low in the Shirasu profile, though difference were observed among the layers, e.g. the contents were relatively higher in layers I and III and lower in layer II (Fig. 4). The very low palmitic and stearic acid contents may imply that layer II was formed under relatively dry conditions, which was also suggested from the composition of the phenolic compounds and opal phytoliths. In the Hosoda profile, however, the yields of palmitic and stearic acids were much higher and relatively constant throughout the profile. Palmitic and stearic acids are considered to originate from the more decomposable lipid components than the wax components. The fatty acid composition of peats may also be correlated with that of specific plant species, which is now under study by authors.

6. General implications

The peaty sediment of the Hosoda profile (23,000–32,000 yBP) was formed during the last glacial maximum era. As it was buried under thick clay layers under anaerobic conditions, organic materials in the sediment may have remained relatively unchanged. Ishida and Nakahori (1987), who conducted a palynological study of the core sample collected in the same wetland, showed that the pollen of *Sphagnum* spp. and *Myrica gale* prevailed in the peaty sediment below the Aira tephra, indicating that the wetland was under bog conditions. The very high contents of soil carbon, phenolic compounds, lipid, and fatty acids as well as the high proportion of palmitic and stearic acids were all consistent with the above assumption. The lowest layer of the Hosoda profile, however, showed also tendencies of fen peat based on the high S/V, C/V, and vanillic acid/vanillin ratios.

The Shirasu profile, on the other hand, was formed after the end of the last glacial period. Based on field observations, the peaty sediment of this profile was divided into four layers. The content of the total phenolic compounds showed a distinct change at each boundary of the four layers, suggesting that there were differences in the types of vegetation as well as in the rate of plant residue accumulation.

Layer IV (ca. 7,000–9,500 yBP) of the Shirasu profile showed a relatively high content of phenolic compounds and a low vanillic acid/vanillin ratio, suggesting the development of anaerobic wetland conditions. The dominant phytolith was that of *Moliniopsis japonica*.

Layer III (ca. 5,000–7,000 yBP) showed a lower content of phenolic compounds and a higher vanillic acid/vanillin ratio, which indicated that relatively aerobic conditions prevailed in this layer. Based on the phytolith analysis, the succession from *Phragmites* spp. (typical fen plant) to *Moliniopsis japonica* (typical transition peatland plant) was inferred. The lipid content was also low in this layer, although the proportion of palmitic and stearic acids was relatively high.

Layer II (ca. 3,600–5,000 yBP) was characterized by the presence of thriving *Pleioblastus* spp., indicating that the wetland was exposed to relatively dry conditions. The high S/V and C/V ratios in the phenolic compounds were consistent with the thriving of *Pleioblastus* spp. The proportion of palmitic and stearic acids were low, indicating the exhaustive decomposition of easily decomposable lipid constituents.

During the period corresponding to the development of layer I (ca. 2,000–3,600 yBP), *Phragmites* spp. and *Moliniopsis japonica* thrived in the wetland. The high yields of the phenolic and lipid compounds indicated the presence of stable anaerobic conditions. Compared with the Hosoda profile, however, layer I of the Shirasu profile was characterized by a lower C/N ratio and lower proportion of palmitic and stearic acids. These characteristics indicated that the state of the wetland corresponded to an eutrophic fen peatland.

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