## DIATOMITE DEPOSIT IN THE BASIN OF LAKE SOIJÄRVI, CENTRAL FINLAND

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Diatomite and underlying diatomaceous gyttja are met with in the overgrown Soijärvi basin at Karttula. Diatomite is considered a material containing abundant diatoms and with a SiO<sub>2</sub> content of 60 %; diatomaceous gyttja has a SiO<sub>2</sub> content of 20—60 %.

The diatom stratigraphy of the Soijärvi sequence was studied. The diatomite and the diatomaceous gyttja are dominated by the comparatively small *Centrales* diatoms, mainly *Melosira distans* and variations. The diatom flora encountered was on the whole very broken.

The chemical composition, porosity and melting temperature were determined on diatomite in a natural state. Porosity was also determined after ingnition at 700°C. The distribution in particle size was determined on diatomite treated with hydrogen peroxide. The specific surface area of the diatomite in a natural state is 20,100 m<sup>2</sup>/kg and, when ignited, 28,800 m<sup>2</sup>/kg.

Key words: diatomite, diatomaceous gyttja, diatom stratigraphy, particle size distribution, specific surface area, porosity, chemical composition, melting temperature.

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### Introduction

Diatomite was found in the course of peat studies in Lake Soijärvi, Karttula ( $62^{\circ} 40' N, 27^{\circ}$ 05' E) (Fig. 1). The diatomite was established by microscopie examination of samples in a natural state based on the ratio of diatom frustules to mineral matter. Diatomite is considered a material in which almost the whole field of view in a preparation made from it is covered with diatoms and in which no mineral grains are visible. Diatomaceous gyttja in contrast is a material that contains diatoms in abundance but in markedly smaller proportions than in diatomite; mineral matter may be present. The microscopic determination of diatomite and diatomaceous gyttja was verified by chemical analysis. The  $SiO_2$  content of the sample is decisive: diatomite assaying over 60 %  $SiO_2$  and diatomaceous gyttja 20—60 %  $SiO_2$  (Grönlund 1982).

The purpose of this paper is to describe the diatom stratigraphy from the diatomite deposit found in the basin of Lake Soijärvi and to discuss some chemical and physical properties of diatomite material for various applications.

#### Description of the site

Soijärvi is an overgrown lake basin in the middle of which there is an open quagmire with



Fig. 1. Soijärvi, Karttula, study lines, sampling point on line AO-A600.

# SOIJÄRVI, Karttula



Fig. 2. The sequence at Soijärvi. Symbols explained in Fig. 3.

a thin layer of peat (10-30 cm) (Fig. 1). The edges are tree mire with birch and spruce and with a layer of peat over one metre deep (Fig. 2). The diatomite deposit was studied from a profile taken at point A 300 (Fig. 1). The layer of diatomite beneath the peat is 130 cm deep (30-160 cm) at the study point. At a depth of 160 cm the diatomite grades into diatomaceous gyttja that constitutes a layer 95 cm thick underlain by gyttja clay from a depth of 255 cm downwards. There is an estimated 187,500 m<sup>3</sup> of diatomite and 6,800 m<sup>3</sup> of diatomaceous gyttja at Soijärvi. Determined at a depth of 70 cm, the dry density of the diatomite is 0.17 g/cm<sup>3</sup>; at a depth of 230 cm the dry density of the diatomaceous gyttja is 0.29 g/m<sup>3</sup>. The content of organic matter in the diatomite is high, the losses on ignition varying between 24 % and 42 % (Fig. 3). The losses are notably smaller for the diatomaceous gyttja and the gyttja clay.

## Methods

## Diatom analysis

Organic matter was removed from the diatom samples by keeping the material in a sand bath in a 30 % solution of hydrogen peroxide for 24 hours at 50°C. Mineral matter was then eliminated by repeated suspending and decanting. Slides were prepared using Clophenharz (Clophen W + Clophen A60 = 5:1) (index of refraction 1.66) as a mounting medium.

Diatoms were taken for analysis at 20 cm intervals, at least 500 frustules being named at each sampling depth.

## Particle size distribution

The distribution of particle size in the Soijärvi diatomite was determined from a sample taken at a depth of 100—105 cm and from which the humus had been removed with hydrogen peroxide. First the sample was wetscreened on  $62 \,\mu\text{m}$ mesh. The material that passed the mesh was studied with an automatic particle size analyser (Sedigraph 5000 D) using accelerated sedimentation and the X-ray technique. For the analysis the density of the diatomite was determined as  $1.897 \text{ g/cm}^3$ ; the density of the water was  $0.9951 \text{ g/cm}^3$ .

## Specific surface area and porosity

The specific surface areas from the material in a natural state and from diatomite ignited at 700°C were determined at the laboratory of Engineering Geology, Tampere University of Technology on a sample taken from a depth of 95 cm using the nitrogen adsorption method, whereby the amount of  $N_2$  adsorped onto the surface of the sample is measured at low temperature and pressure. This method gives the specific surface accurately, the irregularities in shape and porosity included (Nieminen 1982).

The porosity of the Soijärvi diatomite was also investigated at the Tampere University of Technology on samples taken from the same depth (95 cm). This was done using a mercury porosimeter according to a method described in detail by Kellomäki (1982) and by Nieminen and Kellomäki (1982, 1984). Porosity is closely related to the surface area of the particles.

## Chemical composition

The sample was dried at 110°C and ground in an agate mortar. One portion (0.2 g) was fused with sodium hydroxide. The cooled cake was dissolved in hydrochloric acid and an aliquot was taken to measure silica colorimetrically as molybdenum blue. One portion (0.5 g) was decomposed by treatment with hydrofluoric-nitric-perchloric acid, after which aliquots were taken for the determination of aluminium, calcium, magnesium, sodium and potassium by atomic adsorption spectrophotometer. A nitrous oxide acetylene flame was used for aluminium and calcium, and an air-acetylene flame for magnesium, sodium and potassium. Total iron was analysed

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colorimetrically using the 1.14 - HCl method. One portion (1.0 g) of the sample was heated for 1 hr at 1000°C and loss on ignition was measured by weighing.

## Melting temperature

The sintering, softening, fusion and fluid temperatures of the ashes were determined on the Soijärvi diatomite (depth 120 cm) and underlying diatomaceous gyttja (depth 200 cm) with a Leitz Wetzlar heating microscope (DIN 51731).

## Results

## Diatom stratigraphy

Diatoms were abundant throughout the sequence except in the basal gyttja clay. All the diatoms encountered were fresh-water species. Altogether 144 species and 179 taxa of 32 different diatom genera were named from the profile studied. The diatomite contains 99 species and 156 taxa from 25 diatom genera.

The diatom succession is presented in Fig. 3,



Fig. 3. Diatom diagram of Soijärvi, selected species, pH spectrum of diatoms and curve for loss on ignition. 1 = peat, 2 = diatomite, 3 = diatomaceous gyttja, 4 = gyttja clay, 5 = clay, 6 = acf. + acb., 7 = ind. + unknown, 8 = alkf. + alkb.

which gives the loss on ignition curve and the depth and stratigraphic sequence followed by the names of the individual diatoms that account for more than 2 % of the whole species. The pH-spectrum of the diatoms is also presented, the diatoms being divided into ecological groups according to their pH-requirements (Meriläinen 1967, 1969, Miller 1971, Foged 1973, 1980, Mölder & Tynni 1967—1973, Tynni 1975—1980).

The *Centrales* and *Pennales* ratio is shown in the diagram reflecting roughly the planktonic and littoral ratio in the diatom flora. The diatom analysis was hampered by the abundance of broken frustules, which in both the diatomite and diatomaceous gyttja deposits occur in such profusion that they carpet the preparation in an even layer. This shows up particularly clearly in Figs. 4 and 5. Some of the diatoms, however, are very well preserved, and the dominant species in the diatomite, *Melosira distans* and its variations, also occurs in well preserved chains. Because the diatom flora is so decomposed some species may have escaped analysis and thus the stronger species are over repre-





Fig. 4. Overall picture of Soijärvi diatomite. Uppermost are chains of *Melosira distans* var. *lirata*. Although the chains break easily, some long ones can be seen. In the figure the longest chains comprise more than ten individuals. Electron microscope image by

K. Hokkanen.

Fig. 5. Broken diatom flora in Soijärvi diatomite. Electron microscope image by K. Hokkanen.

sented. This is implied by the relatively small number of species in the diatom flora.

In the succession of diatoms the diatomaceous gyttja and the diatomite are distinguished clearly from the underlying gyttja clay, which is characterized by alkaliphilic flora. The dominant species in the gyttja clay are *Fragilaria construens* and *F. construens* var. *venter*.

The diatomaceous gyttja and particularly the diatomite are characterized by the abundance of

Melosira species. Altogether 16 different taxa of Melosira species were distinguished. They were determined according to Mölder and Tynni (1967) and Florin (1980). The most common are Melosira distans and M. distans var. lirata. Also present in appreciable numbers were M. lirata var. lacustris and M. lirata var. perglabra, and M. distans var. tenella (Nygaard) M-B Florin, which is a small and squat, broad-celled diatom. All the above Melosira species are acidophilic in their pH ecology. *Melosira* species calling for more alkaline water were also encountered. The majority of these were *M. ambigua* and *M. granulata*, which occurred in profusion in the diatomaceous gyttja. Littoral species met with in the deposit are diatoms of *Frustulia rhomboides* and *Pinnularia* genera. Also worth mentioning is *Cyclotella stelligera*, which, indifferent in pH ecology, occurs abundantly in the diatomite in particular.

### Particle size

The largest particle size measurable with the particle size analyser is 60  $\mu$ m, which, according to the size classification, is the upper limit of fine sand. The dominant species in the Soijärvi diatomite, Melosira distans and its variations, is box-like in shape and  $4-30 \mu m$  in diameter (Hustedt 1930). The Melosira species may, however, form chains comprising several individuals, in which case the length of the chains exceeds 60 µm (Fig. 4). Many Pinnularia species are also over 60  $\mu$ m in length. Other species usually exceeding 60 µm at Soijärvi include Cymbella hauckii, C. turgida, Eunotia robusta, E. lapponica, E. lunaris, Frustulia rhomboides, Navicula radiosa. Stauroneis phoenicenteron and Tabellaria fenestrata and T. flocculosa. Although the above diatoms are so large that they dominate



Fig. 6. Distribution of particle size in Soijärvi diatomite at depth of 100–105 cm.

the field of view of the microscope their proportion of the Soijärvi species is low, because too little material remained on the mesh during wetscreening for it to be weighed. The distribution of particle size obtained with the analyser is given in Fig. 6. This shows that 52 % of the particles in Soijärvi diatomite are smaller than 2  $\mu$ m, 47 % are from 2 to 20  $\mu$ m, and not even one per cent is from 20 to 60  $\mu$ m. The large number of fragments in the Soijärvi diatomite is thus clearly reflected in the distribution of particle size.

## Specific surface area and porosity

The total calculated area, or specific surface area, of particles from material in a natural state at Soijärvi is 20,100 m<sup>2</sup>/kg and from diatomite ignited at 700°C 28,800 m<sup>2</sup>/kg.

The porosity of the Soijärvi diatomite was determined from both the material in a natural state and the samples ignited at 700°C. The results of the porosity determinations are given in Table 1 and as diagrams in Figs. 7 and 8. Various densities can be obtained for porous materials, depending on what is included in their volume. The geometric volume includes the real volume of the matter and all the pores. Corresponding to this is the bulk density, or weight by volume, of pulverous material, which is obtained with a mercury porosimeter at minimum pressure. At maximum pressure, the mercury fills all the pores with which it comes in contact. This gives the apparent density (Nieminen and Kellomäki 1982). The weight by volume of dried Soijärvi diatomite in a natural state was 0.298 g/cm<sup>3</sup> and of ignited diatomite 0.258/cm<sup>3</sup>. The geometric volume, which was used when calculating the weight by volume, includes all the pores not filled with mercury at minimum pressure (c. 0.03 atm). In the calculation, the pore volume filled with mercury at maximum pressure was subtracted from the geometric volume. The porosity percentage is the percentage of the pore volume of the geometric volume. The apparent density of





Fig. 8. Porosity curves of Soijärvi diatomite ignited at  $700^{\circ}$ C, 1 = cumulative volume, 2 = pore volume distribution, 3 = cumulative surface area.

the Soijärvi raw diatomite is  $0.9233 \text{ g/m}^3$  and of ignited diatomite 1.5499 g/m<sup>3</sup>; the figures for porosity are 68.64 % and 83.34 %, respectively.

The graph presents three curves as a function of pore diameter:

- 1 = cumulative volume curve, or pore volume per pore diameter
- 2 = distribution curve of pore volume, which is a derivative of the curve in 1. It indicates the distribution of the volume of the pores

according to diameter

3 =cumulative surface area curve.

Table 1 reveals that ignition, or the destruction of the organic matter, affected the results. The total pore volume of ignited Soijärvi diatomite is  $3.2 \text{ dm}^3/\text{kg}$  and of material in a natural state  $2.3 \text{ dm}^3/\text{kg}$ . The table also makes it plain that about half the pore volume of the material in a natural state consists of pores of less than  $1 \mu \text{m}$ , whereas in the ignited diatomite about 2/3 of the total volume comprises pores of less than  $1 \mu \text{m}$ .

## Chemical composition

A chemical analysis was performed on the Soijärvi diatomite on a sample taken from a depth of 100—105 cm from the middle of the diatomite layer. The result is as follows:

SiO <sub>2</sub>	_	65.3 %	MgO —	0.3 %
Al <sub>2</sub> O <sub>3</sub>	_	3.0 %	Na <sub>2</sub> O —	0.2 %
Fe <sub>2</sub> O <sub>3</sub>	_	1.3 %	K <sub>2</sub> O —	0.2 %
CaO	_	0.6 %	Loss on-	28.2 %
			ignition	

The organic matter in the Soijärvi diatomite is appreciable, which was already apparent in the other loss on ignition determinations (Fig. 3). Other impurities are few, however; only the aluminium content reaches a few per cent (3).

## Melting temperature

The results of the analyses are as follows:

	diatomite depth 120 cm	diatomaceous gyttja depth 200 cm
sintering temperature	1140°	1110°
softening temperature	1360°	1150°
fusion temperature	>1460°	>1460°
fluid temperature	>1460°	>1460°

Table 1. Results of porosity determinations on Soijärvi diatomite, 1) diatomite in a natural state, 2) diatomite ignited at 700°C. D = diameter ( $\mu$ m) of filled pores, V = filled pore volume (dm<sup>3</sup>/kg of sample), A = cumulative surface area (m<sup>2</sup>/kg of sample)

1. Diaton state	nite in a n	atural	2. Diatomite ignited at 700°C			
Sample we Bulk dens	eight ity 70	.2460 .2896 68.64	Sample weight Bulk density Porosity %		.19 .258149 83.3448	
D UM	V CDM/KG	A SQM/KG	D UM	V CDM/KG	A SQM/KG	
200.5424	0.0000	0	257.843	0	0	
112.8051	.0457	1	138.838	.025045	.555049	
85.9467	.1046	4	72.196	.118396	4.45556	
69.4185	.1600	7	53.0853	.184424	8.80888	
51.5680	.2251	11	45,1225	.210608	10.9559	
40,1085	.2778	16	39.237	.249314	14.6444	
32.8160	.3130	20	31,6649	301682	20 5507	
25.7840	.3614	26	28,6492	342665	26.0002	
22.5610	3948	32	24.7247	385925	32 4942	
19.6183	4273	38	21.7458	426908	39 566	
16 7119	4669	47	20 5102	447399	43 4487	
15 0407	4924	53	19 4075	464476	46 8737	
13 6733	5196	61	17 5233	498628	54 2784	
12 0325	5522	71	15 0726	527080	61 0526	
10 4328	5768	80	15 2058	5/3026	65 120	
0 2517	6181	07	14 2119	570247	72 5642	
9.5517	6191	97	14.2110	.570547	12.3043	
9.3740	.0101	107	13.079	.003303	82.2017	
7.2003	.0392	107	12.0327	.03/310	93.0549	
5.3424	.0880	139	11.5699	.652316	98.0732	
4.1309	./834	220	10.7435	.684189	109.516	
3.3686	.8995	346	10.0272	.713789	120.976	
2.8447	1.0367	524	9.75622	.7229	124.661	
2.4608	1.1430	685	8.03964	.735421	129.864	
2.1682	1.2477	867	5.25021	.832187	191.139	
1.8392	1.3576	1088	4.58921	.897077	244.137	
1.5975	1.5176	1462	4.07917	1.0075	346.397	
1.3577	1.5633	1587	3.33804	1.24315	603.124	
1.1805	1.6099	1735	2.44535	1.59265	1098.37	
.9873	1.6979	2062	1.94849	1.83172	1539.29	
.8484	1.7621	2343	1.77697	1.91027	1708.33	
.7756	1.7972	2517	1.47392	2.06509	2092.66	
.6620	1.8597	2867	1.2677	2.17325	2410.06	
.5774	1.9036	3152	.990278	2.32579	2958.79	
.4844	1.9124	3219	.896978	2.38158	3195.86	
.4483	1.9388	3446	.622169	2.54437	4082.13	
.3592	1.9915	3975	.499917	2.62292	4648.88	
.2996	2.0399	4568	.448967	2.65935	4956.91	
.2569	2.0707	5013	.359573	2.73335	5698.15	
.2117	2.1173	5816	.300363	2.80051	6518.89	
.1801	2.1595	6684	.256428	2.85858	7358.47	
.1386	2.2272	8414	.22538	2.90753	8174.63	
.1060	2.2747	9996	.200145	2.95193	9012.31	
.0901	2.2931	10754	.090306	3.14204	14872.2	
.0721	2.3142	11808	.060131	3.17961	16953.9	
.0601	2.3274	12613	.045263	3.19213	17923.5	
.0258	2.3547	15637	.030109	3.20807	19737.7	
.0180	2.3582	16300	.025808	3.21149	20229.9	
.0116	2.3626	17543	.020067	3.21604	21060.7	
.0090	2.3670	19274	.012065	3.22287	22798.2	
.0072	2.3679	19712	.007206	3.22628	24499.5	
.0060	2.3705	21321	.005956	3.22856	25897.8	

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## Discussion

Only a few diatom floras of diatomite deposits have been described in Finland. The diatom succession from Vähä-Komujärvi in Pyhäjärvi, which is characterized by *Melosira distans* and *M. distans* var. *lirata*, is very similar to that found in Soijärvi, whereas the diatomite from Rätäksuo mire in Hollola is dominated by alkaliphilous *Pennales* diatoms, especially *Fragilaria construens* and *F. construens* var. *venter* (Grönlund 1982).

The diatom floras of the diatomite occurrences situated in a secondary position in Haapajärvi and described by Aario (1966) also differ from the flora in Soijärvi. According to Aario, the occurrences in Haapajärvi are interglacial or interstadial, containing a considerable amount of *Melosira islandica* and its resting spores.

The evolution of the Soijärvi basin is typical of such basins in Finland. The diatomite often deposited in oligotrophic lakes when the changing and silica-bearing water provided the right conditions for a rich diatom flora. The diatoms indicate that as the diatomaceous gyttja started to deposit in the Soijärvi basin the water in the basin was changing from neutral-alkaline to more acidic. As deposition continued the basin became alkaline again but only for a brief period, because the water in the Soijärvi basin was already acidic when the diatomite was deposited. The dominant species grew so rapidly that it hindered competition by other diatoms. Likewise, the diatoms obviously disintegrated very quickly at the sedimentation stage at the same time as the organic matter was deposited.

The use to which diatomite is put depends not only on its physical and chemical properties but also on its purity. It has a wide range of applications (*e.g.* Mölder 1960), one of the most important of which is as a filtration medium: 64 %of the 687,000 metric tons of diatomite produced in the USA in 1981 went for filtration mediums (Meisinger 1981). The next most important application in the USA is as a filler (23 %). This has increased substantially in the last few years and has great promise, particularly in the building materials sector. Diatomite is also used as an insulator (2 %), as an absorption and abrasive material, and as an additive in fertilizers (Meisinger 1981). According to Mölder (1960), the diatomite containing abundant frustules of *Melosira* species, especially *Melosira distans*, is very suitable for use as a polishing material.

In durability, diatomite is comparable with quartz, the only substances being able to dissolve it are strong alkalies and hydrofluoric acid. The Soijärvi diatomite is a rather high-quality material in terms of chemical composition and physical properties. Thanks to its high melting temperature, it makes an excellent heat insulator.

Particle size, specific surface area and the porosity have not been determined before from diatomite and thus there are no data with which to compare the results obtained from the Soijärvi diatomite.

The particle size distribution obtained does not perhaps entirely correspond to the true nature of the diatomite of Soijärvi. More analyses of different kinds of diatomite materials would be needed. The methods used may accentuate somewhat the proportion of small particles, because the big diatoms and diatom chains are inclined to break during wetscreening. Moreover, the elongated ones and those under 62  $\mu$ m in diameter may pass through the mesh. In the analyser the shape of the elongated diatoms may affect their sedimentation rate and mode and thus alter the result. The lightness of the diatomite may also affect its sedimentation process.

Many physical and chemical properties of powdered materials, *e.g.* cation exchange capacity of soils and their ability to retain water, depend on their large surface areas. Large surface areas are possible only because such materials are porous. Determination of the porosity distribution of the specific surface area gives us more classification criteria for the material. We can also establish how the materials behave and how appropriate they are for various purposes. Thus, in his study on the distribution of pores in active carbon, Ranta (1981) states that a high microporosity is beneficial when gases and vapours are being adsorbed. But carbon should also have pores of large diameter, when solutions are being adsorbed. Thus, different pore distributions are suitable for different purposes.

The specific surface area of diatomite is important when assessing the material for technical potential, especially if it is to be used as a fil-

## tration medium because then its large specific surface area has a marked impact on its efficiency.

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