

## 9. CLAY MINERALS AND CHEMISTRY

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### INTRODUCTION

Clay mineral ratios were used in the earlier study of the Pleistocene/Holocene boundary, as reported by Georgala and Jacobsson (in Mörner 1976, Chapter 8). The work was based on X-ray diffraction. From the peak height of selected reflections from kaolinite, chlorite and mica the ratios of these minerals were calculated and plotted *versus* depth. Reproductions of the X-ray curves were presented in the O.R. 1973 as Figs. 1 and 2, but were omitted in Mörner 1976. The work involved laborious pretreatment of the samples and only eight were studied from a core length of about 12 m. Georgala and Jacobsson concluded that the clay mineral ratios could be of use in cases where sedimentation had occurred in salt water.

In the present study it was not possible to carry out a similar detailed study because of the number of samples involved. Rather than reduce the number of samples by selection, we tried to find parameters which could give us information without undue effort. The identification is based on X-ray diffraction (XRD) also in this study. Illite, chlorite, quartz, and feldspars are minerals present in all samples, the relative amounts being influenced by the particle-size distribution. Kaolinite is the mineral which may illustrate variations in the parent material. In the XRD curves, however, the 001–002 basal reflections from kaolinite nearly coincide with the 002–004 reflections of chlorite. The type of chlorite occurring in the samples studied has its 004 reflection at  $25.2^\circ 2\theta$  while the 002 kaolinite reflection appears at  $24.9^\circ 2\theta$  (CuK $\alpha$ -radiation). Where no kaolinite is present the chlorite peak is comparatively narrow.

With increasing kaolinite the peak broadens. Accordingly we used the width of the peak at half height as a measure of the kaolinite content. Smectite is another mineral which might provide information about source material. The smectite is best evaluated from a  $17\text{\AA}$  peak from a glycolated specimen. The sedimented material as a whole does not consist of well crystallized minerals, easy to identify, but includes more or less amorphous material, partly weathering products, partly aggregated silica skeletons, which can be traced by a raised background in the low angle region up to

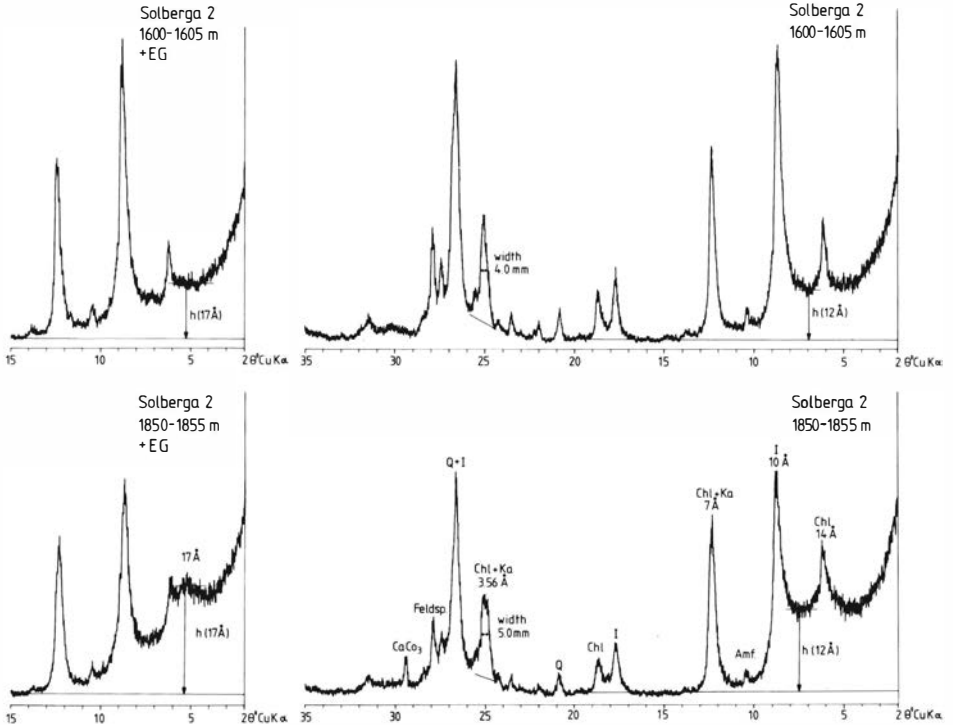


Fig. 9:1. XRD-curves of oriented samples of the clay fraction. CuK $\alpha$ -radiation, goniometer speed 1°2 $\theta$ /min, paper speed 10 mm/min.

Right, air-dried specimen, left, glycolated specimen.

Above: typical XRD-curve above the 18 m level.

Below: typical XRD-curve below the 18 m level.

Chl = chlorite, I = illite, Amf = amphibole, Ka = kaolinite, Q = quartz, Feldsp. = feldspars, CaCO<sub>3</sub> = calcite.

about 10Å (the 001-illite peak). They are here classified as mixed layer material, and the height at 12Å above a constructed background conveys an idea of the amount present. The parameters used may be seen in Fig. 9:1, where curves from two different levels are reproduced. We feel justified in using the above parameters, because of the similarity in the preparation of the specimens, and because the samples from the first core to be studied, Solberga, showed a monotonous character for over 16 m whereafter changes suddenly became evident.

## SAMPLE PREPARATION

The samples were moist on arrival. Without drying, 5 g of each sample were dispersed in 200 ml of distilled water and disintegrated with the help of

ultrasonic vibration and manual stirring. Some of the samples coagulated because of the presence of salt. The supernatant solution was decanted and a new portion of distilled water added. After settling, a portion (15 ml) was withdrawn, calculated to contain particles  $<2 \mu\text{m}$ , and filtered through a membrane filter (Millipore, size 47 mm diam.,  $0.45 \mu\text{m}$  pore size). The clay cake on the filter was transferred to a glass slide (Drever 1973), dried in air and XRD curves were made. The specimen was then placed in an ethylene glycol (EG) vapour bath at  $60^\circ\text{C}$ , and left there at least over night. New XRD curves were taken of the EG-specimens.

### CHEMICAL ANALYSIS

It was considered of interest to know whether variations in the chemical composition, *i.e.* preferably the trace elements, of the sediments could give information on the source material. A “direct” survey of the freeze-dried powdered material was made by X-ray fluorescence. The errors can be great by this method but, because of the similarity of the samples and the fact that the analytical work was performed on one occasion, incline to believe that the values are comparable. From the data, CaO and S, and the relationship Rb/Sr and K/Rb were extracted and plotted *versus* depth.

The cores from Brastad and Solberga were both studied in this way. The results may be seen in Figs. 9:2 and 9:3, while the analytical data are listed in Tables 9:1 and 9:2.

### CORES STUDIED

- Solberga – 35 samples were selected for the XRD-work and 41 samples for the chemical determinations.
- Brastad – From this core 22 samples were selected for the XRD work and the chemical determinations.
- Moltemyr– From this core too 22 samples were selected. XRD work only.
- Vägen – A preliminary survey, only, was made including 10 samples.

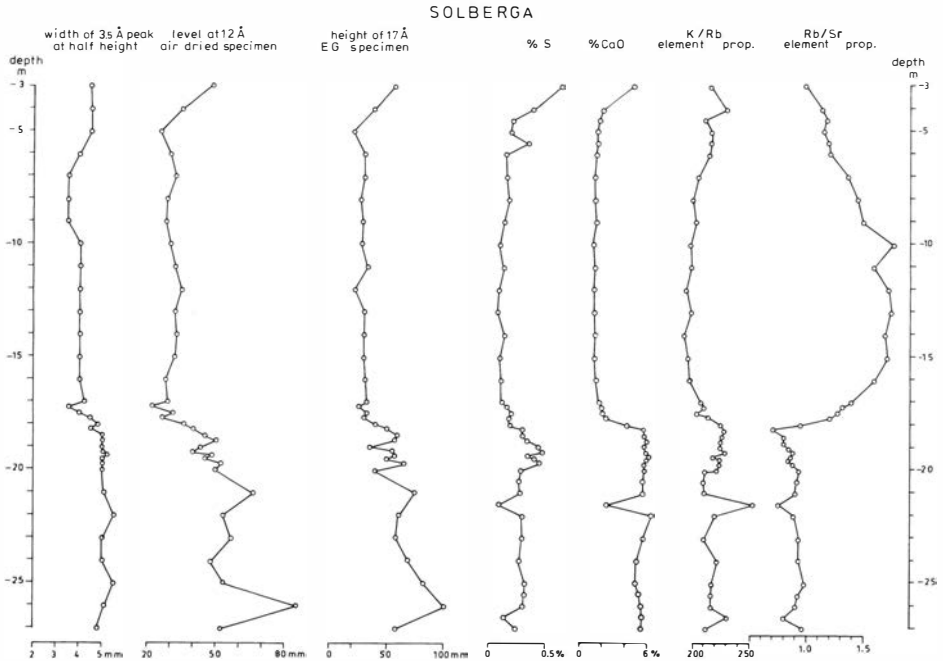


Fig. 9:2. Results from the Solberga core.

## RESULTS

*Solberga*— The results from the chemical analysis are listed in Table 9:1. The XRD work is compiled in Fig. 9:2, which also includes % S, % CaO and the elementary proportions of K/Rb and Rb/Sr.

At about 18–17 m a change occurs in the sedimentary material. From here upwards the sediment is very monotonous, we have no calcite in the fine fraction, very low frequency of smectite components and a relatively lower content of kaolinite than is found below this level. From between 17 and 18 m downwards the sediments have a different character. They hold kaolinite, fine-grained calcite, smectite and weathered material of poorly crystallized phyllosilicates. There is also a higher sulphur content, and at 18 m gypsum is present.

The CaO-curve shows a marked change between 18 and 17.7 m depending on a change in the calcite content. The deviation of the CaO-curve at the level 21.50–21.55 m, reflected also in the other chemical components, has been checked by X-ray diffraction of a nonfractionated sample at this level and of the samples above and below. The anomalous sample shows a lower clay content and higher contents of quartz and

TABLE 9:1. SOLBERGA. Chemical analyses of freeze dried samples, element ratio of Rb/Sr and K/Rb.

IDENT	depth m	Na <sub>2</sub> O %	MgO %	Al <sub>2</sub> O <sub>3</sub> %	SiO <sub>2</sub> %	P <sub>2</sub> O <sub>5</sub> %	K <sub>2</sub> O %	CaO %	TiO <sub>2</sub> %	MnO %	Fe <sub>2</sub> O <sub>3</sub> % tot	S %	Rb ppm	Sr ppm	Rb/Sr	K/Rb
S 1	3.00	2.10	3.61	18.01	57.7	.17	4.32	4.57	.77	.08	7.29	.62	183	188	0.97	214
S 2	4.00	2.51	3.43	18.78	57.4	.18	4.57	2.05	.70	.09	7.21	.37	183	163	1.12	227
S 2B	4.50	3.31	3.38	18.48	60.3	.19	4.83	1.74	.73	.10	7.24	.20	209	180	1.16	209
S 3	5.00	2.99	3.37	18.28	59.9	.19	4.75	1.54	.71	.10	7.22	.18	200	175	1.14	215
S 3B	5.50	3.02	3.41	18.21	58.9	.18	4.72	1.50	.69	.09	7.58	.33	200	169	1.18	214
S 4	6.00	2.93	3.30	17.96	56.9	.18	4.59	1.43	.68	.09	7.22	.15	195	164	1.19	214
S 5	7.00	2.96	3.41	19.18	57.3	.19	4.76	1.35	.66	.09	7.93	.15	212	157	1.35	203
S 6	8.00	2.97	3.53	19.52	57.2	.19	4.83	1.36	.69	.10	8.39	.16	221	154	1.44	198
S 7	9.00	2.95	3.59	19.69	58.5	.21	5.03	1.39	.70	.10	8.12	.13	226	153	1.48	202
S 8	10.00	2.72	3.87	20.67	56.8	.20	5.28	1.21	.72	.10	8.74	.09	243	138	1.76	197
S 9	11.00	2.72	3.63	19.98	56.9	.19	5.06	1.30	.68	.10	8.39	.12	232	147	1.58	197
S 10	12.00	2.78	3.71	20.37	57.7	.20	5.20	1.18	.71	.09	8.31	.09	244	143	1.71	193
S 11	13.00	2.66	3.76	20.43	57.3	.19	5.20	1.24	.73	.10	8.71	.06	238	137	1.74	198
S 12	14.00	2.67	3.74	20.13	57.2	.20	5.19	1.34	.76	.10	8.94	.13	246	146	1.68	191
S 13	15.00	2.67	3.83	20.20	56.6	.20	5.21	1.32	.73	.11	9.13	.08	243	143	1.70	195
S 14	16.00	2.78	3.74	20.10	57.0	.20	5.14	1.43	.75	.11	8.80	.10	236	149	1.58	197
S 15	17.00	2.80	3.51	19.13	57.8	.20	5.03	1.69	.73	.10	7.86	.11	220	158	1.39	207
S 16	17.25	2.82	3.48	19.18	59.0	.20	4.96	1.94	.74	.11	7.91	.14	217	166	1.31	208
S 17	17.50	2.90	3.43	18.95	59.3	.20	4.91	2.06	.72	.10	7.76	.18	218	172	1.27	204
S 18	17.75	2.88	3.32	18.90	59.7	.20	4.86	2.26	.72	.10	7.33	.17	208	173	1.20	212
S 19	18.00	2.45	3.23	17.21	56.8	.18	4.32	4.11	.73	.09	6.75	.19	175	186	0.94	224
S 20	18.25	2.26	3.23	16.45	55.6	.18	4.02	5.57	.74	.09	6.62	.29	161	229	0.70	226
S 21	18.50	2.10	3.22	16.42	56.3	.17	3.95	5.64	.74	.09	6.53	.29	159	200	0.80	225
S 22	18.75	2.01	3.17	15.96	54.8	.17	3.85	5.85	.75	.09	6.54	.32	156	196	0.80	224
S 23	19.00	2.00	3.22	16.45	54.7	.17	3.85	5.57	.74	.10	6.84	.42	157	187	0.84	223
S 24	19.25	2.01	3.36	16.69	55.6	.17	3.90	5.85	.76	.10	7.13	.46	156	179	0.87	227
S 25	19.45	1.92	3.43	16.84	56.9	.18	4.00	6.12	.79	.10	6.98	.33	167	195	0.86	217
S 26	19.55	1.97	3.30	16.25	56.2	.17	3.85	5.81	.76	.10	6.91	.39	157	186	0.84	223
S 27	19.75	1.97	3.33	16.29	56.7	.17	3.93	5.69	.77	.11	7.06	.43	160	184	0.87	222
S 28	20.00	2.01	3.37	16.72	57.9	.18	4.05	5.70	.79	.09	7.03	.27	174	187	0.93	211
S 28B	20.50	2.06	3.36	16.93	56.9	.19	4.15	5.61	.79	.11	7.37	.25	180	197	0.91	209
S 29	21.00	2.21	3.44	17.19	57.4	.20	4.22	5.53	.79	.11	7.56	.27	183	203	0.90	210
S 29B	21.50	3.04	2.54	16.27	64.2	.21	4.46	2.27	.69	.10	5.19	.08	160	214	0.75	252
S 30	22.00	1.80	3.37	16.92	54.8	.18	4.05	6.19	.80	.09	7.41	.29	169	192	0.88	218
S 31	23.00	1.79	3.38	17.34	56.8	.21	4.16	5.56	.80	.11	7.54	.29	179	194	0.92	210
S 32	24.00	1.86	3.33	17.26	56.8	.20	4.14	5.02	.77	.11	7.48	.26	170	183	0.93	221
S 33	25.00	1.68	3.37	17.64	56.8	.19	4.26	4.85	.78	.09	7.50	.31	178	181	0.98	217
S 33B	25.50	1.66	3.36	17.11	55.5	.19	4.11	5.15	.78	.09	7.23	.31	172	187	0.92	216
S 34	26.00	1.64	3.39	17.27	56.8	.19	4.18	5.40	.78	.09	7.26	.29	175	194	0.90	216
S 34B	26.50	1.62	3.33	17.34	56.2	.18	4.18	5.49	.75	.09	6.52	.13	165	207	0.80	229
S 35	27.00	1.72	3.48	18.37	57.2	.18	4.57	5.26	.81	.10	7.45	.23	196	205	0.96	211

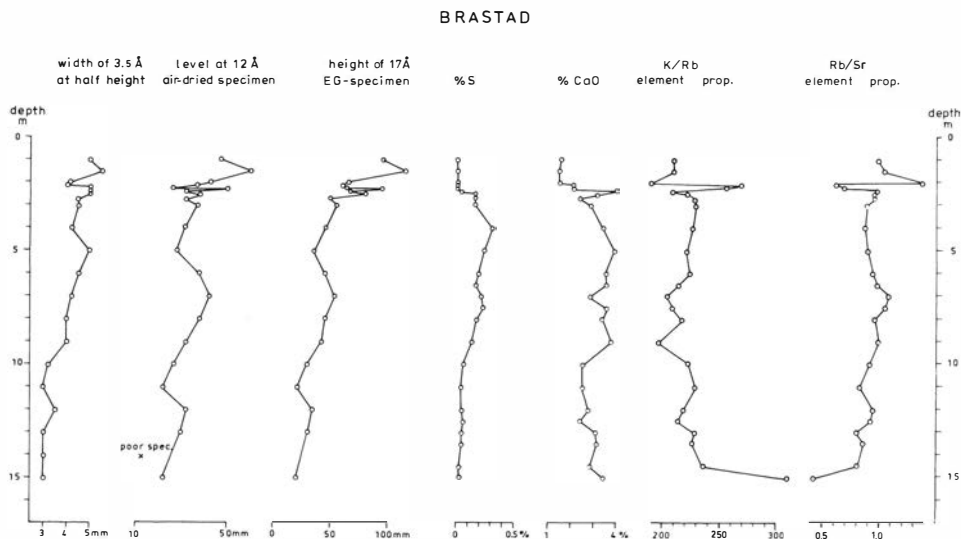


Fig. 9:3. Results from the Brastad core.

feldspar than the surrounding samples. The proportion of potassium feldspar to plagioclase is higher in the anomalous than in the surrounding samples where it is quite low. Table 9:1 indicates that  $K_2O$  has a peak at the level in question. The K/Rb relation also shows a deviation which may be traced to the potassium feldspar. It may be mentioned that just above this layer, low in clay minerals, a clay peak has been registered at 21.40–21.45 m.

The relationship K/Rb for different minerals was studied by *inter alia* Reynolds (1963) who found that K/Rb in feldspars tends to be higher than K/Rb in micas. The implication for Solberga would be a higher mica content from about 18 m upwards, and/or an altogether different origin of the parent material.

In the profile the change in the Rb/Sr proportion follows the change in the CaO-content, Sr being closely related in chemistry to Ca. A high Ca concentration is accompanied by high Sr and in consequence a low Rb/Sr proportion.

*Brastad* – This core shows a different development from the Solberga one. From 15 m upwards there is an increase in both the kaolinite content and the smectite material, and above 2.5 m the layers seem to be disturbed. An increase in the smectitic layers can be observed, but may be due to secondary weathering.

TABLE 9.2. BRASTAD. Chemical analyses of freeze dried samples, element ratio of Rb/Sr and K/Rb.

IDENT	depth m	Na <sub>2</sub> O %	MgO %	Al <sub>2</sub> O <sub>3</sub> %	SiO <sub>2</sub> %	P <sub>2</sub> O <sub>5</sub> %	K <sub>2</sub> O %	CaO %	TiO <sub>2</sub> %	MnO %	Fe <sub>2</sub> O <sub>3</sub> tot %	S %	Rb ppm	Sr ppm	Rb/Sr	K/Rb
B 1	100-105	2.09	2.83	17.23	62.1	.18	4.28	1.60	.78	.08	7.00	.01	185	188	0.98	210
B 2	150-155	1.89	3.01	17.69	61.8	.20	4.35	1.52	.78	.07	7.05	.01	188	181	1.04	210
B 3	200-205	1.99	3.25	18.31	60.8	.20	4.72	1.53	.77	.09	8.69	.01	226	164	1.38	190
B 4	215-220	2.66	2.01	14.97	66.8	.22	4.18	2.09	.60	.08	4.27	.01	141	227	0.62	269
B 5	225-230	2.76	2.16	15.95	66.8	.22	4.47	2.12	.69	.08	4.84	.01	158	230	0.69	256
B 7	240-245	1.87	3.38	18.06	60.2	.19	4.39	3.99	.80	.10	7.32	.04	191	194	0.98	209
B 8	250-255	1.90	3.28	18.29	61.3	.19	4.39	3.20	.79	.12	6.84	.16	180	188	0.96	221
B 9	275-280	1.97	3.27	18.11	62.8	.19	4.36	2.42	.76	.10	6.27	.16	177	184	0.96	224
B 10	300-305	1.97	3.30	17.91	62.8	.19	4.30	2.87	.76	.09	6.15	.16	170	191	0.89	229
B 11	400-405	2.27	3.47	17.80	61.0	.19	4.47	3.41	.76	.10	6.85	.31	179	206	0.87	227
B 12	500-505	1.94	3.47	17.90	59.4	.19	4.47	3.99	.77	.10	6.94	.24	184	205	0.90	221
B 13	600-605	1.97	3.46	17.45	58.1	.18	4.46	3.52	.77	.10	6.91	.19	180	192	0.94	224
B 13B	650-655	2.02	3.56	18.59	60.0	.19	4.63	3.41	.79	.10	7.00	.17	196	198	0.99	214
B 14	700-705	1.92	3.69	18.51	59.2	.19	4.78	3.52	.83	.10	7.54	.21	213	197	1.08	204
B 14B	750-755	1.86	3.71	19.05	58.5	.19	4.71	3.75	.81	.10	7.57	.23	205	195	1.05	208
B 15	800-805	2.23	3.61	17.52	58.9	.18	4.57	2.86	.80	.11	7.18	.18	191	198	0.96	217
B 16	900-905	2.11	3.79	18.01	59.5	.18	4.71	3.57	.83	.11	5.44	.14	205	208	0.99	196
B 17	1000-1005	2.47	3.71	18.79	60.2	.18	4.54	2.54	.79	.13	6.91	.06	185	202	0.92	222
B 18	1100	2.54	3.60	18.06	61.8	.18	4.45	2.55	.77	.12	6.22	.04	176	212	0.83	229
B 19	1200	2.39	3.88	18.33	60.0	.18	4.64	2.80	.82	.14	7.11	.05	192	202	0.95	219
B 19B	1250	2.59	3.75	18.19	60.9	.19	4.59	2.44	.80	.13	6.74	.06	195	213	0.92	214
B 20	1300	2.42	3.50	18.27	61.3	.18	4.45	3.08	.75	.13	6.25	.05	176	221	0.80	229
B 20B	1350	2.34	3.81	17.30	59.1	.18	4.46	3.12	.77	.14	6.56	.05	179	210	0.85	226
B 21	1450	2.44	3.54	17.15	61.5	.18	4.44	2.89	.76	.13	6.13	.03	171	213	0.85	236
B 22	1503-1509	2.98	1.92	14.22	69.7	.16	3.52	3.47	.46	.07	3.19	.03	104	247	0.42	311

*Moltemyr* – The samples along this core all show very similar XRD patterns and no distinct change like that found at Solberga can be observed. From 3.30 m downwards, however, the contributions of kaolinite to the 3.5 Å peak are quite clear and may indicate a change corresponding to the Solberga one at 18 m (see Chapter 20, Fig. 2a). In addition there is a slight increase in the smectite component, although more marked, in the samples from the 3.40 m levels downwards. It is very difficult to define a boundary as the material seems to be very consistent throughout the core, and some variations may even depend on variations in the preparation of the XRD-mounts. Variations in the rate of sedimentation seem more likely than an altogether different origin of the material. No chemical analysis has been made of this core.

The results from Vågen are preliminary and will not be discussed in detail in this report.

## CONCLUSION AND DISCUSSION

At Solberga all the results indicate a change in the sedimentation conditions close to a depth of 18 m. Below this level the sedimentation was relatively slow. The parent material was rich in weathering products and is similar to deposits now present in Quaternary clays in Skåne and Denmark. Calcite is present and may derive from chalkey material. Above 18 m the sediment is monotonous up to the top of the core. No calcite is present in the clay fraction and weathered material is scarce apart from the very top. Illite, chlorite, quartz, and feldspars are the chief components, minerals normally found in Quaternary clays in central Sweden. The change seems to have occurred, when large quantities of meltwater brought material from northern and eastern Sweden to the south-western region.

It may be of interest to compare the CaO-curve (chiefly representing  $\text{CaCO}_3$ ) at Solberga with the results from core B873 (Mörner 1976, p. 255) and Tuve (Cato 1981). The low CaO-content between 4 and 18 m at Solberga may be correlated with the section in core B873 between 3 and 13.5 m which shows a low calcite content apart from a few isolated peaks. At 13.5 m there is a sudden increase in calcite similar to the finding at Solberga at about 18.5 m. At Tuve the section between 4.5 and 7.5 m is low in calcite and may correspond to the above-mentioned section in core B873 and the interval 4–18 m at Solberga.

As regards the mineralogy a direct comparison of the results reported by Georgala and Jacobsson (1976) is difficult because of the few samples studied and the different techniques used in presenting the findings. Nevertheless thanks to Georgala, I had the opportunity to see reproductions



of the X-ray curves from the report quoted as O.R. 1973: Figs. 1 and 2. These curves clearly show that in core B873 the sample 113 at 13.9 m is similar to samples from the lower part of the Solberga core, *i.e.* below 18.5 m, the background level at  $12\text{\AA}$  is high, and both smectite and interstratified minerals are present. The sample 105, in core B873 close to 12.8 m, is clearly of the type above 17 m at Solberga, low in background level at  $12\text{\AA}$  and poor in smectite minerals. Judging by the diagram Fig. 8:3 in Georgala and Jacobsson (1976) there is an increase in kaolinite between the two samples mentioned (113 and 105), corresponding to the findings in the Solberga core between 18 and 17 m. The two upper samples of core B873 (*viz.* Nos 1 and 15 above 2.5 m) again show an increase in the  $12\text{\AA}$  background level and the smectite content, as also found at Solberga above 5 m, which in the present case was interpreted as due to secondary weathering.

It may be concluded from the comparison of results that the change in mineralogy reported between levels 13.9 and 12.8 m in core B873 corresponds to the change at Solberga between 18 and 17 m.

The Brastad core is more difficult to interpret. The fluctuations at the top may well be due to secondary weathering or to displacement of the sediments.

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