MINERALOGY OF THE ORDOVICIAN BENTONITE BEDS AT KINNEKULLE SWEDEN

BY

ANN MARIE BYSTRÖM

WITH 4 PLATES

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ABSTRACT

The investigation of the Ordovician bentonites (Chasmops layers) at Kinnekulle, Sweden, has shown that the main part of the bentonite beds consists of clay minerals belonging to the type described as 'mixed layer' minerals of illite and montmorillonite in random interstratification. Two characteristic combinations of layers have been found. They are determined by the potassium content of the clay minerals. *Type I* from the main bed (2 m thick) is similar to montmorillonite and is characterized by the following data: $K_2O \sim 2.7$ %, base exchange capacity 65—70 meq/100 g and inner basal reflexions of glycerol-treated specimens at 18 Å and 9.3 Å. *Type II* from the upper thin beds (15 cm each) has the corresponding data: $K_2O \sim 5$ %, base exchange capacity 46 meq/100 g and inner basal reflexions at 14 Å and 9.6 Å.

From the chemical analyses the following structural formulae were found:

Type I:

$$(Si_{7.58}Al_{0.42})(Al_{3.01}Ti_{0.02}Fe^{3+}{}_{0.20}Fe^{2+}{}_{0.08}Mg_{0.77})K_{0.43} \overset{\uparrow M^+{}_{0.58}}{O_{20}(OH)_4}$$

Type II:

$$(Si_{7.37}Al_{0.63})(Al_{3.14}Ti_{0.04}Fe^{3+}{}_{0.17}Fe^{2+}{}_{0.06}Mg_{0.60})K_{0.86} \overset{\uparrow M^+{}_{0.36}}{O_{20}(OH)_4}$$
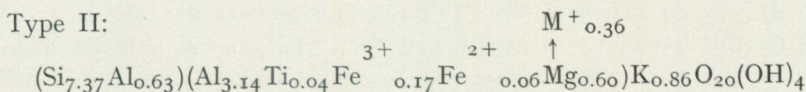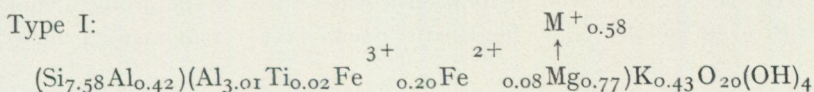
The methods of investigation used are chemical analyses, studies of base exchange capacities, X-ray analyses, DTA-analyses, acid-extractions and electron micrographs.

From the thick bed phenocrysts of biotite, quartz, kaolinized plagioclase and a potassium feldspar, found to be a sanidine, have been isolated and described. The phenocrysts indicate that the bentonite beds are of volcanic origin.

Preface.

The material from the Ordovician bentonite beds at Kinnekulle in the south-west of Sweden, will be described here rather extensively, since the deposit is the first in Sweden of its type which has been investigated comprehensively by chemical and physical methods. At the outset difficulties arose

as to the methods which could best be used in the diagnosis of the clay minerals. The methods currently in use were still tentative, clay research having only recently become the subject of any extensive detailed attention. An inductive line has therefore been followed and knowledge of the bentonites has been achieved step by step. A similar method has been followed in presenting the details of the investigation. The aim has not been so much to elucidate the technical side of the bentonite material as to examine in detail the clay minerals present, so that on the basis of such knowledge there might arise greater possibilities of a full technical investigation.

Introduction.

Previous Work.

A reinvestigation of the strata at Kinnekulle has recently been undertaken in connection with borings made in 1941 by the Geological Survey of Sweden and in 1944 by the Paleontological Institution of the University of Uppsala (Waern, Thorslund and Henningsmoen, 1948). Thorslund (1945) found that certain layers most probably consisted of bentonites as defined by Ross and Shannon (1926) who state that "bentonite is a rock composed essentially of a crystalline clay-like material formed by the devitrification and the accompanying chemical alteration of glassy igneous material, usually a tuff or volcanic ash". At Kinnekulle the bentonite layers were chiefly found in the Chasmops series belonging to the Caradocian period. From samples obtained during the deep boring through Ordovician and Silurian strata in 1944, and also from diggings made in connection with the boring as well as at later dates, the bentonite beds were described by Thorslund (1948). A fairly large number of bentonite beds were found of various thicknesses from an inch up to about six feet. The deposit was considered to be of such interest that a more detailed investigation was planned and started in 1950 at the Chemical Laboratory of the Geological Survey at the suggestion of Dr. G. Assarsson.

From the results of the preliminary investigation made by Thorslund (1947, 1948) it is seen that the bentonite beds at Kinnekulle show a strong resemblance to similar findings in North America, where deposits of bentonites of Ordovician origin have earlier been found. These have been described, *inter alia*, by Ross (1928), and Fox and Grant (1944). The Ordovician bentonites behave somewhat differently from bentonites of later origin and the term m e t a b e n t o n i t e has been used to distinguish them from the bentonites of the Tertiary age, now used as a valuable commercial raw material. Ross and Hendricks (1945), however, have expressed the opinion that the term metabentonite should not be used without discrimination, and they consider it most appropriate to use the term metabentonite exclusively for material showing a proper metamorphism. In a recent investigation of Ordovician bentonites from Pennsylvania, Weaver and Bates (1952) assigned the name p o t a s s i u m - b e n t o n i t e to their material, indicating the high potassium content which is responsible for its characteristic properties. In the following description the Ordovician bentonites at Kinnekulle will be referred to as bentonites only, in conformity with the original definition.

Before the discovery of the bentonite beds at Kinnekulle, Dr. J. Eklund at the Geological Survey of Sweden had already suggested that old ash deposits could be expected (Thorslund 1945). It was he who made the first estimation of the mineral content of the Kinnekulle material (Thorslund 1947). From his calculations based on a chemical analysis of material from the thick bed, he deduced a composition of the bentonite material which gave 63 % montmorillonite, 22 % muscovite and approximately 13 % quartz. Using material from Bornholm, he found a much lower content of montmorillonite, the calculations giving 31 % montmorillonite, 55 % muscovite and 12 % quartz. According to Eklund the higher content of muscovite in the Bornholm material shows that the reaction between the ash products and the sea water, during which the potassium ions in the sea water react with the montmorillonite, to give muscovite, proceeded further in this material than in the Kinnekulle material. He finds this increased reaction natural as a result of the situation of Bornholm as compared with that of Kinnekulle. Against such an argument, the more detailed investigation of Kinnekulle has revealed the presence of bentonite layers with material very similar to that from Bornholm and has shown other factors of importance apart from the situation relative to the volcanic origin. At Kinnekulle, material from the thin beds as compared with that from the thick main bed, shows a relatively higher potassium content and thus a calculated higher muscovite content. According to the description by Funkquist (1919) the material analysed from Bornholm had been collected from a very thin bed, only an inch thick. From a paper by Gry (1948) on the bentonite material from Bornholm, it can be seen that thicker beds also occur in the Bornholm strata. At least one has a thickness of about three feet. In this bed one could expect to find material similar to that from the thick bed at Kinnekulle, that is with the lower potassium content and thus a calculated higher content of montmorillonite. All X-ray photographs hitherto taken on the Bornholm material, however, have given illite diagrams which correspond to material with a relatively high potassium content resembling the material analysed before (Gry 1948 p. 378).

As will be shown, there is a marked difference between the thin and the thick layers at Kinnekulle and a similar difference might be expected at Bornholm. Until further details are known therefore, care must be taken when comparing layers at Kinnekulle and at Bornholm.

Description of the Material.

Figure 1 shows a diagram from the section at Mossen, Kinnekulle. The diagram is reproduced from the paper by Thorslund (1948). The arrows have been added to indicate the approximate levels at which the material was collected for this investigation. Material was taken only from the upper two thin beds and from the thick bed where exposed, as at
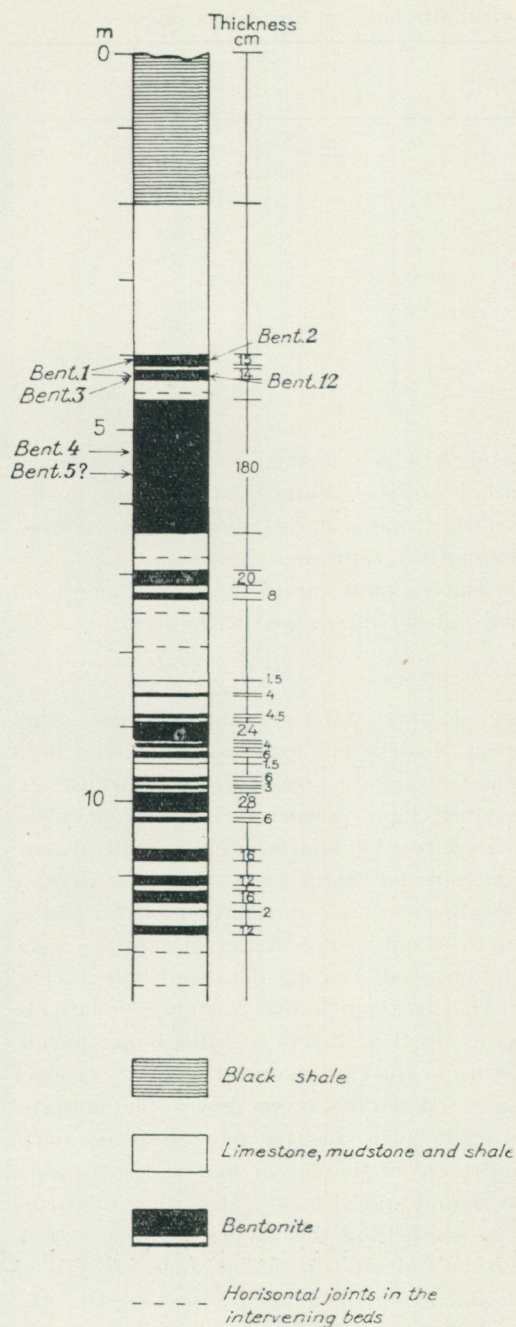
Fig. 1. Diagram of the section at Mossen, Kinnekulle, Sweden. The levels of specimens investigated are marked. (Thorslund 1948, p. 351.)

the time of the boring the presence of the bentonite beds was not fully known and part of the material was carried away with the drilling mud. When this paper was in a state to be published, samples from the lower beds of the Kullatorp core became available, and have been given a superficial study only. In Table I the investigated samples are grouped together. Of samples Bent. 1— Bent. 7 and Bent. 12 there were only fairly small quantities of 100—200 grams each. Bent. 8 comprised about 1000 grams. About 25 kg. of samples Bent. 14 and Bent. 15 were available.

Bent. 1, 2 and 3. Samples from the upper thin beds similar in appearance consisted of small grey slabs up to an inch in diameter. Flakes of biotite were clearly visible as dark spots in the grey mass. Fractures perpendicular to the slabs showed them to be strongly laminated.

Bent. 4. An apparently homogeneous dark grey sample with a laminated structure and easily cleavable parallel to the layers. The fractures had a lustrous appearance and were soapy to the touch, as was the case with most of the bentonite specimens. Fractures perpendicular to the cleavage planes showed conchoidal features. Biotite flakes were abundant.

Bent. 5. A fairly light grey material with no visible biotite grains. All fractures were conchoidal and the rock seemed to have originated from a clay without coarser phenocrysts.

Table 1. Samples from the bentonite beds at Kinnekulle, Sweden.

Number		Place of sampling	Date & Sampler			Approximate level	Bed
Bent.	1	Mossen	2/9	1945	Thorslund	4.0—4.3 m	upper thin bed
Bent.	2	"	14/10	"	"	4.0—4.15 m	upper thin beds
Bent.	3	"	"	"	"	4.2—4.3 m	second upper thin bed
Bent.	4	"	"	"	"	5.5 m	thick bed
Bent.	5	"	26/5	"	"	?	thick bed?
Bent.	6	Nordskagen	14/10	"	"	?	upper thin beds
Bent.	7	"	"	"	"	?	thick bed
Bent.	8	?		"			upper thin beds
Bent.	12	Mossen	/6	"	"	?	upper thin beds
Bent.	14	near Mossen	July 1951 Höganäs-Billesholms AB			?	thick bed
Bent.	15	near Mossen	July 1951 Skånska Cement AB			?	thick bed

Bent. 6. A very light grey specimen which seemed to have been more exposed to weathering than the other samples. Large biotite grains dotted the surface and isolated veins of darker material ran through the sample.

Bent. 7. Resembled Bent. 5. No biotite grains were visible.

Bent. 8. Resembled Bent. 1. The material was considerably weathered and had disintegrated to a finely divided powder intermixed with small pieces of non-weathered material.

Bent. 12. Resembled Bent. 1.

Bent. 14. The sample was collected from material quarried some years earlier by Höganäs-Billesholm AB near Mossen. The material, which had been unprotected during the interval, was considerably weathered and whilst the greater part consisted of a fine-grained light powder, specimens could be selected of weights up to approximately two kg. which had not disintegrated. These appeared markedly adverse in character. Some parts resembled Bent. 5 with a dense smooth clay-like appearance. Other parts resembled Bent. 4 with its pronounced layer-like structure and visible flakes of biotite. Some of the specimens showed a stratification of alternating dark and light layers, each only a few millimeters thick. The light parts always showed relatively large flakes of biotite and quartz grains. In these layers with the larger phenocrysts it is obvious that the weathering in the clay material is much stronger than in the dense fine-grained layers. When breaking down, the material first of all splits up along the weathered layers and the more resistant parts then appear as thin plates. Here and there in the denser material small hard balls of a dark green colour could be found and also elongated rods appearing to consist of fine-grained clay material whirled together. When cut the "nodes" showed a very fine featherlike striation and often included small crystals of pyrites. Pyrites were quite often found as small octahedra scattered in the material.

Bent. 15 was a sample from the quarry of Skånska Cement AB near Mossen.[1] This material was more homogeneous than Bent. 14 and consisted of specimens

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[1] 2 mm N second r in "Övergården" on the topographical map no. 53, Mariestad 1 : 100000.

weighing some kilograms each and resembling Bent. 4, *i. e.*, fairly dark grey material with a slaty structure. Between the layers, quite irregularly, thin sheets of limestone extended, and the material split preferably along these.

Of the specimens here described Bent. 1, Bent. 4, Bent. 8, and Bent. 15 have been subject to a more detailed investigation, and the other specimens have been classified accordingly, using one or two methods of determination only.

Methods of Investigation — General Survey.

Clay minerals constitute by far the greater part of the bentonite beds giving them a basic uniformity. At the same time, as has been described here, samples differ considerably in appearance. The phenocrysts although present only in small quantities contribute greatly to the visible differences between the bentonite samples. The biotite with its dark colour and flaky character is especially prominent. It can be seen from the layers with alternating larger

Fig. 2. Thin section of sample from thick bed, cut perpendicularly to the plane of layers. 3 ×. (Photo C. Larsson.)

and smaller grains that at some time a fractionation of the material must have occurred. Fig. 2 shows a typical example of a bentonite specimen where the parallel orientation of the flakes can clearly be seen. The main part of the investigation has been concerned with the determination of the nature of the clay minerals since in most specimens these constitute 80 % or more of the material. The phenocrysts, which consist chiefly of quartz, and, in smaller quantities, biotite and fresh and altered feldspars, have been investigated mainly to get some knowledge of the genesis of the material.

Chemical analyses, studies of cation exchange capacity, X-ray analyses and differential thermal analyses were the chief methods of investigation used. The material has been examined both in its original state and after fractionation. The fractionation was carried out in order to obtain either fine fractions

containing chiefly clay materials, or coarser fractions from which the pheno-
crysts could be isolated for a closer investigation. The methods have not
been applied to give completely quantitative results, but have rather been
used qualitatively with the primary object of identifying the minerals present.

Beside the methods mentioned, extraction experiments and some micro-
scopical determinations were undertaken. The electron microscope was used
on a few samples.

Table II. K$_2$O content of bentonite material from Kinnekulle, on dry basis 110°C.

Specimen	Bed	natural sample % K$_2$O	fraction < 0.02 mm % K$_2$O	fraction < 0.5 μ % K$_2$O	
Bent. 1	upper thin	5.40	5.26	—	Type II
Bent. 4	thick	2.52	2.47	—	Type I
Bent. 5	thick?	—	—	4.32	Type II
Bent. 6	upper thin	—	4.77	4.78	Type II
Bent. 7	thick	2.88	—	3.19	Type I
Bent. 8b...	upper thin	5.36	—	4.51	Type II
Bent. 12	upper thin	—	5.42	—	Type II
Bent. 14	thick	3.08	—	—	Type I
Bent. 15	thick	2.80	—	2.77	Type I
analyses No. 2461	thick	2.66	—	—	Type I

In order to obtain a general picture X-ray photographs were taken of the
various samples, when it was found that the specimens from the thin beds
gave somewhat different diagrams from those of the thick bed. The swelling
capacity also differed for material from different beds. The potassium content
of most of the specimens was determined and the results have been listed in
Table II. From this it can be seen that there are distinct differences of the
K$_2$O content of the different layers and that the material from the thin beds
always shows a higher potassium content. In some cases a partial fractionation
has been carried out but there are no essential differences as compared with
the natural material. Material from the thick bed is referred to as Type I,
and material from the two upper thin beds as Type II.

Investigation of the Clay Material.

Dispersion and Fractionation.

Sedimentation analyses were carried out to obtain fractionated material
for further investigation, and to acquire information about the particle size
distribution. The bentonite material disintegrates fairly rapidly when placed
in water, and when placed in a solution of sodium pyrophosphate large pieces
weighing several kilograms will fall to pieces in a few minutes. The clay
suspensions, however, are not completely dispersed, but mainly contain flaky
aggregates ranging in size from a few millimeters downwards. The greater
part of these disperse only after drying and repeated treatment with sodium
pyrophosphate solution.

Table III. Sedimentary analyses of bentonite material from Kinnekulle, The analyses were made on Bent. 8 (for pretreatment see below).

	slow rotation, 16 hours			shaking, 16 hours	
dispersion media	dest. H_2O	NH_3 0.1 N		$Na_4P_2O_7$ 0.005 m	
material	8a 0.5—0.2 mm	8 natural sample[1]	8a ground 12 h.[1]	8 natural sample	8b < 0.2 mm
fraction mm	%	%	%	%	%
2—0.6	—	3.4	—	⎱ 20	⎱ 14
0.6—0.2	57	24.0	0.9		
0.2—0.06	11	25.4	17.5	⎰	⎰
0.06—0.02	3	15.4	25.4	7	12
0.02—0.006	4	6.6	9.8	11	8
0.006—0.002	4	3.5	5.6	15	14
< 0.002	14	21.1	38.2	50	53

Bent. 8 $\xrightarrow[\text{0.2 mm}]{\text{sieving}}$ fraction > 0.2 mm → sieving (slightly crushed)
⟶ 8b < 0.2 mm
→ 8a 0.2—0.5 mm → part ground for 12 h
↘ 8c > 0.5 mm

Table III sets out data from the sedimentation experiments. At first all experiments were carried out on sample Bent. 8, as more of this specimen was available than of the others. As mentioned above Bent. 8 was a strongly weathered specimen and to avoid the most finely divided material, it was partially fractionated by sieving and very slight crushing before the sedimentation analyses were carried out. The fractions obtained can be seen at the bottom of Table III.

The first column of Table III gives the range of particle sizes in mm and the other columns give the quantities of the different sizes obtained by using various dispersion media. Distilled water in connection with slow rotation gave a small fraction of particles with apparent grain size less than 2 microns. When ammonium hydroxide solution was used, a better result was obtained, but the clay fraction was still very low. Some of the material was ground in a ball mill for 12 hours prior to dispersion in ammonium hydroxide solution. The result can be seen in Column 4. The clay fraction is nearly twice as great as for the unground sample, but is not as great as might have been expected after this rigorous treatment of a soft material. The last two columns give the results of dispersion in sodium pyrophosphate solution, with more powerful agitation. In these cases the dispersion is much greater, the clay fraction making up half of the material, but the coarser fractions still contain clay mineral aggregates. With alternating drying and re-dispersion, some of these could be broken down, but there always remained some aggregates which resisted dispersion. These have been further described in the second part of this paper.

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[1] Analyses made by B. Berselius, Geological Survey of Sweden.

As can be seen from Table III the particle size distribution is strongly dependent on the pretreatment of the material and on the dispersion conditions and no further attempts were made to obtain a quantitative determination of particle sizes. Sedimentations were performed later, but only when it was necessary to fractionate the material for the further investigation.

The material Bent. 8 used in the dispersion experiments described here was of Type II from the thin beds and to obtain information concerning material of Type I from the thick bed a large specimen of Bent. 15 (about 3 kilograms) was selected for fractionation. The specimen had a typical layer structure. It was dotted with biotite flakes and irregularly interspersed with thin sheets of calcium carbonate. Before dispersion the sample was leached with weak hydrochloric acid (1 : 100) to prevent flocculation by removing the calcium carbonate present. When only traces of calcium persisted in the decanted solutions the material was washed with water and then fractionated. The clay fractions were used for the chemical analyses, the other fractions being used in the further investigation of the clay minerals, and for the separation of non-clay materials, since in this case an especially large amount of the initial material had been used.

As such a large part of the bentonite material was comprised of clay aggregates, it seemed appropriate to endeavour to establish whether or not these aggregates were built up of the same clay minerals as were obtained in the true clay fraction. The coarser fractions from the sedimentation experiments were therefore further fractionated in heavy liquids, mixtures of bromoform and carbon tetrachloride being used. From a liquid with a specific gravity of 2.36 the top fraction was collected for further investigation of the clay aggregates. Most of these floated in liquids with specific gravity 2.50. There was no sharp limit, however, and the clay aggregates showed rather arbitrary specific gravities since they absorbed the separation liquid to a certain extent and also held inclusions of heavier minerals such as quartz and biotite. A fraction with specific gravity considerably below that of quartz was therefore chosen in the hope of getting a fairly pure clay mineral.

Chemical Analyses.

The following samples were chosen for the chemical analyses. Of Type I from the thick bed, two clay fractions were selected with apparent particle sizes less than 0.5 microns and 0.5—2 microns respectively. The analyses are given in Table IV, Columns 5 and 6. The analysis given in Column 7 is also of a sample from the thick bed, but from a natural specimen. The first four columns give analyses from Type II from the thin beds. In Column 1 there will be found an analysis from a natural specimen and, in Columns 2, 3 and 4, three from the sedimentation experiments. Thus two clay fractions with particles less than 2 microns were chosen, one from material dispersed in water and the other from material dispersed in ammonium hydroxide solution. The third sample was a clay aggregate fraction with apparent specific gravity less than 2.36 and particles > 0.06 mm.

Table IV. Chemical analyses of bentonite material from Kinnekulle.

	upper thin beds			thick bed		
	Bent. 1	Bent. 8a			Bent. 15		
	1. No. 2652	2. An. 105	3. An. 103	4. An. 101	5. An. 126	6. An. 127	7. No. 2461
SiO_2	50.37	52.86	53.86	53.13	58.87	53.17	55.99
TiO_2	0.39	0.36	0.34	0.38	0.18	0.20	0.14
Al_2O_3	22.37	22.97	23.53	23.19	22.34	20.43	18.75
Fe_2O_3	1.11	1.64	2.09	1.68	2.53	1.86	0.76
FeO	1.28	0.55	not det.	0.37	0.36	0.65	1.85
MgO	3.70	3.11	3.26	3.61	4.23	3.90	3.92
CaO	1.25	1.40	0.18	1.10	0.12	0.20	2.30
Na_2O	0.05	0.0	0.0	0.0	0.16	0.15	0.08
K_2O	4.96	4.83	4.94	4.89	2.75	2.35	2.48
$H_2O > 110° C$	6.26	6.76	7.82	7.58	7.75	6.12	6.05
$H_2O < 110° C$	8.20	5.79	4.17	4.25	0.77	11.40	6.90
CO_2.........	0.09	0.05					0.84
	100.03	100.32	100.19	100.18	100.06	100.43	100.06

1. No. 2652 Bent. 1   Not fractionated material.
2. (An. 105) Bent. 8a   Material dispersed in H_2O; clay fraction $< 2 \mu$.
3. (An. 103) Bent. 8a   Material ground for 12 hours, dispersed in NH_3, HCl washed; clay fraction $< 2 \mu$.
4. (An. 101) Bent. 8a   Material dispersed in H_2O, fraction > 0.06 mm, and specific gravity < 2.36.
5. (An. 126) Bent. 15,   Material leached with HCl (1 : 100); clay fraction $< 0.5 \mu$.
           No. 387
6. (An. 127) Bent. 15,   Material leached with HCl (1 : 100); clay fraction $0.5—2 \mu$.
           No. 388
7. No. 2461   Sample from the Kullatorp core at 68.90 m. Other determinations made on this material: MnO = 0.02 %, BaO = 0.0 %, P_2O_5 = = 0.05 %, S = 0.0 % and F = 0.02 %. (Thorslund 1948.)

Analyses 1—4 by Mr. A. Aaremäe, Geological Survey of Sweden.

Table V gives a recalculation on dry basis + 110° C of the analyses given in Table IV in order to facilitate a comparison of the values. Data from ion exchange determinations for three of the substances are included in the lower part of Table V. Where the total exchange capacity differs from the sum of the different cations the difference is due to hydrogen ions, which have not been directly determined.

We see that the analyses from the different fractions of Bent. 8 show a strong resemblance to one another, and judging from the chemical analyses only, the clay substance occurring in the finest fraction seems to be the same as that present in the aggregates. The magnesium content is slightly higher for the clay aggregates, which might be due to the presence of tiny flakes of biotite, rich in magnesium, interfoliated between the aggregated clay flakes. For the clay fraction isolated by dispersion in ammonium hydroxide solution the analysis shows a very low calcium content which is, however, quite natural as the material was neutralized with dilute HCl and then washed with water and alcohol, during which treatment the calcium ions were exchanged and a H-bentonite was obtained. The analysis of an unfractionated sample of Bent. 1, from another part of the thin bed, is very similar to those of Bent. 8. The FeO content is higher but the total iron content is not correspondingly

Table V. Chemical analyses given in Table IV recalculated on dry basis 110°C.

	upper thin beds			thick bed		
	Bent. 1	Bent. 8a			Bent. 15		
	1. No. 2652	2. An. 105	3. An. 103	4. An. 101	5. An. 126	6. An. 127	7. No. 2461
SiO_2	54.87	56.11	56.20	55.49	59.33	60.01	60.14
TiO_2	0.42	0.38	0.35	0.40	0.18	0.22	0.15
Al_2O_3	24.37	24.38	24.55	24.22	22.51	23.06	20.14
Fe_2O_3	1.21	1.74	2.18	1.75	2.55	2.10	0.82
FeO	1.39	0.58	non det.	0.39	0.36	0.73	1.99
MgO	4.03	3.30	3.40	3.77	4.26	4.40	4.21
CaO	1.36	1.49	0.19	1.15	0.12	0.22	2.47
Na_2O	0.05	0.0	0.0	0.0	0.16	0.17	0.08
K_2O	5.40	5.13	5.15	5.11	2.77	2.65	2.66
$H_2O > 110°$ C	6.82	7.17	8.16	7.92	7.81	6.91	6.50
CO_2	0.10	0.05					0.90
	100.02	100.33	100.18	100.20	100.05	100.47	100.06
ion exchange capacities	eq/100 g						
total		0.046	0.043		0.070	0.077	
$^1/_2Ca^{2+}$		0.039	0.001		0.008	0.003	
$^1/_2Mg^{2+}$		0.011	0.003		0.018	0.014	
Na+		0.0007	—		0.004	0.002	
K+		0.002	—		0.005	0.002	
H+ (calc.)			0.039		0.035	0.056	
$H_2O > 208°$ C		5.82	6.08		6.04(> 200° C)		
$H_2O > 300°$ C					4.89	4.90	

For key to the analyses see Table IV.

high and the difference is probably due to a partial oxidation of the ferro iron during the treatment of Bent. 8. The biotite in the non-fractionated material contributes to the high FeO content as well as to the fairly high magnesium value. An X-ray photograph of Bent. 1 shows the presence of quartz, which is, however, in a very fine-grained form and difficult to determine quantitatively. By the method of Line and Aradine (1937), in which the silicates are extracted with fluoboric acid (HBF_4), a value of only 1 % was obtained (Table IX). The amorphous SiO_2 as determined from extraction with a soda solution was less than 0.5 %.

The two analyses of Bent. 15 from the thick bed were made from specimens very similar to one another. For both analyses clay fractions were used; for the analyses in Column 5 the fraction with an apparent particle size of less than 0.5 μ, and for that in Column 6 the fraction with particles between 0.5—2 μ. The results of the analyses are practically identical and show no material difference between the clay minerals in these finer fractions. Both

materials have been transformed to hydrogen bentonites and thus show a low calcium content. Comparing the clay fractions with the natural specimen, No. 2461, also from the thick bed, it can be seen that the impurities of the natural specimen do not influence the analysis to any great extent. The admixture of quartz tends to make the aluminium value low and the difference in the calcium content is due to the pretreatment of the fractionated material. The resemblance to the analyses from the thin beds can be seen; only the values for the potassium content diverge appreciably, being half of those from the thin beds.

Calculations based on the Chemical Analyses.

Structural formulae have been calculated using five of the analyses given in Table V, *i. e.*, Nos. 2, 3 and 4 from Bent. 8, Type II, and Nos. 5 and 6 from Bent. 15, Type I. The results will be found in Table VI. The calculations are based on the method used by Ross and Hendricks (1945) for montmorillonites using the ideal formulae for pyrophyllite, $Si_8Al_4O_{20}(OH)_4$, and muscovite, $(Si_6Al_2)Al_4O_{20}(OH)_4K_2$ as a basis. The substitution of some of the atoms in the different layers results in minerals with intermediate formulae. The calculations of structural formulae for the clay minerals are therefore based upon the compensation of the 44 negative charges of the oxygens and hydroxyls ($20\ O + 4OH$) by as many positive charges. The atoms contributing the positive charges are: in the *tetrahedral layer*, Si and part of the Al, to such an extent that this layer is always filled with 8 atoms; in the *octahedral layer*, the rest of the Al, the Ti, Fe, and Mg atoms; and, in the *inter-layer*, the K atoms and the equivalents of the exchangeable ions, such as Ca^{2+}, Mg^{2+}, Na^+ and H^+.

It has not been possible to obtain a reliable value for the exchangeable H^+ ions by direct determination and for the H-bentonites the value of H^+ has been taken as the difference between the total cation-exchange capacity and the sum of the exchanged ions determined.

It is not quite certain that, as has been assumed here, the titanium forms part of the clay mineral structure. It is plausible, however, that it does, as there is very little variation in the Ti-content for different fractions of the same material. In addition it has not been possible from the X-ray diagrams of the analysed samples to identify any specific titanium mineral. This would, however, not be easy with the small quantities involved. The biotite isolated from the thick bed has a Ti content as high as 1.40 %, but the amount of admixed biotite is negligible in all analysed specimens except the clay aggregate sample (Analysis An. 101) which was observed under the microscope to contain some flakes of biotite, roughly estimated at 2 per cent and for which the analysis has been corrected.

From Table VI it can be seen that in all the analyses the octahedral layer is filled with very nearly the theoretical number of 4 atoms, as in the ideal pyrophyllite formula. The number of inter-layer atoms in the ideal muscovite

Table VI. Cell contents of clay minerals, Type II and Type I, from the bentonite beds at Kinnekulle.

Calculated from analyses given in Table V.

		Type II Bent. 8, upper thin beds				Type I Bent. 15, thick bed		
No. of analysis		An. 105		An. 103	An. 101	An. 127	An. 126	
method of calculation		b	a	a	a¹	a	a	b
tetrahedral layer	Si	7.31	7.37	7.34	7.37	7.58	7.61	7.54
	Al	0.69	0.63	0.66	0.63	0.42	0.39	0.46
	sum	8.00	8.00	8.00	8.00	8.00	8.00	8.00
octahedral layer	Al	3.05	3.14	3.12	3.15	3.01	3.01	2.92
	Ti	0.037	0.037	0.037	0.037	0.020	0.017	0.017
	Fe^{3+}	0.170	0.172	0.214	0.173	0.199	0.246	0.244
	Fe^{2+}	0.063	0.064	—	0.002	0.077	0.038	0.038
	Mg	0.597	0.602	0.649	0.650	0.774	0.744	0.738
	sum	3.92	4.01	4.02	4.01	4.08	4.05	3.95
inter-layer fixed	K	0.852	0.859	0.858	0.867	0.427	0.453	0.449
	H_3O^+	0.353						0.375
	sum	1.20	0.86	0.86	0.87	0.43	0.45	0.82
exchangeable	eq.	0.36	0.36	0.34		0.58	0.54	0.53
total		1.56	1.22	1.20		1.01	0.99	1.47
exchangeable ions	H+calc.		—	0.31		0.42	0.27	
	K+		0.02	—		0.01	0.04	
	Na+		0.0	—		0.01	0.03	
	$^1/_2Ca^{2+}$		0.31	0.01		0.02	0.06	
	$^1/_2Mg^{2+}$		0.09	0.02		0.11	0.14	
H_2O—4(OH)	> 110° C		1.14	1.56		0.70	1.21	
	> 208° C		0.55	0.65			0.45 (> 200° C)	
	> 300° C		—	—		— 0.15	— 0.04	

methods of calculation: a, assuming 20 O + 4(OH)
            b, assuming 24 O and water above 208° C comprising H_3O^+ + 4 (OH) (for An. 126 water above 200° C was used).

formula is 2, consisting mainly of potassium, and in the montmorillonite formula approximately 0.7, consisting of exchangeable ions such as calcium and sodium. The clay minerals investigated here have intermediate values which place them between the muscovites and the montmorillonites. If the clay minerals are regarded as mixed minerals composed of montmorillonite layers and muscovite layers, a rough estimate of the relative proportion of

[1] Corrected for 2 % biotite of composition found in Table XVII.

the two different layers can be obtained from the analyses by assuming that all layers holding potassium (*i. e.*, K layers) are of the muscovite type and the others not holding potassium (*i. e.*, 2-K layers for the structural formula here used) are of the montmorillonite type. For Bent. 15, Type I, the ratio of K/2-K is 21 : 79, and for Bent. 8, Type II, 43 : 57, so that the approximate ratio of muscovite to montmorillonite layers is 1 : 4 in Type I and 2 : 3 in Type II.

Ross and Hendricks (1945) have found that for most montmorillonite minerals the base-exchange capacity is very nearly one-third of an equivalent for each layer (using half the structure formula here used) and, combining this value with the proportion of montmorillonite layers found above, we get a calculated base-exchange capacity of 0.53 equivalents for Bent. 15, Type I, corresponding to 69 meq/100 g material. The observed value was 77 meq/100 g for An. 127. Similar calculations for Type II, Bent. 8, give 48 meq/100 g where the observed value is 46 meq. The values show a close agreement and, as a first estimate of the different layers, the calculations seem well founded.

By these calculations we can distinguish non-swelling layers, characterized as potassium-fixed muscovite layers, and swelling layers characterized as montmorillonite layers. It must, however, be taken into account that the non-swelling layers can be fixed in other ways than by potassium, as for instance is the case in illite, with a layer distance of 10 Å as in muscovite but with a lower potassium content. The lack of potassium is compensated for by a higher water content which has been thought to replace the potassium in some form. The water must therefore also be included in the calculations. Somewhat different results are thus obtained if the non-swelling layers are assumed to be illite layers.

Brown and Norrish (1952), in calculations on illite minerals, assumed that part of the potassium was replaced by H_3O^+ and, to obtain a value for H_3O^+, the water content above 110° C was regarded as comprising $4(OH) + H_3O^+$. Such calculations may be justified for the illites but are not so clearly applicable to the Kinnekulle clay minerals which also contain swelling layers of variable hydration. At 110° C the X-ray diagrams show inter-layer distances greater than 10 Å and only at 200° C is the retraction complete. The loss-of-weight curves (Fig. 3) also show that the first dehydration is only completed at about 200° C. The calculations should therefore preferably be based upon water lost above this temperature. This assumes that the H_3O^+ has such a strong binding effect on the layers that it is not lost below 200° C. For two of the samples the cell content has been calculated assuming 24 oxygens in the cell as before but including H_3O^+ for which a value was obtained after reduction of 4 hydroxyls from water lost above 200° C. The result can be seen in Columns b in Table VI. For Type II the number of non-swelling layers is found to be 1.20 of the two possible ones, which gives a proportion of 3 : 2 for non swelling to swelling layers, a plausible value considering other properties. For Type I the corresponding relation is 2 : 3, which is a high value in comparison with

other properties, and probably the water involved in the swelling layers has not been completely removed at this temperature.
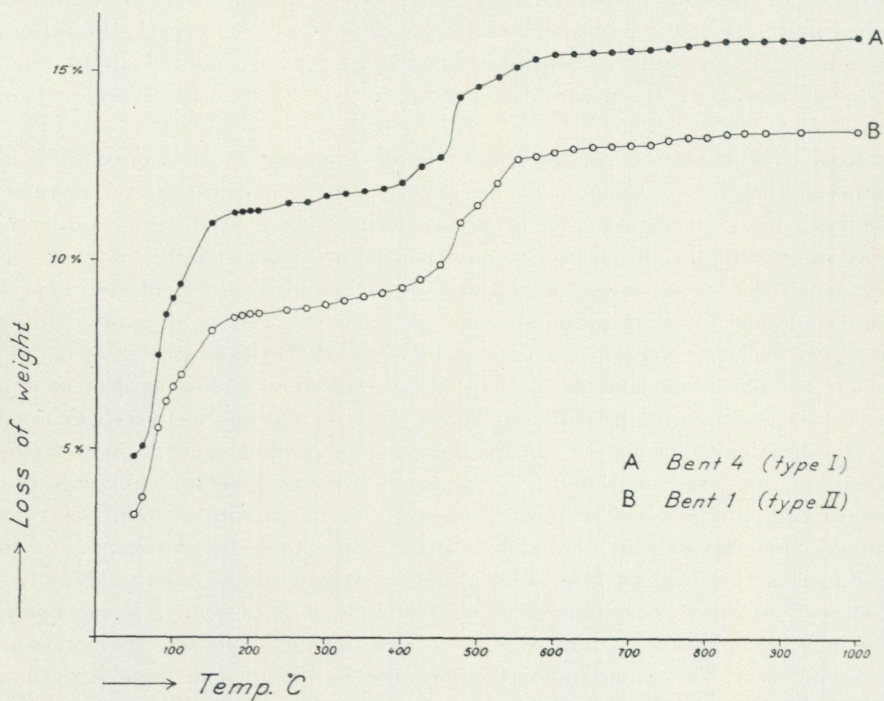
Fig. 3. Loss of weight curves for two bentonite specimens from Kinnekulle. A, Bent. 4, Type I and B, Bent. 1, Type II.

A determination of water lost above 300° C was made. It can be seen that it very nearly corresponds to 4 OH and none is left for water in other positions. This result was also reached by Ross and Hendricks (1945) for the pure montmorillonite minerals.

When dealing with clay minerals such as those under investigation the many uncertain factors involved make the calculation of the proportions of the different layers rather arbitrary. When the structural formulae, however, are considered, the close agreement of the number of octahedrally-bound atoms with the theoretical value is striking, indicating that the minerals are of the dioctahedral type, and making it probable that mineral components of a very different character could not be present. On the other hand the assumption that non-swelling and swelling layers are present makes it probable that these have different compositions. In such calculations it might be assumed that when potassium is fixed as an inter-layer atom the layers tend to attain a muscovite-like arrangement. In the case of Type I the replacement of Si by Al is just compensated for by the potassium and the rest of the layers have a composition very typical of a montmorillonite. This is not so in the case of Type II and either some of the potassium must be com-

pensated for by substitutions in the octahedral layer or a marked excess of silica is present. These conditions might cause the more complex nature of Type II, which, as will be seen later when discussing the X-ray data, seems to contain layers of intermediate swelling-power as well.

Table VII. Cell contents of clay minerals Type II and Type I from the bentonite beds, Kinnekulle, compared with a muscovite and a potassium bentonite.

atoms		1. muscovite	2. K-bent.	3. Bent. 8 Type II	4. Bent. 15 Type I
in tetrahedral layer	Si	6.00	7.10	7.37	7.58
	Al	2.00	0.90	0.63	0.42
		8.00	8.00	8.00	8.00
in octahedral layer	Al	3.68	3.28	3.14	3.01
	Ti	—	—	0.04	0.02
	Fe^{3+}	0.10	0.04	0.17	0.20
	Fe^{2+}	0.14	—	0.06	0.08
	Mg	0.08	0.68	0.60	0.77
	Li	0.10	—	—	—
		4.10	4.00	4.01	4.08
in inter-layer	K	1.48	1.28	0.86	0.43
	Na	0.16	0.04	0.0	0.01
	Ca+Mg	0.02	0.14	0.18	0.29
		1.66	1.44	1.04	0.73
potassium calculated for lowest multiples of 0.43		$4 \times 0.43 = 1.72$	$3 \times 0.43 = 1.29$	$2 \times 0.43 = 0.86$	$1 \times 0.43 = 0.43$

1. Muscovite, described by Maugin (1928), cited by Bragg, W. L., in Atomic Structures of Minerals (1936) p. 213.
2. K-bentonite, described by Weaver (1953).
3. Bent. 8, clay mineral, Type II, from Kinnekulle, Sweden (An. 105, Table V).
4. Bent. 15, clay mineral, Type I, from Kinnekulle, Sweden (An. 127, Table V).

In Table VII the cell contents of the two types of Kinnekulle clays are grouped together with a muscovite (Maugin, 1928) and a potassium bentonite (Weaver, 1953). The simple relationship between the potassium atoms, which form a series of integral multiples of the lowest value of potassium, 0.43, can be seen from the bottom line of Table VII. This appearance of integer multiples might be considered fortuitous. It could on the other hand be interpreted as an indication that, when placed in certain positions, potassium makes the structure more stable. It might explain why certain distinct types dominate when continuous transitions of mixed layers of muscovite and montmorillonite could just as well be expected. The muscovite has been included to show that, not even in this well-crystallized mineral, is the inter-layer completely filled

and among the analyses of muscovite given in the literature hardly any example could be found of the exact theoretical number of 2 inter-layer atoms. It is possible that the structure is only stable when it holds slightly less than 2 potassium atoms distributed statistically over the possible positions or when it contains a number of smaller atoms such as Na.

This discussion on the composition of the respective layers is an attempt to elucidate the clay minerals from different points of view. The question as to the right interpretation of the chemical analyses must be left open for the moment.

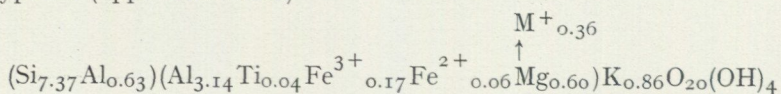The mean composition, however, as found from the calculations assuming 20 oxygens and 4 hydroxyls in the cell for the two types of clay found in the bentonite beds at Kinnekulle, can be expressed in the following structural formulae:

Type I (thick bed)

$$(Si_{7.58}Al_{0.42})(Al_{3.01}Ti_{0.02}Fe^{3+}{}_{0.20}Fe^{2+}{}_{0.08}Mg_{0.77}) \overset{M^+{}_{0.58}}{\underset{\uparrow}{K_{0.43}}} O_{20}(OH)_4$$

Type II (upper thin beds)

$$(Si_{7.37}Al_{0.63})(Al_{3.14}Ti_{0.04}Fe^{3+}{}_{0.17}Fe^{2+}{}_{0.06}Mg_{0.60}) \overset{M^+{}_{0.36}}{\underset{\uparrow}{K_{0.86}}} O_{20}(OH)_4$$
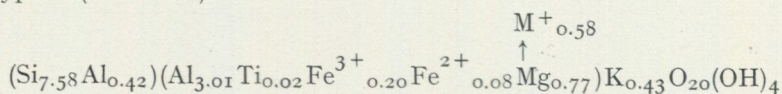
Studies of Cation-Exchange Capacities.

When investigating clay minerals, studies of base exchange capacities are usually made, the results of which, together with a knowledge of the exchanged ions originally belonging to the material are of valuable help when forming an opinion as to the qualities of the clays. The exchange capacity is generally given as the number of milli-equivalents exchanged in 100 g material on a 110° C dry basis and varies greatly for different clay minerals (from 3 meq for kaolin up to 150 meq for vermiculite). Many factors have an effect upon the ion-exchange capacity and there is no distinct value attached to a specific clay mineral. On the contrary, values spread over a considerable range have been recorded, e. g., from 3—15 meq for the kaolin minerals, from 10—40 meq for illites and chlorites, and from 80—150 meq for the montmorillonites. The determination consequently gives no absolute characterization of the clays but is useful in combination with other methods. A review of the exchange capacities of clays containing a large number of references has recently been made by Grim (1953).

There are several methods for determining base-exchange capacities, of which that described by M. D. Forster (1951) has been found to be convenient, and to give reproducible results. This method has been used to obtain the values given in this paper. Neutral ammonium chloride is used to extract

the exchangeable cations, after which, Ca, Mg, K and Na are determined in the solution. The ammonium taken up is determined from the residual powder by distillation. Bower et al. (1952) stated that ammonium is partly fixed when such solutions are used for extraction of the exchangeable ions. This tends to give low values for the total exchange capacity when this is determined by distillation of ammonium, and the sum of the exchanged ions is considered to give a better value. During the investigation of the material from Kinnekulle, however, it was shown that the reproducibility of the total capacity was much greater when it was determined by the direct distillation method than when it was calculated from the sum of the ions in solution, since the aggregated errors of analyses were too great to give comparable values. Furthermore, most of the specimens contained small amounts of carbonate. This was also extracted by the ammonium chloride and, although the CO_2-content in the material could be determined and Ca^{++} in the solution thereby corrected, another source of error was involved. Hence the solutions were analysed to ascertain the character of the exchangeable ions only, the total capacity being determined from the ammonium taken up.

Prior to the extraction with NH_4Cl the specimens were in some cases leached with distilled water to determine the water soluble salts and also the pH. The pH value for the water solutions was at the beginning about 6.1—6.3 but slowly rose to about 6.8—7.2 and only the solutions from material with very low carbonate content retained a fairly steady pH-value of about 6.3. The amount of the water soluble salts was quite insignificant and a quantitative estimate was made in one case only, giving a value of less than 1 meq/100 g for the extracted ions recalculated as calcium.

Method. About 2 g of sample is mixed with 30 ml of a neutralized 1N, NH_4Cl-solution and vigorously shaken. The solution is left overnight or longer and the clear solution is then decanted through a filter paper (oo), as little as possible of the substance being transferred to the filter. Another 30 ml of the NH_4-solution is added and the sample shaken. When clear, the solution is again decanted. This procedure is repeated 4—5 times after which the sample is washed with alcohol diluted with water for the first washings to obtain a quicker extraction of the ammonium chloride, and then with 95 % alcohol. The sample is transferred to the filter paper and washed until the filtrate does not show a chloride reaction. The solutions are evaporated and the extracted ions, *i. e.*, Si, Fe, Al, Ca, Mg, Na and K, determined by ordinary methods of analyses. To determine the ammonium ions in the residual powder the filter paper with its content is transferred to a distillation apparatus. 2 g $Ba(OH)_2$ is added to drive off the ammonium, which is taken up in a 2—3 % solution of boric acid to which has been added a mixed indicator of bromo-chresol-green and methyl-red (Ma and Zuazuga 1942). The ammonia in the boric acid solution is directly titrated with a HCl-solution (0.1 N).

In Table VIII are collected some results from ion-exchange capacity determinations on material from Kinnekulle. Samples of Bent. 1, 4, 5 and 6 were slightly crushed and passed through a sieve (200 mesh) and the ion-exchange capacity was determined for both fractions of each sample. This was done in order to get the more weathered and finely divided powder into one fraction and the unweathered part into the other and to obtain from the results of the separate determinations a knowledge of possible differences. As can be seen from Table VIII, however, these were not significant. The slightly lower values for the coarse fractions were probably due to the smaller

Table VIII. Base exchange capacities of bentonite samples from Kinnekulle.

| Type | samples | fraction in mm. | % H₂O < 110°C | ½CO₃⁻⁻ | cations in extract solution | | | | | | total B.E.C. from NH₄ dest. |
					½Ca++ total	½Ca++ corr. for CO₃⁻⁻	½Mg++	K+	Na+	Sum	
II	Bent. 1	< 0.075	7.48	4.5	40.7	36.2	10.4	—	—	49	46
		> 0.075	7.34	4.5	38.4	33.9	—	2.2	0.7	47	45
II	Bent. 2	< 0.5	7.79	5.4	41.4	36.0	11.3	1.9	0.8	50	46
II	Bent. 5	< 0.075	7.62	10.8	47.0	36.2	—	3.0	0.8	54	47
		> 0.075	7.80	8.4	43.2	34.8	14.4	—	—	53	46
II	Bent. 6	< 0.075	8.36	0.5	42.0	41.5	—	2.6	0.8	55	52
		> 0.075	8.45	0.5	40.5	40.0	10.3	—	—	54	51
II	Bent. 8b	< 0.2	8.10	2	41.2	39.2	11.5	—	—	—	46
I	Bent. 4	< 0.075	8.42	18.3	58.0	39.7	—	2.2	0.6	53	57
		> 0.075	8.64	12.4	53.2	40.8	10.6	—	—	54	56
I	Bent. 7	< 0.2	6.36	4.2	44.0	39.8	14.1	4.2	1.0	59	52

surface of the coarser grains. The values are recalculated on dry basis 110° C and the water loss below 110° C is also included in the table. The CO_2 content was determined to get a correction for the extracted calcium ions, and this has been recalculated to milli-equivalents of CO_3^{--}. Table VIII also gives the values of the extracted ions and as can be seen the sum of these for each sample is about 5—15 % greater than that determined from the ammonium distillation. In those cases where all the ions were not determined for one fraction of the sample, values have been taken from the other fraction as these were in general very similar and small differences would not appreciably affect the total sum.

The table shows that the ion-exchange capacities for the samples Bent. 1, 2 and 8 b (all of Type II from the thin beds) are very much alike, at about 46 meq/100 g. Bent. 5 has the same value and X-ray photographs show it to belong to Type II; unfortunately it is not certain from which bed this sample was taken. Of the other samples, Bent. 4, from the middle part of the thick bed, shows the highest exchange capacity, 57 meq/100 g. Bent. 6 and 7 give intermediate values.

All the values given in Table VIII are obtained from natural samples which contain appreciable quantities of other minerals, chiefly quartz, which have no base-exchange capacity. The values found are consequently lower than those which would be shown by the pure clay mineral. Attempts to determine the quartz content were made by the method described by Line and Aradine (1937), using fluoboric acid to extract silicates present and determining the quartz from the insoluble residue. When very fine-grained quartz is present large errors are introduced by the solution of this mineral. The method has nevertheless been used here to give an indication of the quantity of quartz present. The values are listed in Table IX together with the exchange capacities both as determined and as corrected for quartz. The quartz content is considerable in the samples from the thick beds. The cor-

rected value for the exchange capacity of these specimens, which give X-ray photographs of Type I, is markedly higher than that for those showing X-ray diagrams of Type II and approach the value for montmorillonite.

Table IX. Base exchange capacity and potassium content of bentonite samples from Kinnekulle. Values of B. E. C. also corrected for quartz present.

type	sample	quartz %	B. E. C. meq/100 g		potassium content calculated as		K^+ exchang. meq/100 g
			determ.	corr.	% K_2O	K^+ meq/100g	
II	Bent. 1	1	46	46	5.3	110	2.2
II	Bent. 2	1	46	46	—	—	1.9
II	Bent. 5	3	47	49	4.3	90	3.0
II	Bent. 6	2	52	53	4.8	100	2.6
II	Bent. 8b	3	46	47	5.4	112	5
I	Bent. 4	13	57	66	2.5	52	2.2
I	Bent. 7	20	52	65	2.9	61	4.2

In Table IX the values of exchanged potassium ions have been included as well as the potassium content of the natural samples to show how small a part of the original potassium content is really exchanged. It has also been learnt by other experiments, including leaching with solutions of hydrochloric acid as later described in this paper, that the potassium is strongly fixed by the bentonite.

The high quartz content of the material from the thick bed made it desirable to investigate the distribution of the quartz over the fractions of different particle sizes. A knowledge of the base-exchange capacity of different fractions of dispersed and sedimented material was also considered to be of value. For these experiments material from Bent. 15 was chosen as this was a very large sample and the fractions obtained when preparing material for the chemical analyses could be used. As has been described above Bent. 15 contains a considerable quantity of calcium carbonate and weak solutions of HCl were used to remove this substance forming hydrogen bentonites. When extracted with NH_4Cl-solutions in the determination of exchange capacities the H-bentonites lower the pH of the extracting solutions to such an extent (pH 3.2) that considerable amounts of Al and Fe are dissolved. The material was therefore neutralized with NaOH and thus partly transformed to Na-bentonites. To make certain that there was no excess NaOH the samples were shaken with distilled H_2O and the pH determined in the solutions. As can be seen from Table X, the values lie between 6.8—7 and, as can also be seen, the acid treatment had not been strong enough to remove all the calcium, part of the material still consisting of Ca-bentonites.

We see that the quartz content varies widely for the different fractions with a substantial maximum value for the fraction with sizes 2—6 μ. The quartz content decreases in the coarser fractions. The exchange capacity has been corrected for the quartz determined and is given in the last column of Table X. Except for the finest fractions the corrected value for base-

Table X. Base exchange capacity and quartz content of different fractions ot Bent. 15 (material neutralized with NaOH). On dry basis 110°C.

No.	Particle size mm	pH in H_2O sol.	quartz %	cations in extract solution					B.E.C. from NH_4 dest.	
				$\frac{1}{2}$Ca++	$\frac{1}{2}$Mg++	K+	Na+	sum	determ.	corr. for quartz
404	< 0.002	—	2	35	10	—	48	93	83	85
392	0.002—0.006	7	40	21	6	1	19	47	39	65
393	0.006—0.01	7	16	28	7	2	22	59	52	62
394	0.01—0.02	6.8	—	31	9	3	24	67	62	—
395	0.02—0.06	6.8	11	30	8	2	24	64	59	66
397[1]	0.02—0.06	6.9	—	30	9	2	17	58	60	—

[1] Aggregates extra dispersed.

exchange capacity has a fairly constant value of around 65 meq/100 g which is somewhat lower than the values found for the true clay fractions — earlier determinations of different clay fractions had given values of 70—77 meq. The high value of 83 has been found only for No. 404. X-ray photographs of the samples show that some kaolin mineral is present in the fractions $> 2 \mu$. The exact quantity is difficult to ascertain but is estimated at about 10 %. This admixture of kaolin contributes to a lowered base-exchange capacity and that of the three-layer clay mineral probably lies somewhat above 70 meq. This brings it close to the value for pure montmorillonite. The fact that the kaolin has accumulated in the coarse fractions was at first quite astonishing but it was later explained when, as will be described later in this paper, the origin of the kaolin was found to be the plagioclase phenocrysts.

Table XI. Cation exchange capacities of different fractions of Bent. 15., transformed to H-bentonites, two of which were then treated with NaCl.

No.	particle size mm	treatment	cations in extract solution							B. E. C. from NH_4 dest.
			$^1/_3$Al^{3+}	$^1/_3$Fe^{3+}	$\frac{1}{2}$Ca^{2+}	$\frac{1}{2}$Mg^{2+}	K+	Na+	H+	
388	< 0.002	HCl	38	9	3	14	2	2	40	77
390	0.002—0.06	"	—	—	—	—	—	—	31	49
389	> 0.06	"	31	6	3	10	1	2	37	59
390	0.002—0.06	HCl + NaCl	8		1	3	2	40	—	52
389	> 0.06	" "	8		1	5	4	44	—	59

Determinations of exchange capacity were also performed on different fractions of Bent. 15, which had been transformed to H-bentonites (Table XI). It will be seen that because of the low pH, caused by introduction of the H^+-ions, some aluminium and iron were dissolved. Attempts were made to determine the exchanged H^+ by direct titration of the extract solution with

NaOH, but no good value could be obtained. The aluminium complexes probably tended at first to buffer the solution and at higher pH a precipitate was formed. No attempts to remove the disturbing ions have been made. Two of the fractions were transformed to Na-bentonites, by shaking with NaCl and washing, to see if the ion-exchange capacity could be increased. The Na-ions had no notable influence in this case.

These experiments with different fractions have shown that the coarse fractions contain considerable amounts of clay mineral in the form of aggregates, very difficult to disperse, and that in material from the thick bed the quartz phenocrysts have accumulated in the fraction 2—6 μ.

Rolfe and Jeffries (1952) found that for certain micaceous soils an estimate of the degree of weathering could be made by a study of the changes of basal reflexions after treatment of the material with different solutions. The unweathered soil has a constant value of 10 Å as a repeat distance for the basal layers, while the values for the partly-weathered samples varies from 10—14 Å. To obtain homogeneous preparations the authors treated their samples with a magnesium salt solution and obtained two distinct reflexions, one at 10 Å, due to the still unweathered material and the other, near to 14 Å, due to the weathered part. From the intensities of the two reflexions the ratio of non-weathered to weathered material could be stated. By treating with a potassium salt solution the weathered part also retracted to 10 Å and could be distinguished from the chlorites and the montmorillonites.

The relatively high potassium content of the bentonite material from Kinnekulle makes it reasonable to suppose that part of the material could be muscovite which had been weathered and some experiments were performed according to Rolfe and Jeffries (1952). Samples of three specimens (Bent. 1, Bent. 8 b and Bent. 15, No. 388 clay-fraction) were treated with either a 1N KAc-solution or a 0.8N MgAc$_2$-solution by warming for 3 hours and then shaking for 16 hours. The clear liquid was decanted and the samples were washed first with water and then with alcohol and dried in the air for some weeks, after which the loss of weight at 110° C was determined. X-ray photographs were taken and the treated samples were further used for determinations of exchange capacities. The cations in the extract solutions were determined spectro-chemically with no claim to a very great accuracy. In Table XII data from these experiments are collected together with data for the untreated specimens. Thermal-analysis curves were also run and these are given in Fig. 8.

It is interesting to note the way in which the two different types of bentonite react to the treatments described above. The effects are in each case similar in kind although each type retains its individual differences. The magnesium-treated samples are not very different from the natural materials but the potassium-treated ones show more remarkable changes of the basal cell dimensions. The values for the two inner reflexions of the glycerol complexes are given in the last column of Table XII. Type I gives an inner reflexion of about 13 Å as compared with 17.6 Å and Type II has the 13.7 Å reflexion retracted

Table XII. Base-exchange capacities and X-ray reflexions for bentonite material from Kinnekulle treated with KAc-or MgAc$_2$-solutions. Water below 110°C and extracted cations are also given.

No.	material & treatment	%H$_2$O < 110° C	ratio mol. H$_2$O to eq. exch. ion	B. E. C. from NH$_4$dest.	½Ca++	½Mg++	K+	Na+	I	d$_{hkl}$	I	d$_{hkl}$
				meq/100 g dried 110° C	extracted cations				inner basal reflexions, glycerol-treated spec.			
Type II	*Bent. 1*											
—	no treatm.	7.4	—	46	35	10	2	≤1	st	13.7	st	9.4
398	KAc 1 N	3.5	—	45	14	<5	15	≤1	st	11.6	—	—
399	MgAc$_2$ 0.8 N . .	5.8	—	45	6	61	<5	≤1	m	13.6	st	9.6
Type II	*Bent. 8b*											
—	no treatm.	8.1	—	46	31	12	<5	≤1	w	14.1	st	9.6
400	KAc 1 N	3.4	4.6	43	26	<5	17	≤1	st	11.8	—	—
401	MgAc$_2$ 0.8 N . .	6.0	7.5	46	3	180?	<5	≤1	not determined			
Type I	*Bent. 15, No.388* (clay fraction)											
388	no treatm.	11.4	—	77	3	14	2	2	vst	17.8	m	9.30
402	KAc 1 N	5.2	4.2	73	5	<5	68	2	vst	13.1	—	—
403	MgAc$_2$ 0.8 N . .	9.4	7.5	78	7	83	<8	2	vst	17.6	st	9.20

to 11.7 Å. For none of the types does the reflexion appear near to 9 Å. In no case is there a complete retraction to 10 Å. The layer distances as shown from the X-ray photographs are clearly related to the hydration of the exchangeable ions. An indication of this is found in the values for water lost below 110° C. These are much lower for the potassium-treated samples than for the others. The ratio of water molecules to equivalents of exchangeable ions has been calculated (Column 4, Table XII). The difference for the magnesium- and the potassium-treated samples can clearly be seen, as can the constant value for the two types of clay minerals subjected to the same treatment. An investigation of water lost at 200° C would have given a better basis for calculating hydration water but the difference already found in the water loss at 110° C is notable. The low hydration water content of the potassium-treated samples can also be seen from the differential thermal curves (Fig. 8) where the low endothermic peak between 100°—200° C is not nearly as pronounced as that for the magnesium-treated samples.

The magnesium ions have a greater ability to replace the calcium than the potassium ions have. In spite of the great excess of potassium ions about half of the calcium still remains in exchangeable positions and is only removed by subsequent treatment with ammonium chloride. The hydrogen seems to be more easily replaced by potassium (Bent. 15 No. 388). The exchange capacity for two of the specimens treated with KAc-solution shows a slightly lower value than the original material, which might indicate that a few layers have been fixed by potassium. Most of the potassium, however, could again be replaced by ammonium.

The few experiments made here do not give much information about the possibility of fixing potassium ions and more work is needed before definite statements can be made. It can, however, be said that the main part of the Kinne-

kulle bentonites is not composed of muscovite, or of weathered products from this mineral blended with montmorillonite. The two types found behave rather as specific minerals with qualities intermediate to those of the minerals mentioned. The differences between the two types probably arise from the quantity and distribution of the potassium atoms in inter-layer positions, the layers being fairly similar throughout the whole material. Using ion-exchange data a rough estimate of the composition was made in connection with the calculations of the chemical analyses. It will be sufficient here to mention that the values found are intermediate to those for illite and montmorillonite, and that the determinations made further emphasize that the material can be divided into two types; one low in potassium with an exchange capacity nearly reaching that of montmorillonite, and the other, higher in potassium, with a capacity of about 45 meq/100 g. Further studies along the same lines to determine the behaviour of the mixed-layer minerals towards different cations might help to give a clearer picture of these minerals.

X-Ray Study.

A large number of X-ray photographs were taken of the bentonite material from Kinnekulle. Most of the exposures were made with filtered Cu-radiation using a Philips camera of 11.4 cm diameter, with a small adjustment of the beam catcher[1] to make it possible to register reflexions with d-values up to at least 30 Å. The powder preparations were either mounted in small capillary tubes of Lindemann glass or were formed into thin rods by rolling the powder with a drop of glycerol on a glass plate. Glycerol is widely used in X-ray investigations of clays. It gives definite complexes with the montmorillonite minerals and the preparations are not dependent on the water content or on air conditions (Bradley, 1945; MacEwan, 1946). Non-swelling substances are not affected by the glycerol admixture. The rolling of the preparations orients the layers to some extent and photographs are obtained in which the basal reflexions are enhanced. Completely oriented layers have been obtained by the method described by Nagelschmidt (1941) somewhat modified. Thin films of the clay substances are obtained by allowing settling to take place from a suspension on to a glass plate, or preferably on to a sheet of plexiglass, from which the film can be loosened more easily. A strip of the film is fixed by means of a drop of glycerol on to a plastic rod of 10 mm diameter and the rod is mounted eccentrically in the camera with the incident beam just grazing the surface of the strip. Only basal reflexions are registered from such preparations and they can be identified more easily. On the other hand the reflexions cannot be measured very accurately as they are registered only on one side of the film and the centre is not clearly defined. Reference films of clays with an admixture of quartz showed, however, that agreement was good between values obtained from strip preparations and those from a powder mounted in a capillary tube.

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[1] Designed at the Swedish Cement and Concrete Research Institute, Stockholm.

In Table XXI, XXII, and XXIII results have been collected from photographs of bentonites from Kinnekulle using the different techniques just described. Table XXI gives values from samples with the lower potassium content (Type I), and Table XXII gives similar data for samples with the higher potassium content (Type II). The diagrams from different specimens of the same type are practically identical, the small differences observed quite possibly being due to somewhat different conditions during the exposures. The specimens tend to give broadened lines which extend to bands difficult to distinguish from the background of the films. This is very pronounced, particularly in the regions of higher reflexion angles. The lack of definition of the lines makes it difficult to determine their exact position, but the visually estimated maxima of blackening were used and no corrections have been applied to the measured values.

The few strong and fairly sharp lines, typical of illites and montmorillonites, were found in all diagrams. Tables XXI and XXII give indices for hk-reflexions and also d_{hk} values, calculated for a montmorillonoid with $a_o = 5.20$ kX and $b_o = 9.00$ kX (MacEwan 1951). From the reflexions (26, 40) and (33, 06) respectively, values for a_o and b_o have been calculated for the Kinnekulle clays and are set at the foot of the tables. The variations are very small and the two types could not be differentiated by means of the hk-reflexions. It is true that the a_o and b_o values have been calculated each from one reflexion only and must be regarded rather schematically, but they show clearly enough that both types of minerals belong to the dioctahedral micas.

When considering the basal reflexions the differences between the two types become more obvious. In Tables XXI and XXII this can clearly be seen for the inner reflexions, whilst in Table XXIII, which contains data from oriented specimens giving mainly basal reflexions, the two types show quite different diagrams. It has not been possible to assign indices which refer to unit cells of moderate size, but the reflexions are such as could be expected from minerals built up of mixed layers of different c-spacing in a more or less random interstratification. With bravaisite Bradley (1945) first showed an example of such minerals where layers of illite and montmorillonite are randomly mixed. Later Brown and MacEwan (1951) made calculations of the intensities and d-values which could be expected for different proportions of the randomly mixed layers in two component systems. These curves were used here at first to get an idea of the proportions of the layers in the Kinnekulle clay material, the minerals then being assumed to be built up of only two types of layers $i. e.$, one with a repeat-distance of 10 Å as in illite or muscovite and the other of 17.7 Å as in the glycerol-complex of montmorillonite.

A schematic representation of the reflexions of the types from Kinnekulle is shown in Fig. 4, together with reflexions from a 17.7 Å and a 10 Å mineral (dotted lines). For the two inner reflexions in Fig. 4 the d-values have been taken from the glycerol-treated preparations rolled into thin rods as these were considered likely to give more reliable values than the oriented ones. The Type I from Kinnekulle shows reflexions not very different from those

17,8
001

18

8,9
002

9,3

5,97
003

5,7

5,4

4,45
004

4,5

3,58
005

3,44

2,97
006

3,0

D_{hkl}

$\longrightarrow kx$

14,0

9,5

002
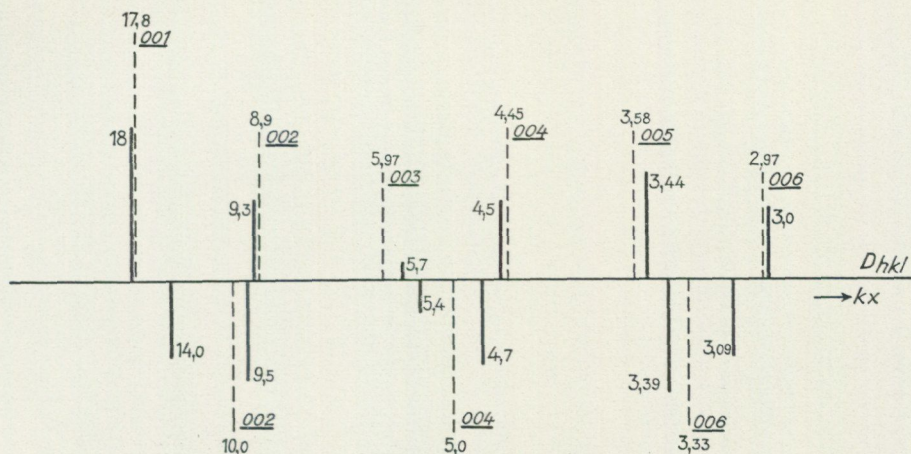10,0

4,7

004
5,0

3,39

3,09

006
3,33

Fig. 4. A schematic representation of reflexions from the two types of 'mixed layer' minerals from Kinnekulle. Full lines represent pointing upwards Type I and downwards Type II. Dotted lines represent montmorillonite (upwards) and muscovite (downwards).

of pure montmorillonite but it is nevertheless obvious that there is a difference, especially when intensities are considered. A rough estimate gives the proportions 1 : 4 of 10 Å to 17 Å layers. For Type II the difference from montmorillonite is more pronounced and from the diagrams the proportions of the respective layers was estimated at 3 : 2. These values, which were in accordance with the results of the chemical analyses and the cation-exchange capacities, were given in a preliminary paper by Byström (1954).

Subsequently MacEwan made more accurate calculations using a more direct method (MacEwan 1953) and reached a different result.[1] For Type I, he found the proportion of 10 Å to 17 Å layers to be higher *i. e.*, 1 : 2. Type II, according to MacEwan is liable to contain a 14 Å component as well, the proportions of the 10 : 14:17 Å layers being calculated as 5.3 : 2 : 2.7 or, taking the 14 Å and 17 Å together as expanding layers, the proportion of non-expanding to expanding layers is 2.3 : 2.

MacEwan suggests that the 14 Å component present in Type II, may be vermiculite. Many of the reactions of this mineral would be masked by the montmorillonite and illite layers so that it would be easy to overlook. At the same time a content of 20 % vermiculite on a magnesium base, as suggested, leaves no magnesium for the other components. This is not plausible, nor is the suggestion that vermiculite is present in Type II and not in Type I with about the same magnesium content. If, however, as has been assumed, the layers are all almost similar in composition and the difference between them is caused mainly by the inter-layer, the intermediate capacity of expansion may be due to a cooperation of the potassium atoms blocking some inter-layers that would otherwise expand.
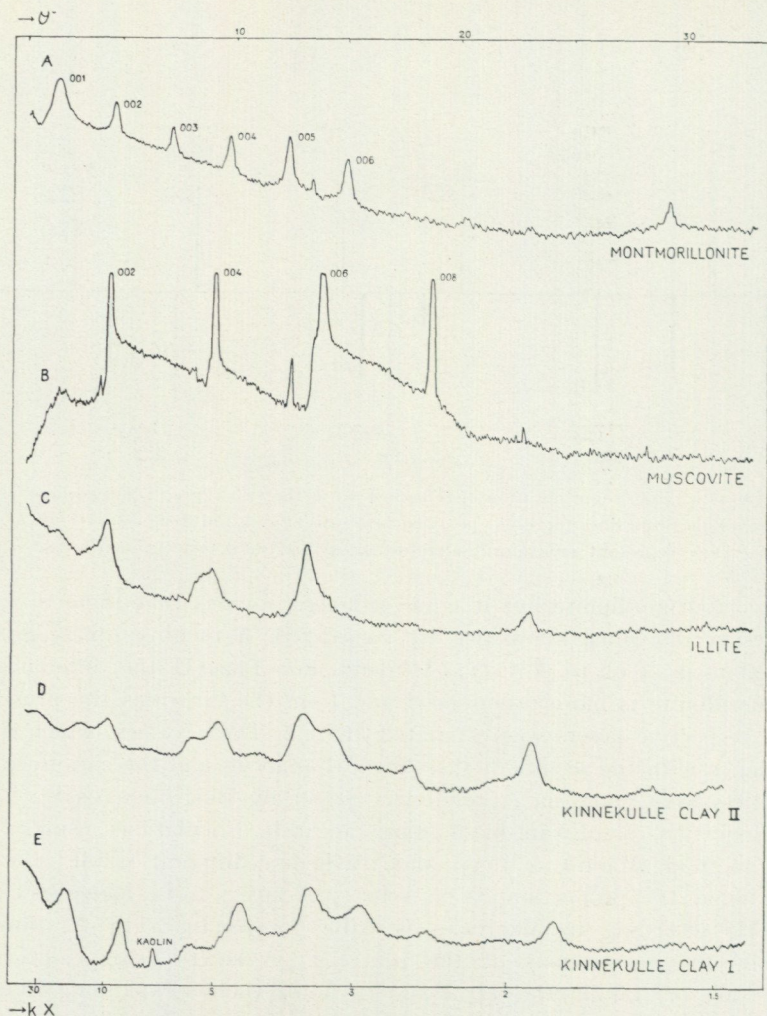
[1] private communication.

Fig. 5. Microphotometer curves of X-ray photographs from glycerol-treated specimens, oriented
parallel to the basal planes. The photographs are reproduced in Fig. 14, Pl. I.
A. Na-montmorillonite (standard material).
B. Thin sheet of muscovite, Skörtorp, Sweden.
C. Illite, Tosterup, Sweden ($K_2O = 6.6$ %).
D. 'Mixed layer' mineral, Type II, from upper thin bentonite beds at Kinnekulle, Sweden.
E.   ”   ”   ”   , Type I, from thick bentonite bed at Kinnekulle, Sweden.

To obtain reliable results in interpreting the X-ray diagrams, it is desir-
able to have sharp and well defined reflexions. Unfortunately, as mentioned
above, these are not obtained in the case of the Kinnekulle bentonites, as
can be seen from Fig. 14, Pl. I where photographs from oriented specimens,
all taken by the same technique, have been reproduced. Table XXIII shows
variations in the values from reflexions within a special type, but these have
not been treated as significant here, since they are considered to a great extent

to depend upon the incomplete technique used. There are other features too which have not been discussed here, in particular the shape and intensity of the lines and the diffuse area of reflexion at very low angles. In a more detailed study these might well contribute to a better knowledge of the clay-minerals. Therefore, for the moment, it is desirable to use the diagrams in a more qualitative way to differentiate between the two types found and await a more complete X-ray analysis for a quantitative estimation. This could be carried out along the lines given by Johns, Grim and Bradley (1954) in a recent paper on quantitative estimations of clay minerals by diffraction methods.

Fig. 5 gives photometer curves of the two types of 'mixed-layer' mineral from Kinnekulle together with those from a Na-montmorillonite and from a muscovite. A curve from an illite is also included which, however, shows a small admixture of some expanding layers. The sharp peaks at definite intervals shown by the pure reference minerals are in clear contrast to the broadened peaks of the Kinnekulle minerals with no integral series of orders related to a simple cell. The features which distinguish the two types under investigation here, both from each other and also from montmorillonite and muscovite, are quite apparent. The X-ray diagrams used to give the photometer curves are seen in Fig. 14. The sheet of muscovite is completely oriented and gives clear spots as in single-crystal diagrams; the clay minerals, on the other hand, give powder diagrams because of the disorder of the layers within the plane. Sometimes, however, during the preparation of thin sheets from the clay suspensions some orientation occurred and from such preparations the intensity of the reflexions is considerably enforced at the middle of the lines. Such preparations always split up very easily along parallel lines and thus behave to a certain extent like very thin single-crystal sheets.

Similar 'mixed-layer' minerals but with other proportions have been described earlier by Bradley (1945) for bravaisite as cited above with a 1 : 1 proportion of illite to montmorillonite layers and by Weaver (1953) who has found in an Ordovician bentonite from Pennsylvania a 'mixed-layer' mineral with non-expanding and expanding layers in the proportion 4 : 1. Type II described here is most nearly related to bravaisite. In Type I the proportions found in the potassium bentonite described by Weaver are inverted.

Photographs from material heated to about 500° C show a retraction of the cell dimensions and a typical illite diagram appears. Type I gives an inner reflexion at 9.92 kX and Type II at 10.02 kX. The other basal reflexions form an integral series of orders and there is no indication of the presence of layer distances deviating from this.

The kaolin reflexion from material of Type I shown in Fig. 4 and in the table arises from weathered fragments of plagioclase phenocrysts and will be described in more detail in the later part of this work.
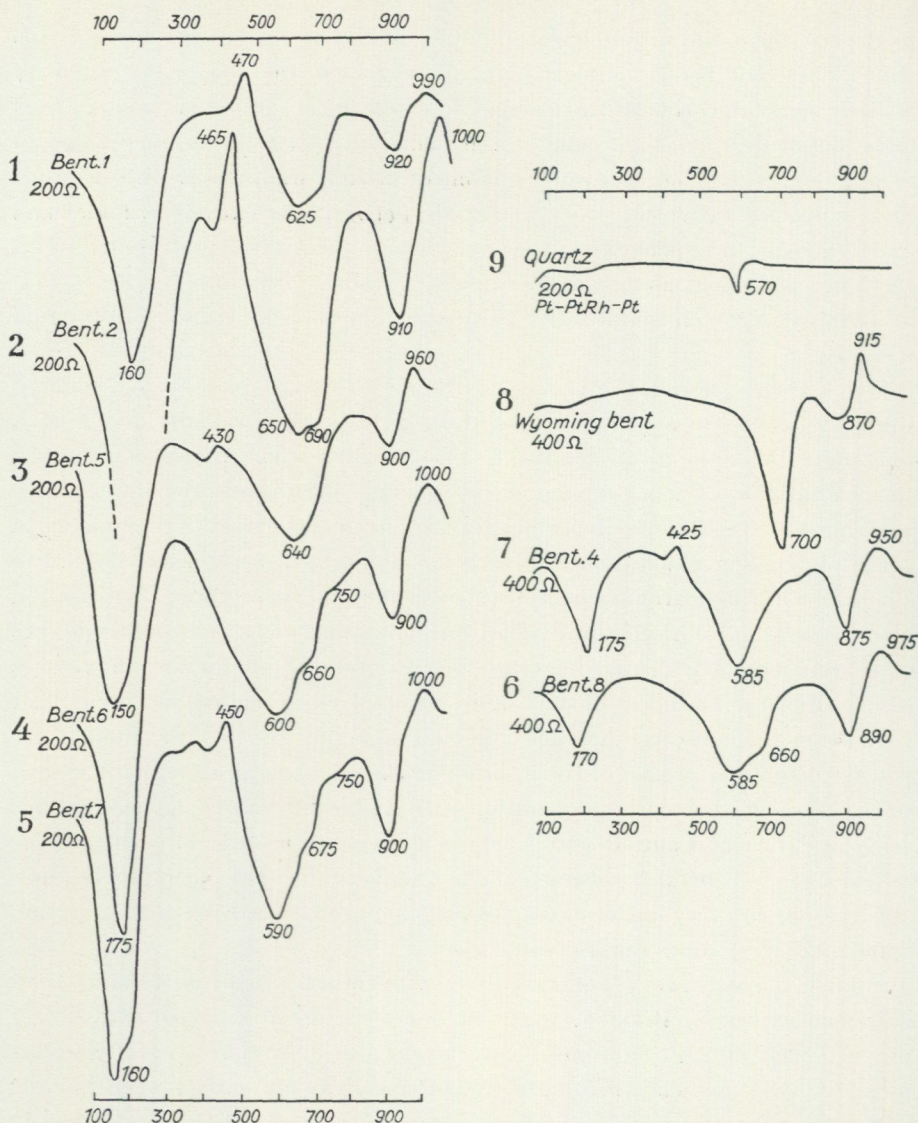
Fig. 6.   DTA-curves from bentonite specimens from Kinnekulle (curves 1—7), a Wyoming bentonite (curve 8) and quartz (curve 9).

Differential Thermal Analyses (DTA).

Figures 6, 7 and 8 show differential thermal analysis curves prepared from the bentonite material from Kinnekulle. A manually operated apparatus was used but the temperature rise could be kept at a fairly constant rate of 11°/min. Chromel-alumel wires, 0.5 mm in diameter were used as differential thermo-couples and the resistance in the circuit was held at either 100, 200, or 400 ohm (the relevant value is given to the left of each curve). The thermal effects were registered with a Moll galvanometer and read once every 60 se-

conds. Precipitated and ignited Al_2O_3 was used as a reference material and both the specimen and the reference material were contained in small platinum crucibles with a volume of 1.5 ml. The apparatus was calibrated with quartz (Curve 9, Fig. 6) and a Wyoming bentonite was used as standard for a montmorillonite mineral (Curve 8, Fig. 6).

Curves 1—7, Fig. 6, show the thermal reactions of natural bentonite specimens from Kinnekulle. The material was only slightly crushed and sieved, the fraction with particles < 0.075 mm being used for the DTA-curves. Before use the material was kept at 60° C for 20 hours. The curves are very similar. There is first a pronounced endothermic peak with a maximum between 150°—175° C, the exact position depending on the time taken for the oven to reach an even temperature rise. This effect is generally attributed to loss of adsorbed water and also to interlayer water. Curves of montmorillonites always show this effect. Curve 8, Fig. 6, is not representative in this respect, as the material had previously been heated to over 200° C.

At 430°—470° C most of the Kinnekulle specimens show an exothermic peak, which is probably best explained as due to oxidation of pyrite (of common occurrence in the bentonite material). Rowland and Lewis (1951) have found a similar effect in a bentonite material containing pyrite and also in a Wyoming bentonite to which 1 % of pyrite had been added.

At higher temperatures the curves of all the specimens show a strong endothermic reaction extending over a large interval. The release of hydroxyl and the associated water loss causes this. As can be seen from the curves the maximum for the bentonite material lies between 585° and 625° C and is followed in most of the specimens by a very small reaction at a temperature about 50—100° higher. Grim and Rowland (1942) found that bravaisite also gave two peaks, and interpreted the first peak as arising from the illite layers and the second peak from the montmorillonite layers. This explanation, however, does not seem plausible in this case for, although the Kinnekulle material is considered to be built up of layers similar to those of bravaisite, but in different proportions, the relative sizes of the two effects show no relation to the proportions of the layers found by other methods. For Type I, with definitely more expanding layers, the second peak ought to be more pronounced than the first peak. It would also be expected to be larger than the second peak of Type II, which has fewer swelling layers. As can be seen from Fig. 6, the second peak in both cases is very small and there is scarcely any difference between the two types. There is actually no reason to expect the curves to incorporate the separate effects from the different layers as they are shown by the respective pure minerals, since the clays investigated here are regarded as consisting, not of a mere blend of illite and montmorillonite, but of intimately crystallised layers, similar in composition to those of the pure minerals, but forming specific minerals with characteristic properties.

Weaver (1953) also found double effects between 500°—800° C in his Ordovician bentonites from Pennsylvania. However he interpreted the peak at the lower temperature of about 600° C as coming from impurities of chlorite
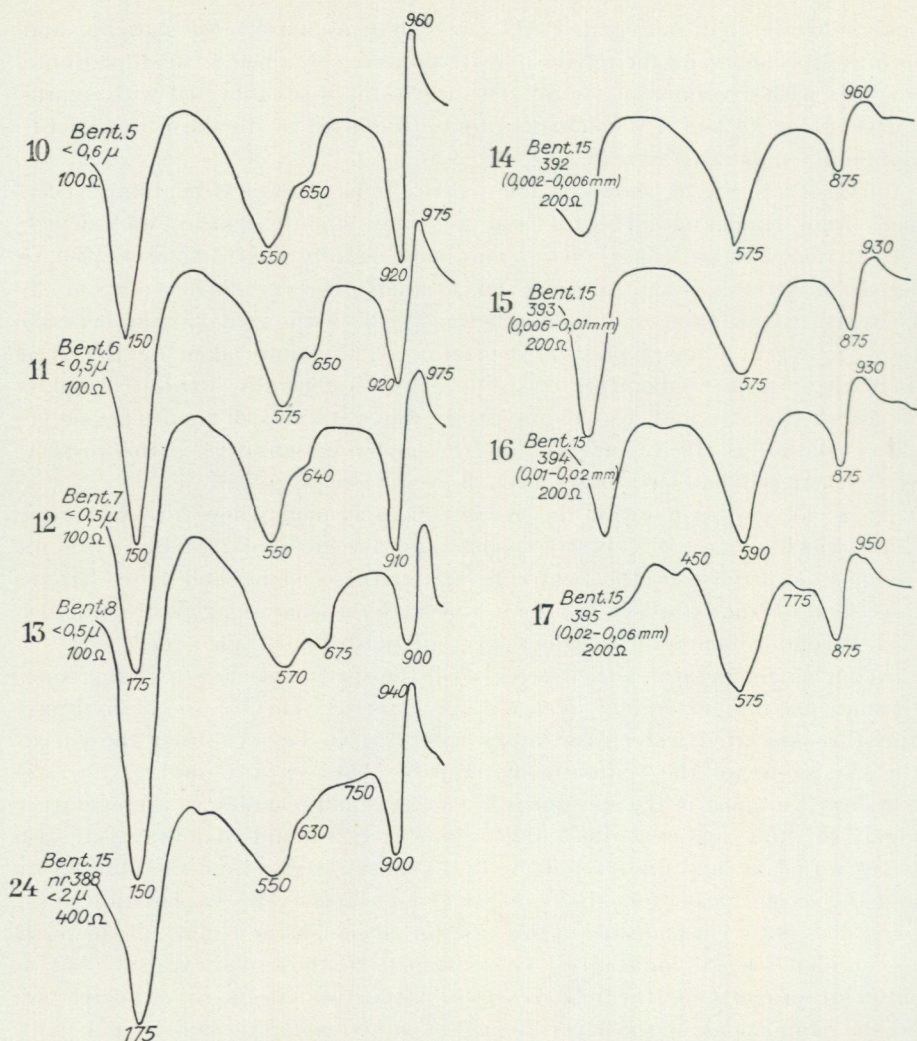
Fig. 7. DTA-curves of bentonite material from Kinnekulle: curves 10—13 and 24 from clay fraction of acid treated material, curves 14—17 from fractionated material neutralized with NaOH, four different ranges of particle size being used.

and the peak at the higher temperature of about 700° C as coming from the 'mixed-layer' mineral of illite and montmorillonite. He ascribed the relatively high temperature for this last peak to the low iron content (FeO = 0.31 and Fe_2O_3 = 1.28 %) of his material. Most DTA-curves had up to that time been run on illite material with the high iron content of 5—10 % and had shown reactions at a lower temperature (about 500° C). The Kinnekulle material has an iron content of 2.5—3 % and the maximum of the thermal effect lies about 600° C. Although the natural material contains a certain amount of biotite partly changed to chlorite the smaller effect is probably not due to
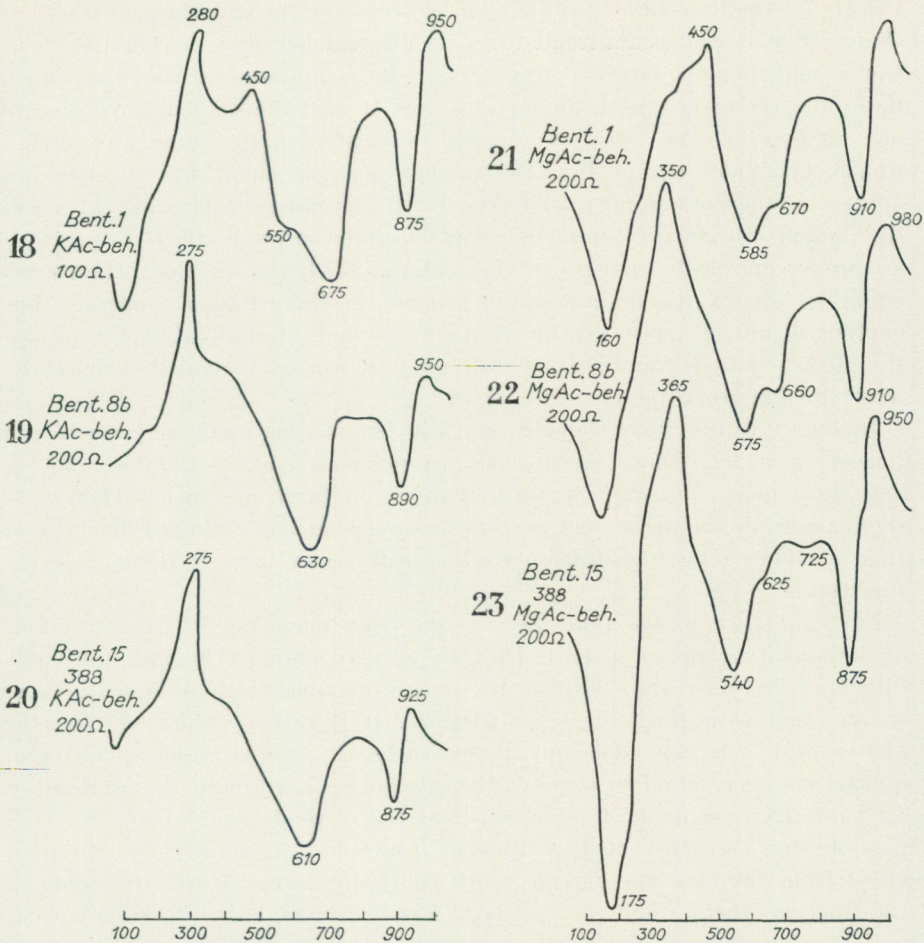
Fig. 8. DTA-curves from three bentonite samples from Kinnekulle treated with either a KAc-solution (curves 18—20) or a MgAc₂-solution (curves 21—23).

chlorite as the reaction is more pronounced in the finest clay fraction of the fractionated material (Fig. 7, Curves 10—13) in which the presence of chlorite has not been proved with certainty.

It would seem that the reaction is dependent upon the kind of exchangeable ions in the interlayer positions. Curves 10—13 in Fig. 7 have all been run on hydrogen-treated material and in these curves the second peak comes out much more distinctly. The other peak comes at a slightly lower and also more constant temperature than for the natural material in which calcium and magnesium are the exchangeable interlayer ions. The effect of the interlayer cations is still more obvious in the curves in Fig. 8, which are from bentonite material treated with KAc- or MgAc₂-solutions respectively (cf Table XII). For specimen Bent. 1 there is a marked difference between the KAc- and

the MgAc₂-treated samples and it can be seen how the endothermal reactions change. For the potassium-treated specimen the smaller one comes first at about 550° C and then the larger at 675° C. For the magnesium-saturated specimen it is quite the reverse with the larger at 585° C and the smaller (a very small one) at 670° C. The other two specimens treated in the same way show a similar behaviour except that the smaller peak at about 550° C does not appear for the potassium-treated samples. It has not been possible to extend the present investigation to include further study on these effects but as they are so susceptible to changes in the material further work along these lines ought to give valuable information about the 'mixed-layer' minerals. The exothermic effect registered for the KAc-treated samples at 275° and for the MgAc₂-treated samples at about 350° C is worthy of note but must also await further work for an explanation.

In Fig. 7, Curves 10, 11 and 13 are from Kinnekulle material Type II and Curves 12 and 24 from Type I. They are all made on clay fraction $< 0.5 \mu$ and show more consistent features than the natural specimens. There is a slight tendency for the second peak to be somewhat more marked for Type II than for Type I but the difference is not sufficiently large to distinguish the two types.

Curves 14—17 in the same figure have been made on different fractions of the same specimen of Type I. They are all very similar. The only noticeable difference between the curves is the pyrite reaction which is shown only in the fraction with the largest particle size. It is rather surprising that the quartz peak does not come out more clearly, as a considerable quantity of quartz has been found in some of the specimens, e. g. Bent. 4 and Bent. 7, (cf Table IX) and in the fractionated material of Bent. 15 (cf Table X). It is possible that the generally typical effect from quartz is masked by the larger effect from the clay minerals at nearly the same temperature. It is only in the fraction where about 40 % quartz has been found that there is a clear indication of its presence (Curve 14). In Curve 17 from the coarsest fraction the sharp tip of the peak could also be ascribed to quartz. The X-ray photographs all show quartz to be present, except in the very finest fractions, and the DTA-curves could not therefore be used here as a means of indicating the presence of quartz.

The part of the curves at higher temperatures shows the features generally typical for the illite and montmorillonite minerals, namely an endothermic reaction at about 900° C immediately followed by an exothermic peak at about 1,000° C. The interesting feature here is the different rates at which the exothermic reaction occurs in the natural material as compared with the material treated with different solutions. The hydrogen bentonites react most rapidly and the magnesium-saturated samples come next in this respect. The natural samples, which have calcium as exchangeable ions, and the potassium-treated samples have slower reactions. It seems, therefore, that crystallisation of the high temperature phases, which have not been identified in this investigation, is facilitated by the smaller inter-layer cations.

In summing up the DTA-investigation of the Kinnekulle material it can be said that differences between material from different beds have not been found, and that the curves show the general features of those from illitic material with marked endothermic peaks at about 600° C and 900° C and an exothermic peak at near 1,000° C. The low endothermic peak at about 150° C is more pronounced than is usual for illites and resembles that of montmorillonite minerals. This is another indication of the 'mixed' nature of the Kinnekulle clays. None of the curves show features of a pure montmorillonite nor are they such as could be expected from mere blends of illite and montmorillonite. They could well, however, be in accordance with a more intimate inter-stratification of the two minerals. The lack of differences between the curves prevents the different types being distinguished, as has been possible by other methods, but serves on the other hand to emphasize the basic similarity of the whole bentonite material.

Acid Extractions.

It will be remembered that during the determination of the cation-exchange capacities a very small proportion of the potassium ions took part in the exchange reactions (Table IX), whilst on the other hand, as soon as the pH-value was lowered (as was the case for the hydrogen-saturated bentonites) some alumina and iron went into solution. To obtain further information about the solubility of the different cations of the bentonite material from Kinnekulle several extraction experiments were made. These were designed first to give information as to the resistance of the material to acids and secondly to find out by examining the different rates of solubility of the cations, whether one or several minerals were present.

Table XIII. Chemical analyses of extract solutions from Bent. 15 nr 388, extracted with 0.5 N HCl in periods of 6 hours. Values expressed in milli-atoms/100 g of material, on dry basis 110° C. Type I.

time hours	Si	Al	Fe	Mg	Ca	K	Na	% dissolved	Al/K	Al/Mg	Mg/K
6	25.0	36.4	6.2	12.0	3.3	4.3	0.5	4.6	8.4	3.0	2.8
+ 6	33.4	27.2	2.3	6.8	0.3	2.5	0.3	4.0	10.9	4.0	2.7
+ 6	27.6	23.4	1.5	5.2	—	1.6	0.3	3.3	14.7	4.5	3.2
+ 6	20.9	25.2	1.5	6.8	—	1.9	0.2	3.1	13.3	3.7	3.6
total 24	106.9	112.6	11.5	30.8	3.6	10.3	1.3	15.0	in original material		
% dissolv. of orig. atom	11	25	32	31	100	20	25		7.8	4.5	1.7

The extractions were carried out in the following manner: 2 grams of the samples were heated on a water bath with 100 ml of 0.5 N HCl and after definite intervals of time the solutions were completely decanted and the residues washed twice. The Si, Al, Fe, Ca and Mg present in the extract solu-

Table XIV. Chemical analyses of extract solutions from Bent. 1, extracted with 0.5 N HCl in periods of 6 hours. Values expressed in milli-atoms/100 g of material on dry basis 110˚ C. Type II.

time hours	Si	Al	Fe	Mg	Ca	K	Na	% dissolved	Al/K	Al/Mg	Mg/K
6	22.7	28.2	10.0	17.3	21.2	8.4	0.5	5.8	3.4	1.6	2.1
+ 6	25.5	22.0	2.6	4.8	1.7	4.8	0.3	3.4	4.6	4.6	1.0
+ 6	20.7	17.5	1.2	2.9	—	3.4	0.3	2.5	5.1	6.0	0.9
+ 6	18.1	17.4	0.7	2.9	—	3.7	0.3	2.3	4.7	6.0	0.8
Total 24	87.0	85.1	14.5	27.9	22.9	20.3	1.4	14.0	in clay material		
% dissolv. of orig. atom	10	18	44	28	95	20	15		4.4	6.3	0.7

tions were determined by chemical analysis and the K and Na spectro-chemically. Values are given for two of the samples, one from Type I and the other from Type II, in Tables XIII and XIV. Figures 9 and 10 show the same results in a graphical way. For Type I the partly purified clay fraction of Bent. 15 was used (Analysis No. 127, Table IV) and for Type II the natural sample of Bent. 1 (Analysis No. 2652, Table IV). The natural samples contained some biotite but the earlier fractionation had removed this almost completely from Type I.

Fig. 9. Acid extraction (0.5 N HCl) of bentonite material, Type I, Kinnekulle. a) amount of extracted ions; b) ratio of extracted ions in extract solutions.

For both types all ions except silica were extracted to a much greater extent in the first than in the following extractions. For calcium this was expected, as it is situated in an easily exchangeable position, and the first extraction brought about an almost 100 % removal of this ion. For the rest of the ions the high solubility at the beginning could be related to the presence of biotite

since this easily breaks down under acid treatment and would thus give a high solubility especially for iron and magnesium. This was more pronounced for Bent. 1 (Fig. 10 a), of which the original sample was used, than for Bent. 15 (Fig. 9 a), which, as has been mentioned, had been freed from the greater part of the biotite.
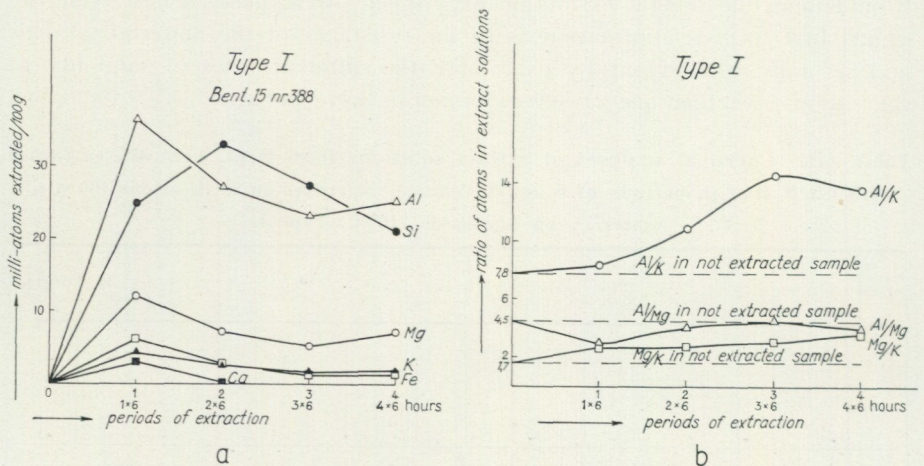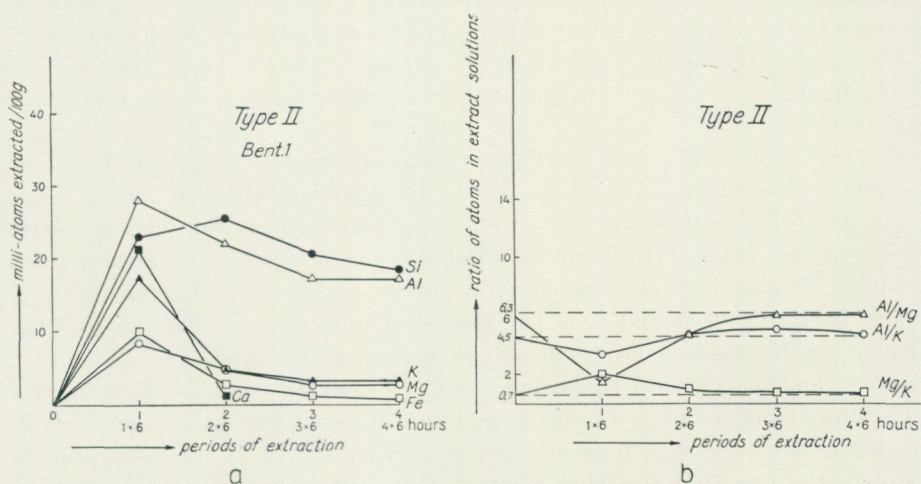

Fig. 10. Acid extraction (0.5 N HCl) of bentonite material, Type II, Kinnekulle. a) amount of extracted ions; b) ratio of extracted ions in extract solutions.

Apart from this similarity in reaction towards the extracting solutions the two different types behaved differently. After the second extraction Type II had already attained a fairly constant rate of solubility for the different ions and the ratios of dissolved Al and Mg to K ions approached very near to that of the original material (Fig. 10 a and 10 b, Table XIV).

According to earlier experiments involving acid treatment of different clay minerals as compiled by Grim (1953, p. 296) montmorillonites have a considerably greater solubility than illites and muscovites. For 'mixed-layer' minerals composed of layers of illite and montmorillonite, as is the case for the clay minerals from Kinnekulle, a preferential solution of the layers of montmorillonite type could be expected. For Type II there is no indication of this and the clay material behaves as though composed of a mineral with homogeneous layers.

Type I, on the other hand, had a considerably higher solubility for aluminium and magnesium as compared with potassium and the ratios Al/K and Mg/K departed markedly from those of the original sample. This might be an indication that layers not fixed by potassium are more easily broken down. A small admixture of pure montmorillonite, not easily detected in a 'mixed-layer' mineral like Type I, could also give a high solubility of aluminium and magnesium and information on this point could perhaps be obtained by prolonged extractions. If, however, the higher ability of aluminium and

magnesium to go into solution is due to a preferential solution of atoms from the layers of montmorillonite type a sufficient number of extractions should finally lead to an enrichment of the potassium-fixed layers. Such a change could possibly, but not necessarily, be revealed by X-ray photographs. Mering (1949) has shown for montmorillonites that, although a considerable part of the octahedrally-bound atoms has been removed, the remaining silica skeleton preserves the original structure without greater modification. Montmorillonites give a much more distinct X-ray diagram than the clay minerals here investigated and small changes in these might well escape observation altogether.

X-ray photographs, however, were made of oriented specimens from the residues after the last extraction, *i. e.* the material extracted for 24 hours with 0.5/N HCl. Both types gave reflexions similar in position and intensity, possibly somewhat broadened, to those for the original material and there was no indication of a change in either of the types. A total of about 15 % had been extracted and it is not possible to judge from what part of the lattice or from which layers the atoms had been dissolved.

A stronger attack on the samples was effected by boiling with 4 N HCl for 6 hours under reflux. From the residues thus obtained we see more clearly how the two types had been affected by the acid. Type II was astonishingly resistant. Even after this strong attack there still remained a base-exchange capacity of 27 meq as compared to 43 meq for the original material and the X-ray diagram of a glycerol-treated specimen showed that the material still contained a certain swelling power. The inner reflexions were found at 13.1 Å and 9.5 Å, where the original material gave reflexions at 14 Å and 9.6 Å. The relative intensities were similar but the reflexions rather more diffuse.

Type I on the other hand had been more affected by the stronger acid. The inner reflexion at about 18 Å of the glycerol-treated sample had disappeared and so had the reflexion at 9.3 Å. Instead a reflexion at 9.5 Å was visible. The inner part of the diagram was diffuse. The sample not treated with glycerol gave a fairly broad reflexion at 11.8 Å. This behaviour of Type I towards the strong acid seems to suggest that the proportion of swelling layers is diminished and, therefore, that these are thus more easily attacked than the potassium-fixed layers.

Except for the changes in the inner reflexions no alterations could be observed in the X-ray diagrams of the acid-treated material and this confirms that the silica framework can keep the structure together, even when a great part of the octahedrally-bound atoms are removed.

Type II seemed to be an extraordinarily stable modification of the 'mixed-layer' minerals and a chemical analysis was made of the residue. The results are given in Table XV. Data for a similar material, not extracted, is given for comparison, the values from the clay fraction of Bent. 8 a being chosen since no complete analysis was available for the Bent. 8 b used in this extraction. (For the different fractions of Bent. 8 see Table III.) Calculated from the TiO_2 content in the natural sample (0.58 %) and in the residue, about

14 % of the material was dissolved during the extraction, Al, Fe, Mg and Ca constituting the main part. The primarily-dissolved silica had been rendered insoluble during the prolonged boiling with the strong acid and only 0.5 % went into solution, as compared with about 10 % for extractions with the weaker acid. This of course makes the silica content very high, as can ben seen from Table XV, and distorts the atomic proportions.

Table XV. Chemical analysis of residue from extraction of Bent. 8b, Type II, with 4N HCl for 6 hours. As comparison, clay fraction of Bent. 8a. On dry basis 110°C.

	Bent. 8b extracted, An. 102			Bent. 8a clay fraction, An. 105	
	%	atomic prop.	cell content — 10 % SiO_2	%	cell content
SiO_2	65.45	1.090	Si 7.31 } IV Al 0.69 }	56.10	Si 7.37 } IV Al 0.63 }
TiO_2	0.67	0.008		0.38	
Al_2O_3	18.47	0.362		24.38	
Fe_2O_3	1.40	0.017	Al 2.01 } Ti 0.06 } VI	1.74	Al 3.14 } Ti 0.04 } VI
FeO	—	—	Fe 0.13 } 2.69	0.58	Fe 0.23 } 4.01
MgO	2.66	0.066	Mg 0.49 }	3.30	Mg 0.60 }
CaO	0.04	—		1.49	
K_2O	4.36	0.092		5.13	
H_2O	7.02	0.78	M+ 0.20 } 0.88 K 0.68 }	7.23	M+ 0.36 } 1.23 K 0.87 }
	100.07		H_2O 3.0	100.33	H_2O 3.1
ion exch...	0.027 eq/100 g			0.046	
ratio:					
Al/K	4.0			4.3	
Al/Mg	5.5			6.3	
Mg/K	0.7			0.7	

M+ exchangeable ion.

An idea of the remaining structural formula is given by Column 3 where the deficiency of atoms in octahedral positions can clearly be seen. In the calculations an estimated excess of 10 % silica has been subtracted. It has been assumed that the proportion of silicium to aluminium in the tetrahedral layer is maintained, an assumption which is based on data from Brindley and Youell (1951) who found that in certain silicates aluminium was more easily removed from the octahedral layer. The ratios Al/K, Al/Mg and Mg/K show a relatively small deviation from those of the original sample, the deviation showing that aluminium is most easily extracted. Very little potassium has been extracted and, what is more astonishing for this type of mineral since the magnesium-montmorillonites are generally more easily decomposed by acid than the aluminium rich ones (Grim, 1953), the same is true of magnesium.

Although the residue described here shows a certain likeness to the original material in exchange capacity and swelling power towards glycerol, the sample has been strongly changed. The plasticity has been lost and the material has taken on a whitish tint, mostly due to extraction of iron from the biotite flakes, which now appear as shiny translucent shales.

The results from the extraction experiments have been included in this description of the bentonites at Kinnekulle as they are considered to elucidate to some extent the clay minerals described and also to underline the difference between the two types found there. These have been described earlier in this paper as minerals of intimately mixed layers, rather than a mechanical mixture, of montmorillonite and illite. This is most evident for Type II and in this mineral the layers seem to have lost their individual character. In Type I there could be observed a preferred decomposition of the swelling layers, which indicates that the different layers have preserved something of their original properties.

Electron Micrographs.

Electron micrographs were made of the bentonite material from Kinnekulle, and a few of these are to be seen in Figs. 15, 16, Pl. II. The micrographs of the two different types are very similar and any special feature characterising one type or the other cannot be distinguished. The micrographs very much resemble those found in the literature (Davis et al., 1950, Grim, 1953) for montmorillonites and also for illites. Irregular flakes are stacked on top of each other and the edges that protrude are more or less bent or rolled giving the particles a fluffy appearance. In a stereographic picture this can be seen very clearly. Some of the flakes are raised on edge and take a position almost perpendicular to the plane of the paper. In a one-dimensional picture such flakes appear as small elongated black spots. Thin grey flakes, scarcely visible from the background, can be seen which seem to have a homogeneous appearance and which have been interpreted as single flakes. These have most often a rectangular form and dimensions of 0.1—0.3 microns. The thickness has not been estimated. Sometimes these single flakes partly cover each other and the overlapping part appears darker.

The samples used to give the micrographs were dispersed in a sodium pyrophosphate solution, the finest fraction being separated and washed with water. A drop of a very dilute suspension was transferred to the preparation holder, already covered with a thin film of collodium, and the drop was allowed to dry. Fig. 15 shows a micrograph from a sample of Bent. 15, Type I, but the micrographs from samples of Type II are very similar. Particles and aggregates of various dimensions below 1 micron can be seen.

Fig. 16 Pl. II reproduces an electron micrograph from material obtained from the upper part of a suspension which had been allowed to stand for several weeks and here there are more homogeneous particles aggregated to a very small extent. Most flakes seem to be either single or double flakes. This electron micrograph is of Type II but here again Type I gave a similar picture. The thin needles that can be seen must have developed during the long period under which the suspensions were settling. They have not been investigated in detail. Sometimes when solutions from the bentonite material

have been decanted and allowed to stand, there has been observed, even macroscopically, a crystallisation of needles, giving a good X-ray diagram with inner reflexions at 9.8 Å and 4.9 Å. As yet the quantity has been very small and there has been no detailed investigation.

The electron micrographs give further evidence of the pronounced flaky structure of the bentonite material and also of its close relationship to the illite and montmorillonite minerals.

Summary of the Investigation of the Clay Minerals.

Summing up the results of the different methods used to identify the clay minerals of the Kinnekulle bentonites, we find that some of the methods accentuate the similarity of the material from the different beds investigated, whilst others underline differences which make it possible to distinguish separate types. The combination of methods gives a fairly good knowledge of the bentonite material and it has been found that the bulk is built up of aggregates of layer minerals of a character intermediate to that of montmorillonite and illite. The structure is related to pyrophyllite and to muscovite and, as can be seen from the chemical analyses and the hk-reflexions of the X-ray diagrams, is clearly of the dioctahedral type. The apparently consistent character of the material is confirmed by the electron micrographs and the DTA-curves which methods have not revealed any differences between the samples. The flaky character of the minerals can be seen both macroscopically and in the electron micrographs, and a parallel orientation of the flakes is easily obtained from settling suspensions. The DTA-curves resemble those from hydro-micas and show that pure montmorillonite, as had been assumed before this investigation, is not the clay mineral present.

The uniformity of the material as shown by these methods is contradicted by the results obtained from determinations of cation-exchange capacity and from X-ray diagrams of oriented specimens. By using these methods two definite types can be distinguished, each of which can be related to samples from a certain bed. The chemical analyses that have served to show the similarity can also be used to underline the differences between the two types when only the potassium content is considered. Thus Type I with K_2O content of 2.7 per cent, a base-exchange capacity of about 70 meq/100 g and inner basal reflexions at about 18 Å and 9.3 Å for glycerol-treated specimens, is found in the main thick bed at Kinnekulle. The other type found in the thin beds just above, only separated by a cherty bed of about one foot has the following corresponding data; $K_2O \infty$ 5 per cent, base exchange capacity ∞ 46 meq/100 g and inner basal reflexions at 14 Å and 9.6 Å.

Some acid extractions have also been performed and help to elucidate the different types. Type II seems to be extraordinarily stable towards acid whilst Type I has layers that are more easily decomposed.

In spite of the information obtained from the different methods of investigation it has not been possible to obtain a definite picture of the clay

minerals. They seem to be 'mixed-layer' minerals of illite and montmorillonite layers, the proportions of the different layers being determined by the potassium content. Type II has been found to contain layers with an intermediate expansion of 14 Å. This fact can possibly be explained by the influence of the larger potassium content, giving rise to a greater amount of non-swelling layers, which prevents some of the swelling layers to expand completely.

Description of Minerals in the Coarser Fractions

In order to investigate the genesis of the bentonite material a study of the coarser fractions was undertaken. For this purpose material from the thick bed was treated as described above (page 14), and the fraction with particle sizes larger than 0.06 mm was used for further concentration of the non-clay minerals. The separation was made in acetylene-tetrabromide-alcohol mixtures and was accelerated by centrifuging, using special tubes (Landergren 1951). In this way four main fractions were isolated containing chiefly the following minerals and having the specific gravities given:

(a) > 2.70, biotite and pyrite.
(b)   2.70—2.60, quartz.
(c)   2.60—2.50, opaque grains of a kaolinized plagioclase and clear crystals of a potassium feldspar, shown to be sanidine.
(d) < 2.50, clay mineral aggregates of the 'mixed-layer' type.

The amount of phenocrysts varies from point to point within the bentonite beds and it is not possible to make a quantitative estimate of the different minerals which were only isolated to make identification possible. Elaborate separations were carried out in order to obtain the minerals in as pure a state as possible. In the following section the different minerals, with the exception of pyrite which is of autogenous origin, will be described in detail.

Biotite.

The biotite gives the bentonite layers their characteristic appearance, the brown colour of this mineral making it clearly visible. The periodical variations in size and quantity of the biotite grains mark the separation of a great number of bentonite layers. The biotite seems to be primary in origin, often showing idiomorphic grains (Fig. 11) and was most probably contained in the ashes which at different times contributed to the formation of the bentonite beds.

Table XVI gives X-ray data for two different biotites, one from the thick bed (Bent. 15) and the other from the upper thin beds (Bent. 8). For comparison a diagram from Nagelschmidt (1937) is included. As can be seen from the table the biotite fraction from Bent. 15 contains a considerable quantity of chlorite whereas none is found in Bent. 8. An optical study of a preparation of the coarse fraction from Bent. 15 showed that the biotite had partly changed. This was most evident in a slide of a preparation of methyl-

Table XVI. D_{hkl} values and intensities for biotite, separated from two different bentonite beds at Kinnekulle, Sweden.

phase	Biotite from Bent. 15 (thick bed) fraction spec. grav. 2.84—2.91					Biotite from Bent. 8 (thin bed) fraction with spec.grav.>2.77		Biotite[1] (Nagelschmidt, 1937)	
	unheated			heated to 700°					
	D_{hkl}	I	hkl	I	D_{hkl}	D_{hkl}	I	D_{hkl}	I
chlorite	14.3	m	001	vst	14.0				
biotite	9.92	vst		st	9.98	10.0	vst	10.1	vst
chlorite	7.07	st	002						
chlorite	4.76	m	003						
biotite				w	4.56	4.59	vw	4.58	w
chlorite	3.56	st	004						
biotite	3.36	vst		st	3.33	3.34	m	3.36	vst
chlorite	2.86	vw	005			—			
biotite	2.66	st		m	2.62	2.64	st	2.65	st
biotite	2.46	vw		w	2.44	2.44	m	2.45	st
biotite	2.19	w				2.18	w	2.183	st
chlorite } biotite }	2.02	m	007						
biotite						2.00	w	2.002	st
biotite	1.68	m				1.67	w	1.67	st
chlorite } biotite }	1.55	st		w	1.54	1.54	m	1.551 / 1.527	st
chlorite	1.44	vw							
chlorite	1.37	m							

vst = very strong, st = strong, m = medium, w = weak and vw = very weak.

A Philips' camera with a diameter of 11.4 cm and filtered copper radiation has been used.

[1] apart from the d-values here given there are some weak reflexions, omitted in this column for greater clearness (vw—3.15, vw—2.91, w—2.51, vw—2.282, vw—1.911, vw—1.752).

metacrylate, Fig. 12, in which the mica flakes had taken a parallel orientation. The thin section was cut perpendicularly to the plane of orientation and showed in this way a marked preponderance of sections parallel to the c-axis with a pronounced zonal character. The methylmetacrylate had caused significant swelling of the mica flakes, giving them a fibrous appearance. Some flakes were quite exfoliated. These might belong to the clay mineral still present in the fraction although they appeared like the biotite with alternative layers of strong and weak pleochroism. The optical properties of the biotite were normal: i. e., brown colour, strong pleochroism (α = light yellow and γ = dark brown), high double refraction (0.040—0.045), and a small axial angle, which could even be zero. The outer parts were seen to have changed to an almost colourless mineral which might be a chlorite (α = colourless and γ = faintly green) and which had almost the same refractive indices as biotite.

The biotite grains showed a considerable variation in specific gravity from 2.7 to over 3.0. A fraction from Bent. 15 with a specific gravity between 2.84—2.91 was separated and subjected to chemical analysis (Table XVII). It could be seen from the analysis that the biotite had greatly changed, the high water content and low potassium content indicating a weathered product.
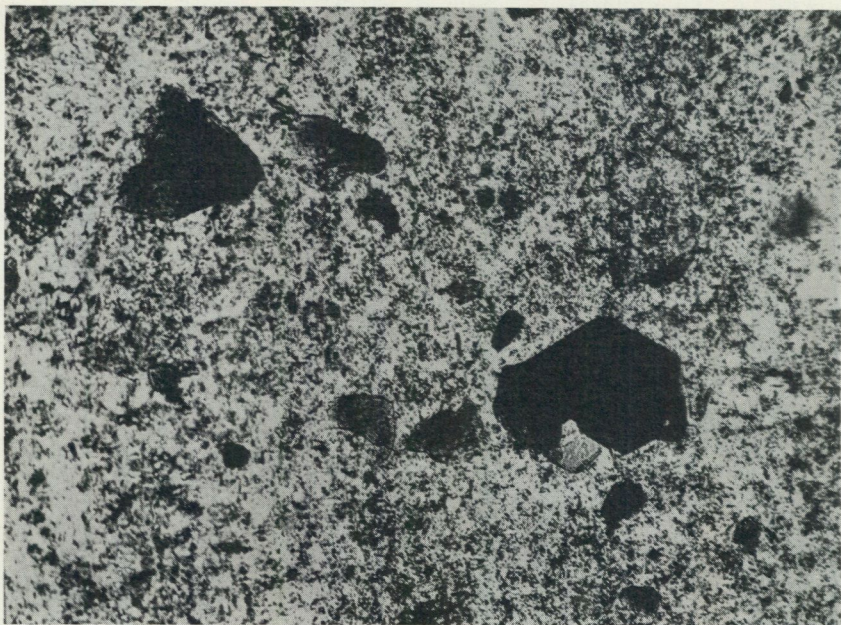
Fig. 11. Thin section of bentonite specimen, cut parallel to plane of layers. Idiomorphic biotite grain can be seen. From lower part of the thick bed (68.8 m), Kinnekulle. 96 ×. (Photo N. Sundius.)

The only mineral present besides biotite was shown from X-ray data to be a chlorite and a rough estimate of the intensities gave about equal quantities of the two minerals. From the chemical analysis a tentative calculation was made of the composition of the two minerals present, and on the basis of the potassium content, the proportion of the biotite was found to approximate 25—30 %, assuming the ideal structural formula as given in Table XVII. When the biotite content was subtracted from the analysis the remaining part gave a feasible formula for a chlorite. This is also given in Table XVII. Some of the silica liberated in the change of biotite to chlorite was treated as remaining and was excluded from the analysis before calculating the formula for the chlorite. The chlorite could be classified as an intermediate to amesite and daphnite.

The X-ray data corresponded to an iron-rich chlorite and the even basal reflexions had a relatively stronger intensity than the uneven ones (Table XVI). The product heated to 700° C gave an enhanced 14 Å reflexion and no reflexion of higher 00l-order for the chlorite phase. A similar case was found for daphnite as described by Brindley and Robinson (1951).

The silica liberated during the weathering of the biotite might have crystallised as quartz but this phase could not with certainty be identified as the strongest reflexion at 3.33 Å coincides with one of the stronger reflexions from biotite.
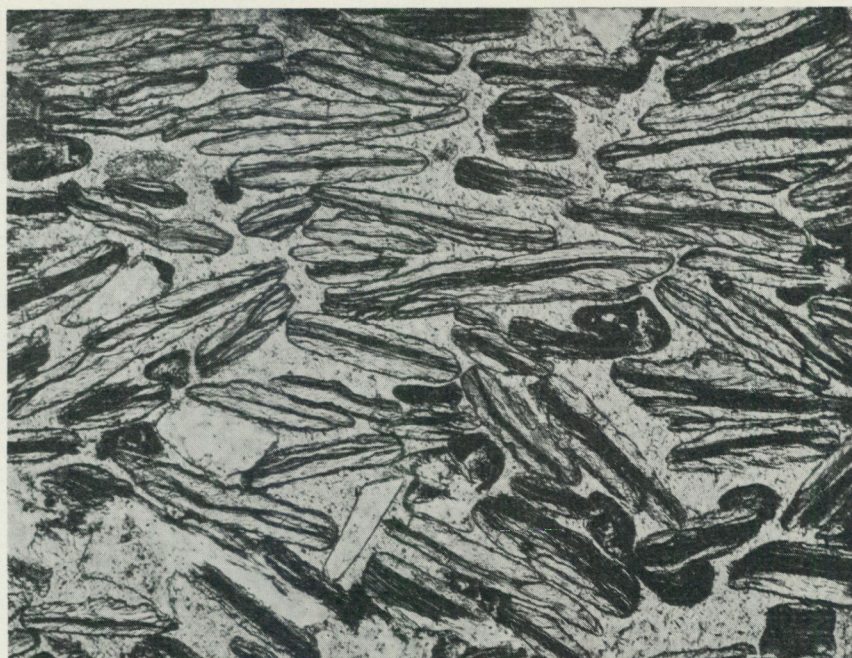
Fig. 12. Biotite grains from Bent. 15. Thin section prepared from fraction > 0.125 mm embedded in methylmetacrylate and cut perpendicularly to the orientation of the flakes. 96 ×. (Photo N. Sundius.)

The high titanium content suggested that a titanium mineral could be present. The stronger reflexions from rutile coincide with the biotite reflexions and no reflexion from anatase was found. The titanium content was included in the biotite formula.

The investigation of the biotite fraction indicated that the biotite in the thick bed had to a great extent changed to a chlorite only about one-fourth remaining as biotite. As can be seen from Table XVI, however, the biotite from the thin beds showed no alteration. A study of thin sections, cut perpendicularly to the bentonite layers, revealed that the biotite differed from layer to layer even within the thick bed. In some cases it was completely unchanged, whereas in others it was partly changed as described above. No detailed investigation has been carried out to discover if there are systematic variations and if these in any way could be connected with variations in the clay material.

It is very difficult to estimate the quantity of biotite present because of its uneven distribution in the bentonite layers. From thin sections an estimate was made by Dr. Sundius. He found a content of 2—3 % (Waern et al. 1948 p. 354) which seems to be a fairly good mean value. During the fractionation of a bentonite sample of about 3 kilograms a biotite-chlorite fraction was separated with apparent particle sizes greater than 0.06 mm. The quantity amounted to about 1 % of the original sample. The fractions with smaller

particle sizes might have a biotite content of about the same magnitude. The biotite grains seldom exceed 0.5 mm in diameter and the greater part seems to be accumulated in the range 0.2—0.01 mm.

Table XVII. Chemical analysis of a biotite fraction (specific gravity 2.84—2.91), separated from Bent. 15 (thick bed). The biotite is partly changed to a chlorite and the proportions have been tentatively calculated.

	chemical analysis		biotite		chlorite		quartz	
	%	prop. of atoms	prop. of atoms	%	prop. of atoms	%	prop. of atoms	% [1]
SiO_2	31.09	0.518	0.168	10.0	0.290	17.5	0.060	3.6
TiO_2	1.40	0.017	0.017	1.40				
Al_2O_3	18.41	0.361	0.056	2.9	0.305	15.6		
Fe_2O_3	2.14	0.030			0.030	2.1		
FeO	18.21	0.253	0.060	4.3	0.193	13.9		
MgO	14.92	0.370	0.091	3.6	0.279	11.2		
MnO	0.10							
CaO	0.04							
Na_2O	0.15	0.002	0.002	0.15				
K_2O	2.52	0.053	0.053	2.52				
$H_2O > 110°$ ...	9.20	1.02	0.112	1.0	0.90	8.1		
$H_2O < 110°$ ...	1.56							
P_2O_5	0.23							
BaO	0.02							
S	0.04							
F	0.14							
Total	100.17			25.9		68.4		3.6

Structure formula used for calculation of the biotite content: $K_2(Al_2Si_6)$ (Mg, Fe)$_6O_{20}(OH)_4$.
Structure formula found for the chlorite: $(Al_{1.4}Si_{2.6})$ (Mg, Fe)$_{4.3}(Al, Fe^{3+})_{1.6}O_{10}(OH)_8$.
Analyst: A. Aaremäe, Geological Survey of Sweden.

Quartz.

Quartz is the most abundant of the phenocrysts present in the bentonite material. The forms commonly found are thin wavy plates, often shaped like wedges, together with thicker particles of irregular form, these latter generally having concave boundaries. Another common type consists of elongated bars like broken icicles, sometimes straight and smooth, but at other times curved and with one or more edges like saw blades. Fig. 17 Pl. III shows a photograph of some grains of this type. The appearance seems to be due to the coalescence of small pyramidal crystals with faces more or less well developed. Individual crystals consisting of hexagonal bipyramids without a subordinate prism and with sharp crystal faces are also to be found, as well as similar crystals in more or less rounded forms. The quartz grains are never quite clear but have a translucent appearance as if impregnated with minute bubbles.

As is revealed in a study of the thin sections, the different forms of quartz phenocrysts are distributed in a random manner. It is likely that they have been deposited at the same time. The bipyramids have forms typical for a quartz porphyric rock, whereas the rod-shaped grains do not have forms

generally connected with such rocks. A description of a similar type has, however, been made by Wittich and Kratzert (1922) who found in rhyolitic ashes from Qualcazar (Mexico) small elongated crystals of quartz with rhombohedral end faces. The quartz phenocrysts from Ordovician bentonites at Bornholm, as described by Gry (1948), closely resemble those found in this investigation.

The amount of quartz in the thick bed was found to be much greater than in the thin beds. From determinations made (Table IX) the thick bed was found to contain between 10—20 % quartz, whereas only a small percentage was found in the thin beds. The phenocrysts are seldom larger than 0.2 mm and the majority of the quartz phenocrysts seems to have accumulated in the fraction 0.006—0.002 mm, which consisted of 40 % quartz (Table X).

Kaolin.

The X-ray photographs from the thick bed had shown that some kaolin was present. The mineral, however, did not seem to be associated with the clay minerals of the 'mixed-layer' type being found in the coarser fractions. A fraction with specific gravity around 2.54 was isolated which consisted

Table XVIII. Intensities and spacings of kaolin grains from Bent. 15.

I	d_{hkl}	phase
vst	7.19	kaolin
diff m	4.38	"
st	4.27	quartz
st	3.59	kaolin
st	3.33	quartz
m	2.57	kaolin
m	2.53	"
m	2.33	"
w	2.29	"
w	1.49	"

Cu-K radiation was used and a Philips camera with diam. 11.4 cm. Beside the reflexions given here, there are some very weak reflexions, which can scarcely be distinguished from the background, and these have not been registered. The d-values, however, indicate that they can result from kaolin and quartz.

chiefly of opaque, colourless grains, which were extremely soft and crushed under the slightest pressure. Under the microscope it could be seen that the grains were not homogeneous but comprised two minerals with somewhat differing refringences, the higher one near to 1.56. Grains having the form of feldspar plates were often to be seen. An X-ray diagram of the material showed that the phases present were quartz and a kaolin mineral (Table XVIII). After heating to 600° C the reflexions from the kaolin phase had disappeared and although the material had not been ground, the photograph showed mainly reflexions from a very fine-grained quartz. Two reflexions belonging to a coarse-grained feldspar could also be distinguished. The only

feldspar found in the bentonite material had been a completely unchanged potassium feldspar. It was at first difficult to understand the origin of a kaolin mineral so distinctly associated with the altered feldspar grains when no transitions were to be found. A detailed study of the kaolin fraction under the microscope revealed, however, that the original ash must have contained a plagioclase which had almost completely weathered to kaolin. Unaltered plagioclase grains are extremely rare and Fig. 18 Pl. III shows one where typical lamellae of albite twins can be seen. The extinction angle of the plagioclase lamellae is small and suggests a composition roughly corresponding to oligoclase or andesine. The grain to the left on the photograph is a typical example of a kaolinized grain.

When the composition and origin of the opaque grains were made clear it was easier to understand the composition of the original ash and the reason why kaolin was found in some preparations and not in others. The plagioclase has weathered to kaolin and quartz. The quartz in a very fine-grained form retains the original form of the plagioclase crystals in those cases where these have not been broken down mechanically. In thin sections the distribution of the plagioclase is very uneven and the grains are fairly difficult to distinguish. In many cases calcium carbonate replaces a considerable proportion of the grains. In slides from the thin beds no altered grains of plagioclase have been found. This accords with observations from the X-ray photographs of preparations from the thin beds in which no kaolin mineral has been identified.

Dr. Sundius in his earlier study of thin sections from the bentonite material (in Waern et al. 1948 p. 354) drew attention to the presence of certain grains which he then considered to be rock fragments. On a re-examination of the slides Dr. Sundius found that the grains could be identical with the plagioclase pseudomorphs which have just been described.

The amount of kaolin indicates that the plagioclase grains could amount to 5—10 % of the material which forms the thick bed. As was mentioned above no indication whatever was found of an unaltered or altered plagioclase in the thin beds but in these beds the phenocrysts were on the whole very rare.

Sanidine

As was stated above, the fraction with specific gravity 2.50—2.60 contained, besides the kaolin grains, about an equal quantity of a clear colourless mineral. This after a close investigation was found to be a sanidine. The mineral was further separated in heavy liquids to obtain as pure a phase as possible. This method did not permit of its complete separation from the accompanying grains of kaolinized plagioclase, and the removal of all the quartz which adhered to the fraction was also difficult. The discovery, however, of an absolutely transparent sanidine in the Ordovician bentonite beds was considered to be of such great interest that a more detailed study was undertaken.

To get a good material for a chemical analysis an elaborate purification was carried out by handpicking the contaminating mineral grains, a little

more than 100 mg being obtained in this way. Sodium and potassium were determined and the following values were found: $K_2O = 12.5$ % and $Na_2O = 2.90$ %. The impurities amounted to 3—5 % and consisted chiefly of quartz, as can be seen from the X-ray powder photograph (Table XXIV) and under the microscope. The analysis gives a composition of 75.2 % (by weight) of $KAlSi_3O_8$ and 24.8 % of $NaAlSi_3O_8$ or, expressed in molecular composition, $Or_{74}An_{26}$. The specific gravity of the mineral is 2.57. In Table XIX, data from the investigation are compiled and a comparison of the optical data is made below with those from another sanidine and a heat-treated orthoclase. The indices of refraction were determined using immersion oils and the optical axial angle was found by the aid of the universal table. Fig. 19 shows some fragments of the sanidine embedded in canada balsam and magnified about 80 ×, Pl. IV.

Table XIX. Properties found for sanidine from Kinnekulle, Sweden.

chemical analysis	composition	spec. grav.	cell dimensions	optical properties
% K_2O 12.5 Na_2O 2.90	wt % $KAlSi_3O_8$ 75 $NaAlSi_3O_8$ 25	2.57	$a = 8.48 \mp 0.02$ kX $b = 12.97 \mp 0.05$ ” $c = 7.16 \mp 0.02$ ” $\beta = 116.1° \mp 0.2°$ $V = 707$ kX³	$n_\alpha = 1.519$ $n_\beta = 1.523$ calc. $n_\gamma = 1.524$ $2V_\alpha = 15°—18°$ $a \wedge a = 3°$ $\beta = b$

Two Weissenberg X-ray photographs were taken, one of the $h01$-zone and the other of the $0k1$-zone. Different crystals were used, but both were prismatic with the prism axis parallel to the a-axis. The crystal used to give the $0k1$-zone was not perfect, giving double spots displaced about $1/2°$, but having the same intensities and the same angles of reflexion. There was no sign which showed the crystals to be microperthitic. The intensities were compared with those found by Cole et al. (1949) and as far as could be judged from the visually estimated intensities there were no remarkable discrepancies.

Specimen	Composition wt%			n_α	n_β	n_γ	$2V_\alpha$	Orientation
	Or	Ab	An					
Sanidine, Kinnekulle	75	25	—	1.519	(1.523)	1.524	15—18°	$a \wedge a = 3°$ $\beta = b$
Sanidine, Eifel[1] ..	78	21	1	1.5201	1.5248	1.5248	17°	
Sanidinized orthoclase[2]	92.2	6.8	2.5	1.5187	1.5227	1.5233	4.4°	$a \wedge a = 5.3°$ $\beta = b$

[1] Sanidine, Eifel, Germany data from Tuttle (1952).
[2] Sanidinized orthoclase, Mogul, Upper Burma (Spec. C, described by Chao et al. (1939), data from Cole et al. (1949)).

A powder photograph was taken, using monochromatic copper radiation and a camera of the Guinier type, to get more accurate cell dimensions. As

an aid in identifying the reflexions, data from Taylor (1933) and Cole et al. (1949) and a rotation photograph around the b-axis were used.

A complete interpretation of the powder photograph was not undertaken but the greater part of the reflexions could be given indices with good agreement between observed and calculated values for the cell dimensions found. This can be seen from Table XXIV, in which the F-values observed by Cole et al. and Taylor are also listed. Data for the cell dimensions are given in Table XIX, where other properties determined are also compiled.

The size of the sanidine fragments seldom exceeds 0.2 mm and these were found in the finer fractions as far down as the resolution of the microscope permitted them to be distinguished. The quantity is again difficult to estimate. In the thin beds there has not been observed any feldspar at all and in the thick bed the uneven distribution of phenocrysts renders a quantitative determination impossible. For the sample investigated, however, the quantity of sanidine may be estimated to approach 5 per cent considering the potassium content of the coarser and the finer fractions and allowing for the different amounts of quartz present.
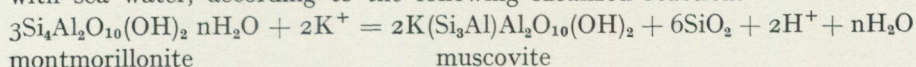
By the investigation here it has been shown that the alkali feldspar present in the Ordovician bentonite layers is a true sanidine and accordingly has crystallized from a melt and at some time has been subjected to a sudden cooling. Through the quenching the homogeneous character of the alkali feldspar has been preserved and this provides good evidence that the bentonite layers originate from volcanic material. The fragmental development of the phenocrysts remains and their uneven distribution makes it probable that ash falls have formed the deposit.

The alkali feldspar seems to be quite stable in the surrounding clay material and does not show any sign of weathering in contrast to the plagioclase in the same layer which has almost completely changed to a kaolin mineral.

Clay Mineral Aggregate Fraction.

The coarser fractions of the bentonite material always consisted to a large extent of clay mineral aggregates which resisted dispersion. To ascertain why some particles behaved like this, the aggregates were isolated from heavier phenocrysts and a fraction with specific gravity less than 2.40 was subjected to further investigation, still using the material from Bent. 15. The X-ray diagrams showed that the main part of the aggregate fraction consisted of the clay mineral of Type I, described in the first part of this paper. One or two reflexions from a kaolin mineral were present and the strongest reflexions of quartz could also be identified. From a photograph of a material which had not been ground, it could be seen that the quartz was present in a very fine grained form, showing smooth lines for an unrotated specimen. When the aggregate was seen with 100 × magnification, it appeared to be made up of very thin colourless sheets laid on top of each other and forming thicker flakes of nearly homogeneous translucent appearance. Only at the edges can the different layers be distinguished.

In immersion oil the flakes show double refractions, as if composed of a network of small needles, and this is probably due to the fact that the thin sheets are not absolutely parallel but have the edges slightly folded up so that thin sections not parallel to the basal planes can be seen. The refractive indices are difficult to determine exactly, but appear to be somewhat higher than quartz. It can be seen that the flakes are not homogeneous but contain another mineral, probably quartz, distributed as small dots. The difficulty in dispersing the flakes can be explained if the aggregates are assumed to consist of very thin clay mineral sheets held together by finely divided quartz. This might originate either from the reaction when the volcanic ash changes to clay minerals and silica is liberated (Bramlette, 1946), or, if montmorillonite is first formed from the volcanic ash, at the succeeding reaction of this mineral with sea water, according to the following idealized reaction:

$$3Si_4Al_2O_{10}(OH)_2 \cdot nH_2O + 2K^+ = 2K(Si_3Al)Al_2O_{10}(OH)_2 + 6SiO_2 + 2H^+ + nH_2O$$
montmorillonite   muscovite

The liberated silica could have crystallized as quartz between the mica flakes thus preventing the flakes dispersing. The greater part of the liberated silica, however, has been transported away from the bentonite beds and is found in the adjoining cherty beds, as has been mentioned by Thorslund (1948) and can be seen in Fig. 13.

Table XX. Chemical analysis of clay aggregate fraction of Bent. 15, No. 396.
No. of analysis 2632.

%	110° C calc. %	atomic proportion	10 % SiO$_2$ + 5 % kaolin deducted	cell content of clay mineral	
SiO$_2$ 58.22	61.60	1.017	0.813	Si 7.56	= 8.0
TiO$_2$ 0.25	0.26	0.003	0.003	Al 0.44	
Al$_2$O$_3$ 19.04	20.14	0.395	0.356	Ti 0.03	
Fe$_2$O$_3$ 1.84	1.95	0.024	0.024	Al 2.86	
FeO 1.17	1.24	0.017	0.017	Fe^{3+} 0.22	= 4.1
MgO 3.78	4.00	0.099	0.099	Fe^{2+} 0.16	
CaO 0.84	0.89	0.016	0.016	Mg 0.83	
Na$_2$O 0.42	0.44	0.014	0.014		
K$_2$O 2.33	2.46	0.052	0.052	Mg 0.09	
H$_2$O > 110° .. 6.72	7.11	0.790	0.71	Ca 0.13	= 0.84
H$_2$O < 110° .. 5.48	—			Na 0.14	
Sum 100.09	100.09			K 0.48	

The cell content might be compared to Table VI.
Analyst: A. Aaremäe, Geological Survey of Sweden.

The analysis made of the aggregate material is given in Table XX. The resemblance to the other clay analyses (Table V) can be seen. The SiO$_2$ content is higher, which is in accordance with the statement made above. The cell content of the clay mineral has been calculated, after subtraction of 10 % quartz and 5 % kaolin, both roughly estimated from the X-ray photographs.

The kaolin belongs to the plagioclase pseudomorphs which have not been quite separated from this fraction. The formula found for the clay mineral does not deviate appreciably from that found for the true clay fraction of Type I after making allowance for the rough estimate of the impurities.

Electron micrographs of the aggregated clay fraction showed that the flakes were similar to those found in the finer fractions although on a larger scale.

The results from the investigation on the clay aggregates all point in the same direction and make it apparent that the clay minerals in the finest fractions and in the aggregates of the coarser fractions are the same.

A similar detailed investigation has not been made for Type II, but a chemical analysis made on an aggregate fraction and on a clay fraction (Table V, An. 101, An. 105) of the same material gave similar results. This aggregate fraction, however, had not been subjected to repeated dispersions and an excess of silica is not noticed.

Discussion on the Origin.

In the description by Thorslund (1948) the bentonite layers were already, from their general appearance and character, considered to be altered ash layers. This has been further substantiated during the present investigation. The phenocrysts described here give an idea of the composition of the parent lava related to the thick bed. The abundance, in certain parts, of quartz phenocrysts (15 %), the presence of potassium feldspar (5 %) and of plagioclase pseudomorphs (10 %) indicate that the lava could have had a composition corresponding to a rhyolite or, more probably, a dacite. The devitrified glass now consists of a clay mineral which has been described as composed of mixed layers of montmorillonite and illite in a random interstratification and with a high proportion of montmorillonite layers (clay, Type I). It is more difficult to draw any conclusions as to the composition of the material which gave rise to the thin beds. Larger phenocrysts are very sparse, idiomorphic biotite grains only being present, indicating that the lack of phenocrysts is not due to a separation during the transport of the ash material. The clay minerals, Type II, connected with these beds, are similar in kind to Type I but differ in the proportions of the layers. A higher potassium content involves a greater number of non-expanding layers.

This difference of the Kinnekulle clays both from each other and from pure montmorillonite appears to be due to the present differences in the potassium content. It is not clear whether these are due to a variation in the composition of the volcanic glass, or result from alteration, caused by sea water or circulating ground water, or a combination of both. A comparison of the most outstanding differences of the bentonite beds, *i. e.* the content of phenocrysts and the thicknesses of the beds, might bring forward some positive information when combined with observations made by other authors.

The low content of phenocrysts in the thin beds could be due to the magma related to these beds having had a higher temperature hindering

the development of crystals prior to the volcanic eruption. The high temperature might have caused the quickly cooled lava to disintegrate into a finely divided powder of high reactivity, higher than that of the ash products related to the thick bed. The subsequent transformation in sea water might have produced a variation in the clay minerals formed.

The different quantities of phenocrysts might also be caused by a difference in the primary composition of the lavas also indicated by a variation in the Ti content of the beds investigated. The influence of the composition has been discussed by Ross and Hendricks (1945) who have found that the bentonites which consist of pure montmorillonites generally have been formed from a less acid glass than has been found for the Kinnekulle bentonites and the parent rock of Ordovician bentonites in North America. The latter mostly holds 5—7 % K_2O and seems originally to have been a potash-rich latite.

Bramlette (1946), however, has found that the original potassium content is removed during the alteration of a volcanic tuff to bentonite and demonstrates this by analyses of fresh tuffitic material, partly altered, and of completely altered material of the same pyroclastic origin. The K_2O content in the fresh tuff is 2.48 and in the bentonite 0.09 %, the partly altered tuffs giving intermediate values. Bramlette does not hold the view that a tuff is altered to bentonite on the sea floor since he found silicification not only in the bed below, but also in that above the bentonite bed. He finds it inconceivable that pyroclastic texture could be preserved in an alteration on the sea floor as bentonite swells and sloughs when immersed in water. The tuff is considered to have been altered by the relatively scant water within the confining strata.

On the other hand, Weaver (1953) points out the influence of the sea water on the potassium bentonites found in Pennsylvania. The parental lava here seems to have been of an intermediate composition, a trachyte or trachyandesite, deposited in the form of volcanic ash in sea water. Weaver presumes that potassium was leached out and a calcium-saturated clay was formed which later absorbed potassium from the sea water forming minerals of illite type, but still containing a certain amount of expanding layers. The bentonite layers described by Weaver are, in general, very thin, measuring only a few inches and being rarely as thick as 10 inches.

The ash related to the Kinnekulle bentonites has obviously been deposited in sea water, the studies of fossils (Thorslund 1948) showing that there is no discordance in the strata related to the bentonite beds. The arguments given by Bramlette against an alteration of the bentonites on the sea floor are not, therefore, valid in this case but may be used as some evidence that this is what might have happened. There are no signs of a pyroclastic texture preserved and there are several indications that the material has been sloughed and swirled. The alternation of layers with larger and smaller phenocrysts can also have been effected by a dispersion of the clay material formed, followed by sedimentation. As can be seen from Fig. 13 (reproduced from the paper by Thorslund 1948), the extreme cherty beds are only found below the bentonite beds.

This seems to be further evidence of the suggestion by Ross and Hendricks (1945) that when potassium-bentonites are formed the alteration of the tuffs has taken place in sea water, whereas when bentonites containing pure montmorillonite are formed the alteration has been effected by the circulating ground water.

Concerning the thicknesses of the beds it has been pointed out that the bentonite material from the thick bed more closely resembles montmorillonite and has a lower potassium content than material from the upper thin beds. Also the potassium bentonites with a still higher potassium content described by Weaver (1953) occurs in very thin beds. This could be an indication that thin beds are more easily accessible to the potassium of the sea water. If this is so a variation of the minerals within a bed could be expected, especially for the thicker beds. In the extremely thin beds the formation of illite should be favoured. Within the thick bed, however, the specimens taken were found to be similar and of Type I, except the single specimen Bent. 5 (whose position is not certainly known).

When the Kullatorp core became available specimens from a greater variety of beds could be investigated. The beds varied greatly in thickness, but were generally thin as compared to the thick bed (Fig. 13). The specimens were superficially studied by X-ray for a first classification and will be given a more detailed study in connection with samples from bentonite beds from other parts of Sweden. Samples 20—26 (Fig. 13) are all very much alike and whilst resembling Type II seem to have somewhat larger proportion of swelling layers. Bents. 27 and 28 from the very thin beds at a much lower level were both similar and clearly of Type II. No samples showed a typical illite diagram and it is clear that accessibility of potassium to the very thin layers is not the only factor contributing to the formation of illite.

A weathering process, widely separated from the devitrification of the volcanic glass, is the alteration of plagioclase to a kaolin mineral and at some time the bentonite beds must have been under conditions favourable to this process.

Thorslund (1948) in his paper mentions an easterly part of the North Sea as a possible source of the volcanic outburst and connects this with the Caradocian periods of volcanicity in Wales and in the Trondheim region (Vogt, 1945). Professor Vogt has kindly made available four specimens of rhyolitic tuffs from the Esphaugen-Hareklett.[1]

Dr. Sundius has kindly made a microscopical examination of the slides prepared from these specimens and has given the following description:

"In the four slides studied it can be seen that the tuff has strongly changed and shows signs of a cataclastic action, manifested in deformed and also broken quartz grains and a parallel arrangement of the mica. All the specimens

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[1] 1   Rhyolitic tuff, quartz porphyry a, Harekletten, Map Melhus 7/7 1943.
   2   »   »   ,   »   »   9. Between Damtjönn and Nordtömme 19/8 1943.
   3   »   » , Hareklett, small burst exposure at dam N. W. Nordtömme, 3/9 1947.
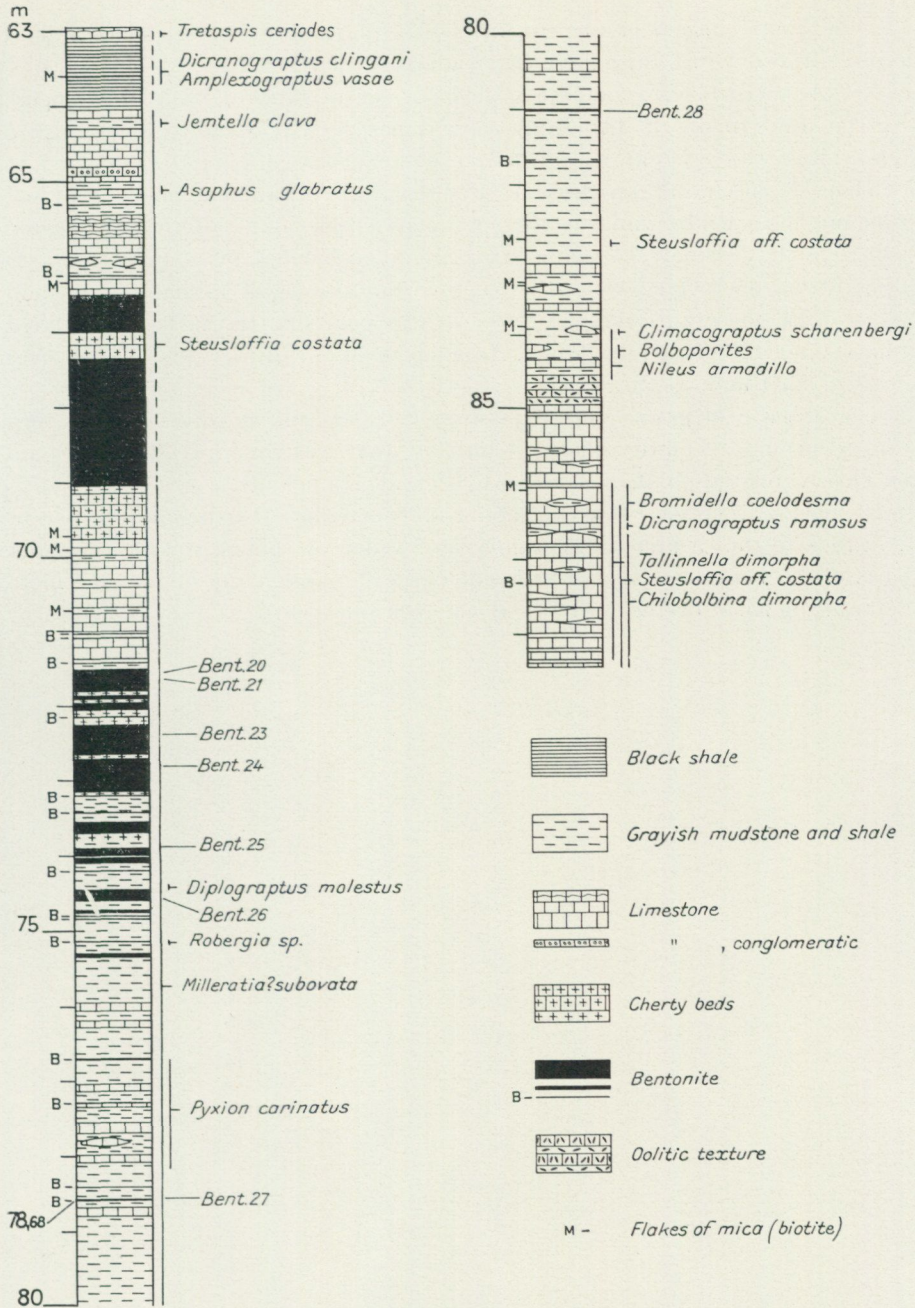   4   »   » , Effusive 1, far to the North, between Esphaugen and Knuthammeren, 6/8 1943.

Fig. 13. Diagram of part of the Kullatorp core. (Thorslund 1948, p. 344.) The specimens taken are marked.

consist of a very fine-grained quartz feldspar matrix, rich in sericite, phenocrysts of quartz and albite, the latter partly clouded by sericite, some zoisite and calcite also being present. In several cases original porphyry fragments

can be distinguished. Some quantity of quartzite, sericite-quartzite and probably also schist may have been admixed in the tuff.

No phenocrysts of a potassium feldspar, or of biotite, fresh or changed, can be seen. In one of the slides only, it has been possible to distinguish a few grains which might possibly be pseudomorphs of a biotite changed to chlorite. It has not been possible to distinguish mica pseudomorphs of potassium feldspar. In some of the specimens check-board albite can be seen which by its intimate twinning structure is considered by some authors to be albitised microcline. But this structure can also be of primary origin and in any case the grains are very few. All this points to the tuff being related to a magma rather rich in sodium. An analysis of one of the tuffs (No. 2) gives 3.03 % K_2O and 2.0 % Na_2O.

The absence of grains of a potassium feldspar, and in any case the very rare occurrence of biotite, makes it unlikely that this rhyolitic effusive should be closely related to the altered ash beds at Kinnekulle."

It appears, therefore, that we should find, in some other region, the parent lava rock to the Ordovician bentonites in Sweden. A comparison on a broader basis of the bentonite beds in different parts of Scandinavia might give more definite evidence of the position of the volcanic centre.

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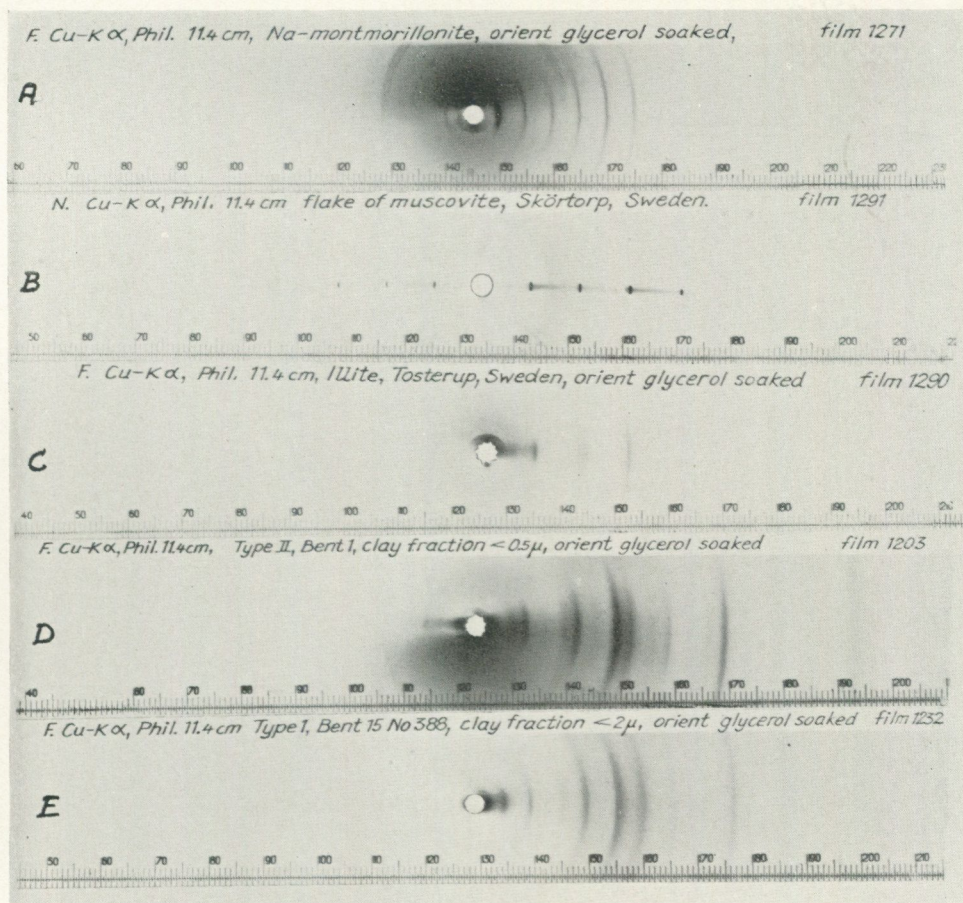
Fig. 14. X-ray photographs from glycerol-treated specimens, oriented parallel to the basal planes. Microphotometer curves of the photographs are given in Fig. 5. (see text note to this figure).
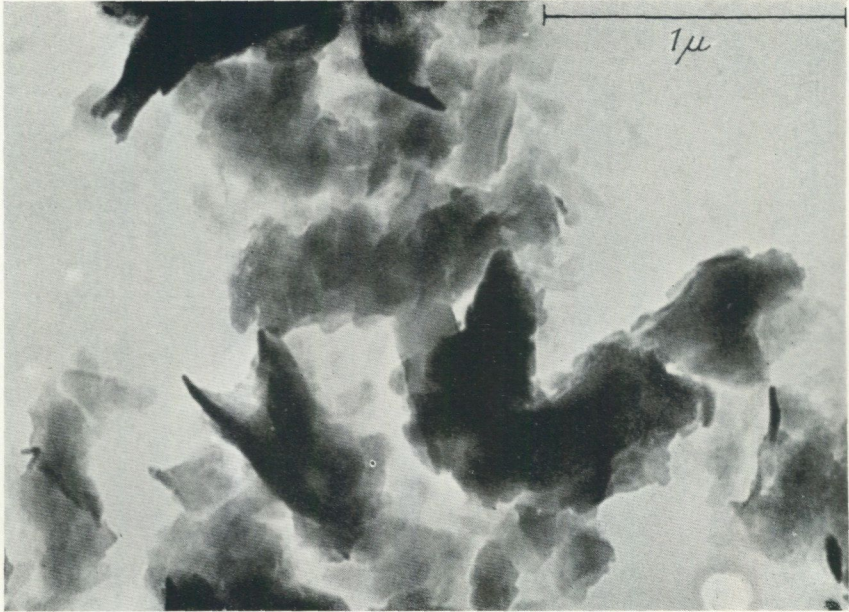
Fig. 15. Electron micrograph of the bentonite clay from Kinnekulle dispersed in sodiumpyrophosphate, fraction $< 1\,\mu$. Type 1, Bent. 15 No 388. 40.000 x.
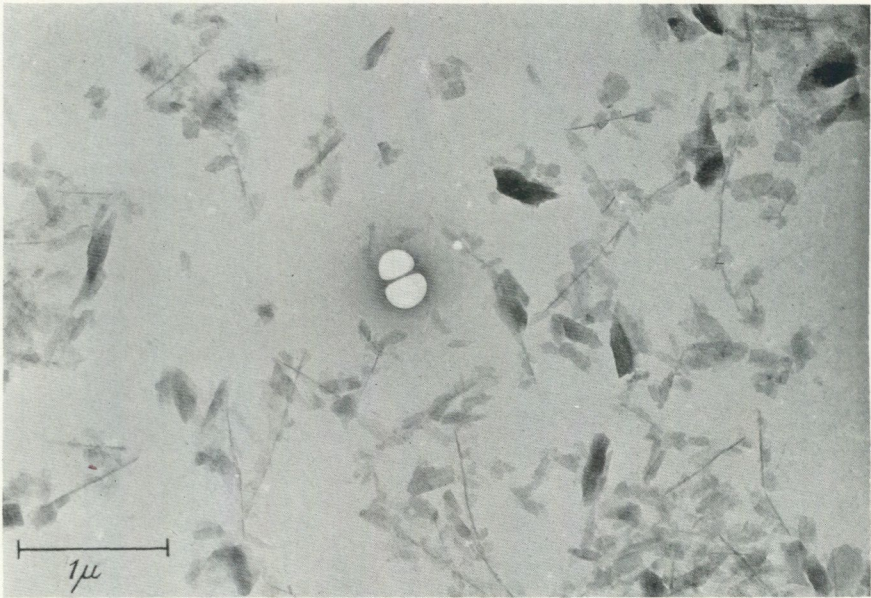
Fig. 16. Electron micrograph of bentonite clay from Kinnekulle, Type II, Bent. 6. Upper part of suspension, allowed to settle for several weeks. 20.000 x.
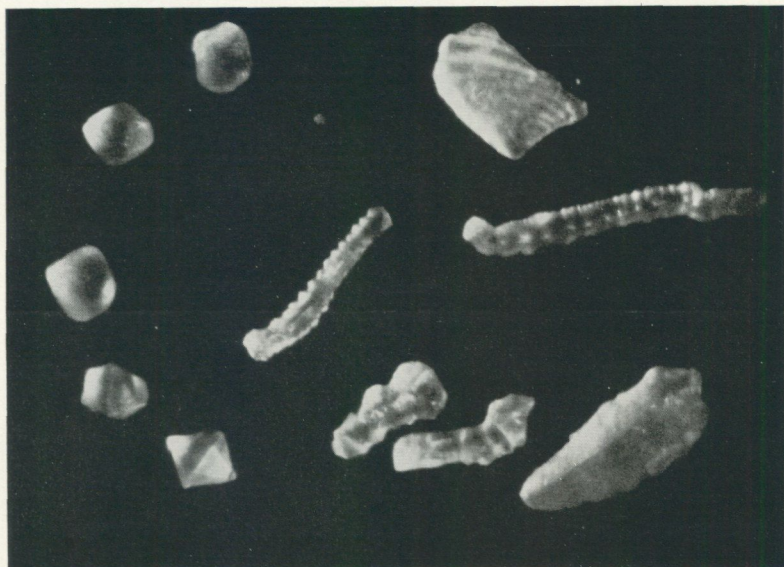
Fig. 17. Quartz grains isolated from Bent. 15. A bipyramid can clearly be seen. 50 x.

photo N. Sundius
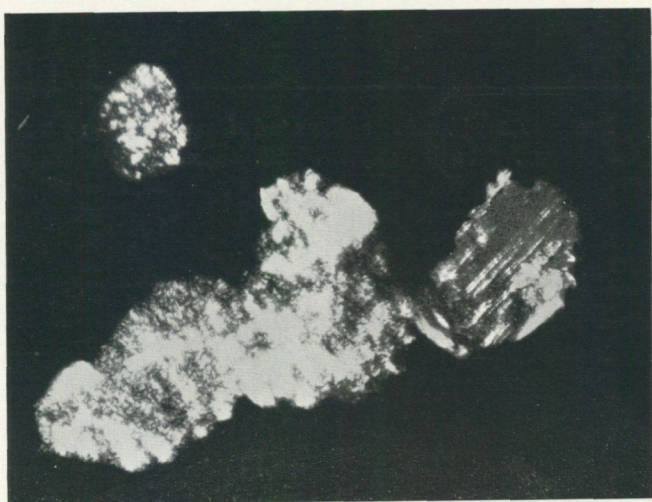
Fig. 18. Kaolinized plagioclase grain isolated from Bent. 15. The grain to the right shows an unaltered plagioclase fragment with typical lamellae of albite twinning. 160 x.

photo C. Larsson

Fig. 19. Fragments of sanidine, isolated from Bent. 15 embedded in canada balsam, tube slightly lowered. 80 x.

photo C. Larsson

Table XXI   S.G.U. SER. C NR. 540

Intensities and spacings from X-ray photographs of bentonite material
from Kinnekulle, with the lower K_2O content of about 2.5 %, Type I.

The specimens were made from clay fraction $< 0.5\mu$ of the H-bentonite

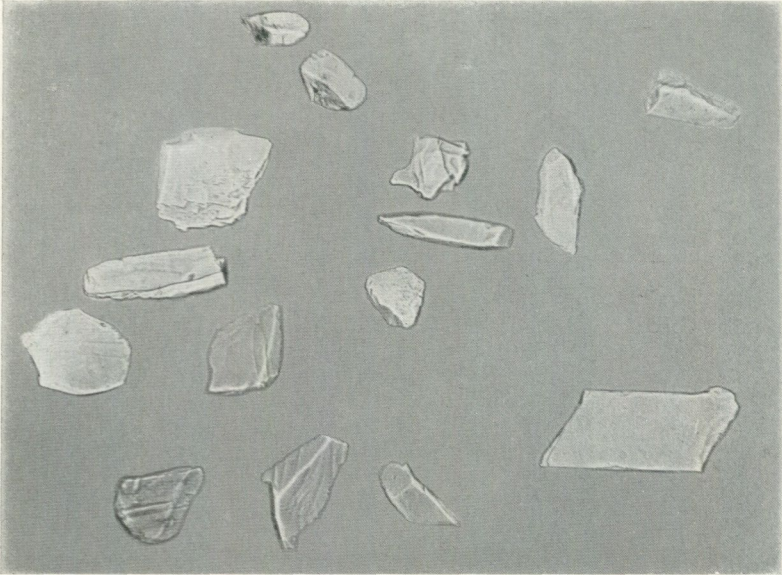| hk indices x)	d_{hk} calc x)	glycerol-treated specimens rolled into thin rods						powder specimens in capillary tubes of Lindemann glass					
		Bent 4.		Bent 7.		Bent 15.		Bent 4.		Bent 7.		Bent 15.	
		I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}
		vst	18.2	st	17.6	vst	17.8						
								st	13.6	vst	14.5	vst	12.1
		st	9.28	st	9.29	st	9.30						
								vw	4.98	w	5.04		
11, 02	4.49	vst	4.46	vst	4.45	vst	4.48	vst	4.48	vst	4.48	vst	4.47
		vw	4.22										
		w	3.48	m	3.45	m	3.48	vw	3.70	w	3.64	w	3.69
		w	3.32									vw	3.31
		vw	⌐3.09	w	⌐3.07			vw	⌐3.25	mbr	⌐3.19	vw	⌐3.05
			⌊2.99			vw	⌊2.98		⌊3.10				
13, 20	2.59	vst	2.54	vst	2.56	st	2.57	vst	2.56	vst	2.56	vst	2.57
		w-	2.36	w	2.38	w	2.36	w	2.36	w	2.38	w	2.37
22, 04	2.25	vw	⌐2.24	vw	⌐2.24	vw	⌐2.25			vw	⌐2.21	w	⌐2.24
			⌊2.12		⌊2.11		⌊2.12	vw	⌊2.17		⌊2.08		
		w+	1.96	w	1.97					vw	1.95		
31, 15, 24	1.703	w	⌐1.70	vw	⌐1.70	vw	⌐1.70	w	⌐1.69	vw	⌐1.70	w	1.70
			⌊1.64		⌊1.62		⌊1.64		⌊1.62	vw	⌊1.63		
33, 06	1.500	vst	1.499	vst	1.492	st	1.500	st	1.499	vst	1.500	vst	1.498
26, 40	1.298	m	1.295	m	1.290	w	1.299	m	1.295	m	1.295	m	1.296
35, 17, 42	1.249	w	1.245	w	1.238	vw	1.245	w	1.245	w	1.245	w	1.248
a_o	5.20		5.18		5.16		5.20		5.18		5.18		5.18
b_o	9.00		8.99		8.95		9.00		8.99		9.00		8.99

a_o and b_o values have been deduced from the observed (33, 06)
and (26, 40) reflexions respectively.

vst=very strong, st=strong, m=middle strong, w=weak, vw=very weak
Those reflexions which are connected together rather denote edges on
a broad band.

Dhkl values are given in kX

x) from Mac Ewan, D.M.C., (1951)

Table XXII   S.G.U. SER. C NR 540

Intensities and spacings from X-ray photographs of bentonite material from Kinnekulle, with the higher K_2O content of about 5 %.

The specimens were made from clay fraction <0.5 μ of the H-bentonite except Bent 8, from the aggregate fraction (An. 101)

hk indices	d_{hk} calc.	glycerol-treated specimens rolled into thin rods								powder specimens in capillary tubes			
		Bent 1.		Bent 5.		Bent 6.		Bent 8.		Bent 1.		Bent 8.	
		I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}
		m	13.9	vw	14.0	m	13.9	w	14.1				
										vst	11.38	vst	11.3
		st	9.58	m	9.55	st	9.45	st	9.46				
										vw	4.92	m	4.98
11, 02	4.49	vst	4.45	st	4.44	vst	4.52	vst	4.49	vst	4.49	vst	4.48
		m	3.42	w	3.39	m	3.46	m	3.37	w br	3.67	w	3.67
										w	3.30	w	3.36
		w	3.09	w	3.11	w	3.10	w	3.10	vw	3.14	vw	3.14
13, 20	2.59	vst	2.56	st	2.56	vst	2.56	vst	2.57	vst	2.57	vst	2.57
		w	2.38	w	2.37	w	2.37	m	2.38	m	2.38	w	2.39
22, 04	2.25	vw	⌈2.23 ⌊2.12	vw	⌈2.25 ⌊2.11	vw	⌈2.24 ⌊2.12	vw	⌈2.25 ⌊2.11	vw	⌈2.23 ⌊2.12	vw	⌈2.25
		w	1.97	w	1.97	m	1.98	w	1.97				
31, 15, 24	1.703	vw	⌈1.70 ⌊1.64	vw	⌈1.70 ⌊1.63	vw	⌈1.70 ⌊1.62	vw	⌈1.70 ⌊1.63	vw	⌈1.70 ⌊1.63	vw	⌈1.70 ⌊1.63
33, 06	1.500	st	1.496	st	1.498	st	1.500	vst	1.495	st	1.495	vst	1.500
26, 40	1.298	m	1.293	m	1.292	m	1.294	m	1.295	m	1.293	m	1.295
33, 17, 42	1.249	w	1.245	w	1.248	w	1.245	w	1.245	w	1.245	w	1.24
a_o	5.20		5.17		5.17		5.18		5.18		5.17		5.18
b_o	9.00		8.98		8.99		9.00		8.97		8.97		9.00

a_o and b_o values have been deduced from the observed (06, 33) and (26. 40) reflexions respectively.

For intensity scale see Table XXI

Table XXIII   S.G.U. SER. C NR 540

Intensities and spacings from basal reflexions of oriented specimens of bentonite material from Kinnekulle. All preparations were treated with glycerol. The % given beneath each material refers to the K_2O content.

Bent 1. 5.2%	Bent 5. 4.3%	Bent 6. 4.8%	Bent 4. 2.5%	Bent 7. 2.7%	Bent 15. No 388 2.8%	Na-montmorillonite 0%	002	Muscovite 11%	002
I d_{hkl}	I d_{hkl}	I d_{hkl}	I d_{hkl}	I d_{hkl}	I d_{hkl}	I d_{hkl}		I d_{hkl}	
			vst 17.7	st 17.7	vst 18.0	vst 17.7	001		
st 13.1	st 13.6	m 13.8						st 10.0	002
vst 9.6	vst 9.3	st 9.6							
			st 9.0	st 9.4	st 9.0				
						st 9.0	002		
						m 5.97	003		
vwbr 7.0									
			w 5.61	vw 5.6	w 5.71				
m 5.46	m 5.24	w 5.50							
								st 4.99	004
st 4.74	st 4.67	m 4.66							
vwbr 4.04			w+ 4.47	m 4.48	st 4.44	st 4.45	004		
						st 3.58	005		
vst 3.44	vst 3.36	vst 3.42	m 3.42	st 3.44	vst 3.42				
								st 3.30	006
st 3.10	m 3.14	m 3.11		vw 3.0 diff		m 2.97	006		
			w 2.94	vw 2.82	st 2.93				
vwbr 2.77									
	vw 2.63								
		w 2.56		vw 2.53	w 2.48	vw 2.56	007		
m 2.45	w 2.47		vw 2.48					st 2.48	008
w 2.12									
st 2.04	m 1.94	st 1.97	m 1.94	st 1.97	st 1.92	w 1.97	008	m 1.97	0010
reflexions not belonging to the mixed layer minerals {			m 7.02	st 7.12	w 7.07	kaolin			
				w 4.70		chlorite			
				m 4.25		quartz			
			w 3.52	st 3.56		kaolin			
				st 3.31		quartz			

For intensity scale see Table XXI

Table XXIV   S.G.U. SER. C NR 540

X-ray data from a powder photograph of sanidine, isolated from the
Ordovician bentonite beds (Bent. 15) Kinnekulle, Sweden, Cu-K
radiation (monochromatized) was used and a focussing camera of
Guinier type.

hkl	d_{obs} kX	I	$\sin^2\theta$ obs	$\sin^2\theta$ calc	F_{obs} Cole et al.	F_{obs} Taylor
020 001	6.58	w	0.0137	0.0141 0.0143	37 24	3
11$\bar{1}$	5.86	w-	0.0172	0.0174		2-3
20$\bar{1}$	4.20	st	0.0337	0.0339	119	
111	3.93	m	0.0384	0.0387		
200 130	3.77	st	0.0417	0.0409 0.0419	41	<1 8
13$\bar{1}$	3.62	m-	0.0452	0.0456		4-5
22$\bar{1}$	3.51	w	0.0479	0.0480		
11$\bar{2}$	3.46	st	0.0495	0.0496		5-6
Quartz (101)	3.34	w+	0.0530	0.0521		
220	3.29	vst	0.0547	0.0550		8
20$\bar{2}$ 040 NaCl(111)	3.25	vst br.	0.0558	0.0555 0.0563 0.0560	148 121	8
002	3.22	vst	0.0570	0.0572	166	8
131	2.98	st	0.0666	0.0668		5
22$\bar{3}$ 041	2.90	m	0.0704	0.0696 0.0706	88	4 5-6
022	2.88	w-	0.0714	0.0713	69	3-4
NaCl(200)		extra st	0.0746	0.0747		
31$\bar{1}$ 13$\bar{2}$	2.75	m	0.0780	0.0780 0.0778		5-6
31$\bar{2}$	2.58	vw	0.0889	0.0889		
24$\bar{1}$ 221	2.56	st	0.0900	0.0902 0.0905		8
112	2.53	w	0.0922	0.0922		
310	2.49	w	0.0955	0.0955		4-5
240	2.48	w-	0.0965	0.0972		2
151	2.41	m	0.1018	0.1019		4-5
33$\bar{1}$ 203	2.36	m	0.1060	0.1060 0.1057	12	
11$\bar{3}$	2.31	w	0.1109	0.1105		3-4
Quartz(102)	2.28	vw-	0.1141	0.1142		
Quartz(111)	2.24	vw-	0.1173	0.1182		
15$\bar{1}$ 330	2.20	vw	0.1225	0.1232 0.1237		2 1
060	2.17	st	0.1262	0.1267	171	8
241	2.11	m	0.1325	0.1328		
40$\bar{1}$ 40$\bar{2}$	2.09	m	0.1360	0.1232 0.1356	72 92	
061 20$\bar{2}$	2.05	m	0.1407	0.1410 0.1406	60 60	3
NaCl(220)		extra st	0.1500	0.1495		
222	1.96	w+	0.1548	0.1547		
$\overline{}51$		-		0.1623		2
400	1.90	w	0.1639	0.1635	125	6-7
40$\bar{3}$	1.89	w	0.1653	0.1645	98	
11$\bar{3}$	1.845	w	0.1742	0.1744		
Quartz(112) 350 42$\bar{3}$	1.815	vw	0.1800	0.1794 0.1800 0.1786		3
26$\bar{2}$	1.803	vw-	0.1823	0.1822		4-5
062 20$\bar{4}$ 043	1.790	st	0.1848	0.1839 0.1846 0.1850	102 178 105	5 5
44$\bar{2}$	1.758	m	0.1920	0.1919		
43$\bar{3}$	1.734	w+	0.1970	0.1962		
NaCl(311)	1.695	st	0.2060	0.2055		
35$\bar{3}$	1.667	vw-	0.2131	0.2129		
NaCl(222) 080	1.625	vst	0.2244	0.2242 0.2253	72	3
13$\bar{4}$ 004	1.609	vw-	0.2291	0.2281 0.2288	31	2 1
-	1.580	w	0.2370			
024	1.560	w	0.2434	0.2429	102	4
063	1.518	m	0.2569	0.2554	59	4
46$\bar{1}$	1.502	m-	0.2624	0.2620		4
280	1.491	st	0.2662	0.2661		8
-	1.464	vw	0.2762			
114	1.442	vw-	0.2852	0.2851		5
-	1.430	w	0.2902			
-	1.418	vw-	0.2947			
NaCl(400) 60$\bar{2}$	1.405	vst	0.2999	0.2989 0.2974	147	
60$\bar{3}$ 402	1.394	vw	0.3056	0.3051 0.3058	34 152	
40$\bar{5}$		-	-	0.3082	112	
-	1.355	w	0.3211			
60$\bar{4}$	1.312	vw-	0.3435	0.3394	103	
-	1.305	vw	0.3476			
005 20$\bar{4}$ 064	1.288	m	0.3566	0.3575 0.3548 0.3555	51 115 64	
48$\bar{2}$	1.280	m	0.3613	0.3609		
282 600 NaCl(420)	1.275 1.258	m vst	0.3655 0.3746	0.3659 0.3679 0.3737	101	

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