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Figs. 1–3, December 1973

VARIATION IN CLAY MINERAL X-RAY DIFFRACTION RESULTS WITH THE QUANTITY OF SAMPLE MOUNTED[1]

PER R. STOKKE[2] and BOBB CARSON
Geological Survey of Norway, P. O. Box 3006, 7001 Trondheim, Norway and
Department of Geological Sciences, Lehigh University, Bethlehem, Pennsylvania 18015

Abstract: Two mounting techniques which employ settling of clay minerals through aqueous solutions, show variations in calculated clay mineral abundances which are directly related to the quantity of sample mounted. Hence, for different mounts of a single sediment sample, calculated values for montmorillonite (17 Å) range from 0–23%, while kaolinite (7 Å) and illite (10 Å) vary from 73–55% and 27–22%, respectively. The change in montmorillonite content is a real artifact of the quantity of sample mounted, whereas fluctuations in the kaolinite and illite values are the result of calculations in a closed number system and the variable montmorillonite concentration. Other mounting techniques, which do not depend upon particle settling, do not show this pattern.

It is suggested that two factors produce the observed effect. The small size of montmorillonite particles, and their resulting low settling velocities, result in a segregation of montmorillonite toward the top of the slide-mounted clay film and an enrichment of illite and kaolinite toward the bottom. For thick mountings, this pattern gives excessively high values for montmorillonite. For thinner mountings, the smaller size of montmorillonite particles (compared to illite and kaolinite) makes it impossible for this mineral to achieve a sufficient degree of preferred basal orientation at very low concentrations, and thus the montmorillonite concentration is underestimated.

Mounting techniques which employ gravitational settling of particles in suspension, give neither true nor consistent results. Therefore, such techniques should not be used.

INTRODUCTION

Several mounting techniques for quantitative clay mineral X-ray diffraction analysis have been developed in the past 30 years (Grim, 1934; Bradley, Grim, and Clark, 1937; Clark, Grim, and Bradley, 1937; Kinter and Diamond, 1956). Each technique has subsequently been used (Biscaye, 1965; Griffin, Windom and Goldberg, 1968; Knebel, Kelly, and Whetten, 1968; Duncan, Kulm, and Griggs, 1970) and evaluated or criticized (Kinter and Diamond, 1956; Kittrick, 1961; Gibbs, 1965; Fenner, 1966; Gibbs, 1968). In order to determine which of the most commonly employed techniques should be used for quantitative clay analysis, Gibbs (1965) examined seven of these procedures and concluded that those involving settling of clay particles in aqueous solutions cause mineral segregation and give erroneous results. Even after this study, however, such techniques were widely used. In 1968, therefore, Gibbs reiterated his 1965 findings and criticized continued use of these mounting methods. Nevertheless, this type of sample-preparation is still employed (Stoffers and Müller, 1972; Windom, Neal, and Kevin, 1971; Venkatarathnam and Ryan, 1971; Morton, 1972).

Perpetuation of techniques which employ gravitational settling is apparently based upon several tenets: the technique is a widely used one; the reproducibility is good, based upon results from closely grouped samples; and the patterns of clay mineral distribution, if not the actual percentages, indicated in studies using these techniques are correct and present a coherent picture. While the first statement above is undoubtedly true, the two latter arguments rest wholly upon the assumption that the relative percentages of clay mineral species are independent of the actual amount of clay sized material deposited on the slide.

In order to test whether a relationship exists between the actual quantity of the clay minerals mounted and the quantitative results of the X-ray diffraction analysis, a study of four common mounting techniques was performed,

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[2] Present Address: Department of Geological Sciences, Lehigh University, Bethlehem, Pennsylvania 18015.

two of which involved settling and two of which did not.

METHODS OF STUDY

Samples

Three different samples were used in this study. Two were samples from naturally occurring sediments, the third sample was an artificial mixture of selected standard clays, mixed with a matrix material to approximate the composition of naturally occurring clay fractions.

Sample A was taken from the lower continental slope off Washington, and originally occurred as a semi-consolidated mudstone. It is high in illite with intermediate amounts of kaolinite and lesser amounts of montmorillonite.

Sample B was taken from the lagoon-side beach of the barrier island at Stone Harbor, New Jersey. It is high in illite, intermediate in kaolinite and very low in montmorillonite.

Sample C is an artificial mixture of Wards Natural Science Establishment's standards, consisting of montmorillonite (WNSE #26), illite (WNSE #35), and kaolinite (WNSE #4). A matrix material (Alundum, abrasive grain) was mixed with the clay fraction such that the sample consisted of 35% clay minerals and 65% matrix material by weight. The matrix material which has no diffraction peaks in the region scanned for clay minerals, was added to bring the peak heights down to levels comparable to those encountered in the natural samples.

Sample preparation

The $< 2\ \mu$ fraction was obtained from samples A and B by dispersion, slaking, settling in distilled water and decantation. The settling times were determined using Stokes' law, and settling and decanting were repeated three times to obtain the complete $< 2\ \mu$ fraction. The rather dilute suspension obtained was allowed to concentrate by evaporation at room temperature. Sample C was obtained by separately preparing the different clays and the matrix material in the same way as samples A and B. The $< 2\ \mu$ fraction of each constituent was dried at 70° C, cooled in a desiccator and carefully weighed. These parts were then mixed with distilled water in the right proportions to a suspension of about the same concentration as those finally obtained from samples A and B.

A total of 72 slides were prepared from these samples. The four mounting techniques investigated are essentially the same as those described in Gibbs (1965): pipette on glass slide, centrifuge on ceramic tile, suction on ceramic tile, and smear on glass slide.

(a) Pipette on glass slide: Starting with the original suspension, a constant amount of thoroughly mixed sample was pipetted onto a preweighed glass slide. Part of the original suspension was then diluted with distilled water and the same amount was, after thorough mixing, pipetted onto another glass slide. Series of increasingly dilute samples were prepared and the slides were dried at room conditions for about 20 hours. Then the slides were weighed and the amount of clay per cm^2 was calculated.

(b) Centrifuge on ceramic tile: The same procedure was used in varying the concentration of the suspensions for mounting on ceramic tiles. The tiles were placed in a holder in and above the base of centrifuge cups. The suspension was poured on top of the tiles in a small well in the holder. By centrifuging at 2,000 rpm for about 10 minutes, the fluid was forced through the tiles down to the bottom of the centrifuge cups, leaving a smooth clay film on the tile. The tiles were dried at 50° C, cooled in a desiccator and weighed. The amount of clay per cm^2 was calculated.

(c) Suction on ceramic tile: Again the dilution procedure gave suspensions of different concentrations. The suspensions were pipetted onto the tiles at about 1 cm depth and the liquid was drawn through the tile by a vacuum, leaving a smooth clay film on the tile. The tiles then were dried at 50° C, cooled in a desiccator and weighed. The amount of clay per cm^2 was calculated.

(d) Smear on glass slide: A portion of the suspension was allowed to evaporate, at room conditions, to a thick paste. The paste was spread across the slide with a standard laboratory spatula. The amount of clay per cm^2 was controlled by the amount originally transferred to the slide.

All slides were glycolated before X-ray analysis according to the method of Brunton (1955).

X-radiation procedure

The samples were X-rayed on a standard Norelco wide angle X-ray diffractometer with geiger counter, using nickel filtered copper K_α radiation at 40 kV and 20mA. Scanning speed was ½° 2θ per minute and chart speed was ½ inch per minute providing 1° 2θ per inch printout for all samples. A constant area of the sample was exposed to the X-ray beam and the scaler of the rate-meter was set to maximize the record of the diffracted beam.

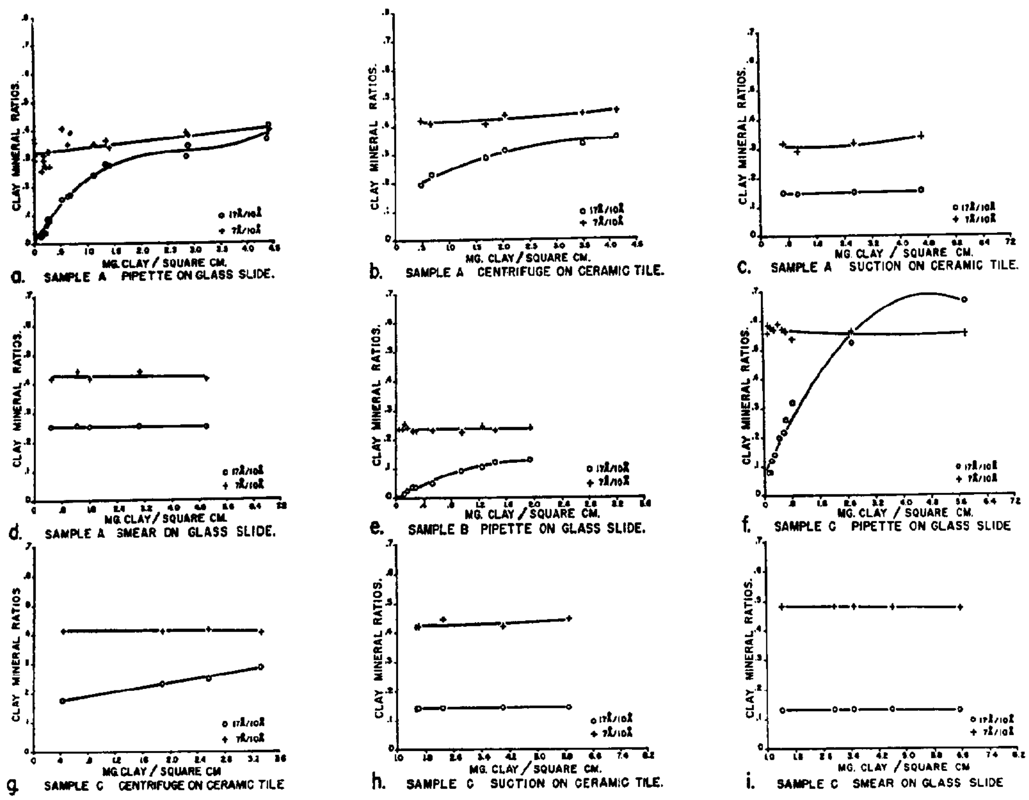

FIG. 1.—17Å/10Å (percentage of montmorillonite relative to illite), and 7Å/10Å (percentage of kaolinite relative to illite) versus mg clay per cm^2 on the slide surface.

Quantitative determination of relative clay mineral concentrations

A polar planimeter was used to measure peak areas. Measurements were made of the 17Å peak (montmorillonite), the 10Å peak (illite), and the 7Å peak (kaolinite). For some samples, the 3.35Å and 3.58Å (illite and kaolinite) peaks were also measured. The semi-quantitative technique of Biscaye (1965) was used for all samples to convert the peak areas to concentrations of clay minerals. Additionally, for some samples calculations were also made using the method of Griffin and Goldberg (1963). The results were different but the effect examined was the same using both methods. Only the results utilizing Biscaye's (1965) method are presented here.

RESULTS

The results of the quantitative X-ray diffraction analysis for all samples are shown in Tables 1, 2, and 3. The variation in percentages of montmorillonite, illite and kaolinite with varying clay concentrations were examined by computing the ratio 17Å/10Å (percentage of montmorillonite relative to illite), and the ratio 7Å/10Å (percentage of kaolinite relative to illite) versus mg clay per cm$_2$ on the slide surface. This was done for each of the three samples and for the different mounting techniques used on each sample. The results are shown in Figure 1.

Pipette on glass slide

The montmorillonite/illite ratio increases sharply with increasing on-slide concentration of clay minerals, while the kaolinite-illite ratio remains fairly constant for all concentrations. This is the case for all three samples (A, B, and C, Fig. 1a, e, and f). It is apparent for sample A (Table 1) that this pattern is due to the variation of montmorillonite from 0% at low clay concentrations to 23% at higher concentrations. Illite and kaolinite also change, but only

TABLE 1.—*Peak areas, clay percentages calculated and mg clay/cm²*

Technique	Slide no.	mg clay / cm² slide	Peak area 17Å	Peak area 10Å	Peak area 7Å	% Clay calculated 17Å	% Clay calculated 10Å	% Clay calculated 7Å
Pipette on glass	A-1	4.420	320	196	158	23	55	22
	A-2	4.378	335	227	180	21	57	22
	A-3	2.882	209	156	119	20	58	22
	A-4	2.844	200	162	130	18	59	23
	A-5	1.400	120	110	76	17	62	21
	A-6	1.330	120	110	80	17	61	22
	A-7	1.111	250	264	187	15	63	22
	A-8	0.677	71	106	81	11	64	25
	A-9	0.626	82	113	80	11	66	23
	A-10	0.524	80	127	104	10	64	26
	A-11	0.297	41	125	68	6	74	20
	A-12	0.273	40	107	68	6	71	23
	A-13	0.255	40	126	81	6	71	23
	A-14	0.234	31	120	64	5	75	20
	A-15	0.193	33	183	101	3	76	21
	A-16	0.172	14	92	57	3	74	23
	A-17	0.164	17	93	53	3	75	22
	A-18	0.139	21	174	90	2	78	20
	A-19	0.008	17	97	62	3	74	23
	A-20	0.008	16	109	63	3	75	22
	A-21	0.004	5	64	46	1	73	26
	A-22	0.004	0	67	50	0	73	27
Centrifuge on ceramic	A-23	4.124	250	178	160	20	55	25
	A-24	3.484	203	148	130	19	56	25
	A-25	2.038	155	120	103	18	57	25
	A-26	1.677	135	112	90	17	59	24
	A-27	0.666	99	105	87	14	61	25
	A-28	0.472	76	95	80	12	62	26
Suction on ceramic	A-29	4.628	155	150	129	15	59	26
	A-30	2.697	138	134	112	15	60	25
	A-31	1.062	172	169	135	15	61	24
	A-32	0.655	67	65	53	15	60	25
Smear on glass	A-33	4.997	139	135	109	15	60	25
	A-34	3.040	150	145	125	15	59	26
	A-35	1.589	139	135	110	15	60	25
	A-36	1.232	194	195	170	15	59	26
	A-37	0.478	188	180	150	15	60	25

to adjust to the changing values of montmorillonite since the kaolinite/illite ratio is fairly constant. In sample B (Table 2) the montmorillonite ranges from 0% at very low clay concentrations to 10% at higher concentrations. In sample C (Table 3), montmorillonite varies from 5% to 30% without any influence on the 7Å/10Å (kaolinite/illite) ratio. Figure 2 illustrates the change in X-ray patterns, and particularly the loss of the 17Å (montmorillonite) peak as one progresses from very high to very low concentrations of clay minerals on the glass slides.

TABLE 2.—*Peak areas, clay percentages calculated and mg clay/cm²*

Technique	Slide no.	mg clay / cm² slide	Peak area 17Å	Peak area 10Å	Peak area 7Å	% Clay calculated 17Å	% Clay calculated 10Å	% Clay calculated 7Å
Pipette on glass	B-1	1.931	102	195	95	10	73	17
	B-2	1.441	90	188	88	9	74	17
	B-3	1.248	82	196	95	8	74	18
	B-4	0.949	50	145	65	7	76	17
	B-5	0.532	25	115	55	4	78	18
	B-6	0.286	16	110	51	3	79	18
	B-7	0.242	17	110	50	3	79	18
	B-8	0.173	9	100	47	2	79	19
	B-9	0.128	3	77	35	1	79	20
	B-10	0.105	0	67	31	0	81	19
	B-11	0.048	0	42	20	0	81	19

Centrifuge on ceramic tile

This mounting technique was used for samples A and C. The variations in the 17Å/10Å (montmorillonite/illite) and 7Å/10Å (kaolinite/illite) ratios are similar to those observed for the pipette on glass slide technique (Fig. 1b and g). In sample A (Fig. 1b) the variations

TABLE 3.—*Peak areas, clay percentages calculated and mg clay/cm²*

Technique	Slide no.	mg clay / cm² slide	Peak area 17Å	Peak area 10Å	Peak area 7Å	% Clay calculated 17Å	% Clay calculated 10Å	% Clay calculated 7Å
Pipette on glass	C-1	5.835	160	60	65	30	45	25
	C-2	2.551	245	120	134	25	48	27
	C-3	0.841	75	60	63	17	54	29
	C-4	0.648	50	50	57	14	55	31
	C-5	0.580	42	50	57	12	56	32
	C-6	0.445	39	49	55	11	56	33
	C-7	0.310	22	40	45	8	58	33
	C-8	0.227	19	38	44	7	59	34
	C-9	0.146	12	38	43	5	60	35
	C-10	0.131	11	36	40	5	61	34
Centrifuge on ceramic	C-11	3.330	135	122	99	17	59	24
	C-12	2.554	110	108	90	15	60	25
	C-13	1.876	57	64	53	14	61	25
	C-14	0.425	80	120	100	11	63	26
Suction on ceramic	C-15	5.920	74	130	110	9	63	28
	C-16	4.033	120	207	170	9	64	27
	C-17	2.310	110	183	159	9	63	28
	C-18	1.627	90	157	130	9	64	27
	C-19	1.577	83	145	130	9	64	27
Smear on glass	C-20	1.441	72	134	131	8	62	30
	C-21	2.933	87	160	158	8	62	30
	C-22	3.488	91	182	176	8	62	30
	C-23	4.590	100	185	177	8	62	30
	C-24	6.551	102	192	182	8	62	30

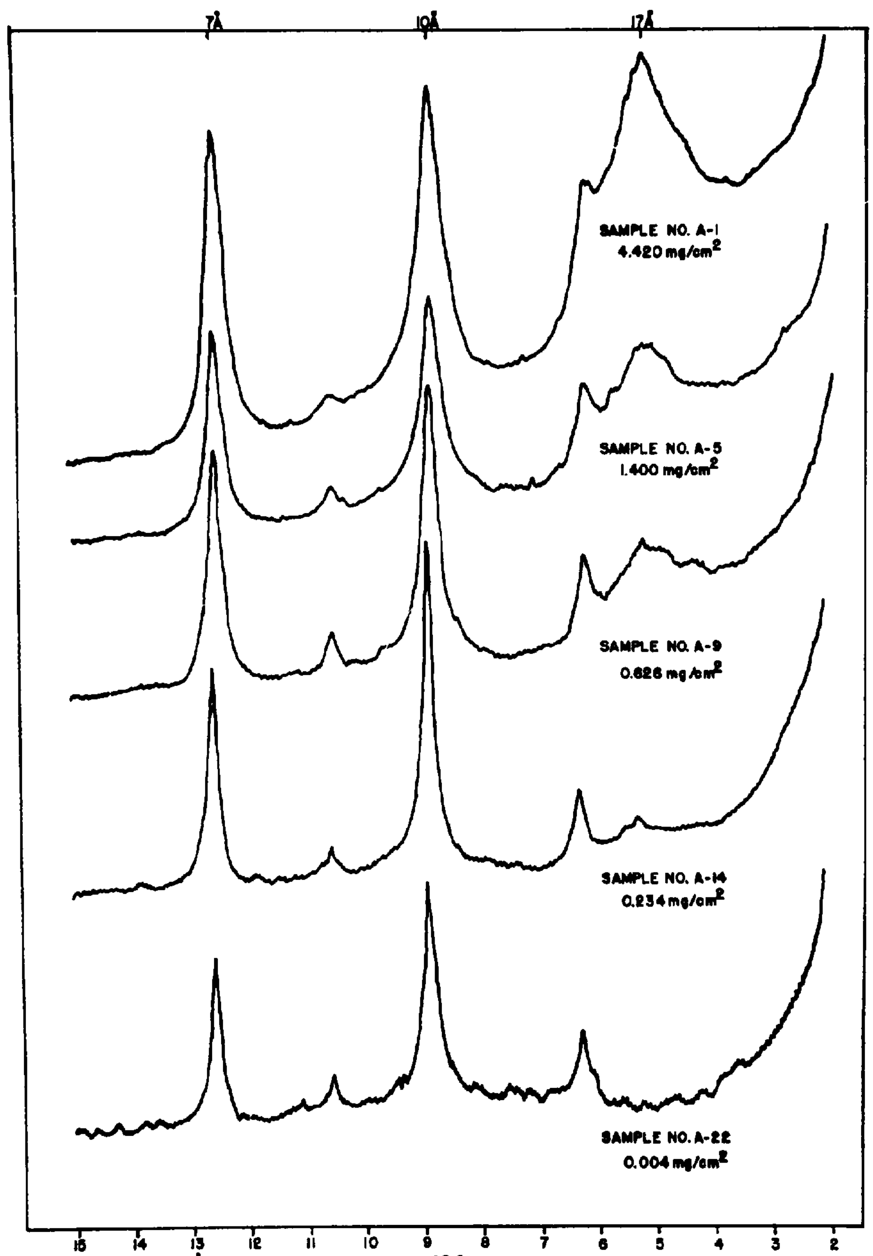

FIG. 2.—X-ray diffraction patterns from sample A, pipette on glass slide technique, with decreasing concentration of clay on the slide surface.

are of very nearly the same magnitude as in the glass slide procedure, but sample C (Fig. 1g), the effect does not seem as pronounced for similar on-slide concentrations. Tables 1 and 3 show the actual montmorillonite (17Å), illite (10Å), and kaolinite (7Å) determinations for samples A and C using the centrifuge on ceramic tile technique.

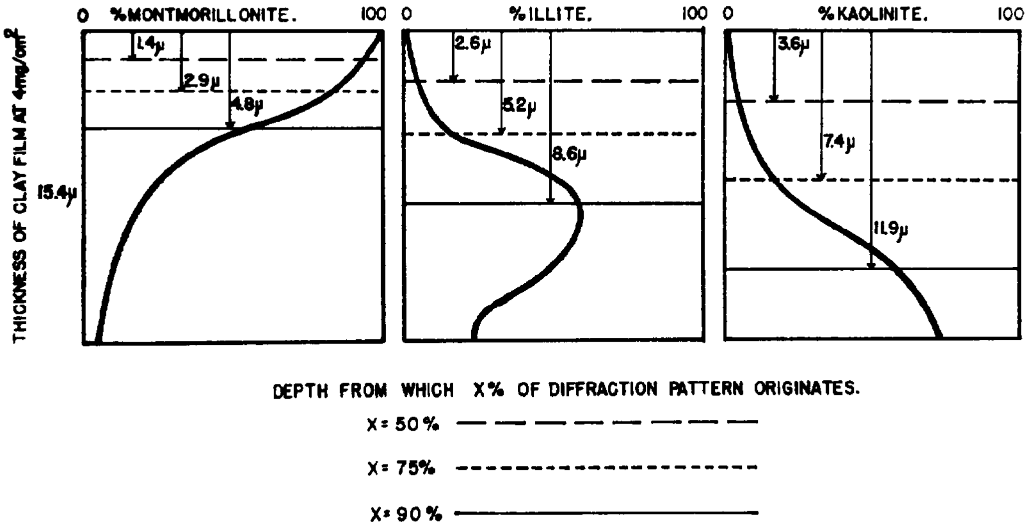

FIG. 3.—Inferred distribution of montmorillonite, illite and kaolinite in a clay film of thickness 15.4 μ made by settling through an aqueous solution, and depth of X-ray penetration for each mineral at 5.2°, 8.9°, and 12.6° 2θ respectively. After Gibbs (1965) and Grim (1968).

Suction on ceramic tile and smear on glass slide

The previous techniques both involved settling of clay particles in a liquid media. The suction on ceramic tile and smear on glass slide techniques should both exclude any particle segregation upon settling, provided the vacuum used in the suction technique is sufficient so that the liquid portion of the suspension is sucked through the tile before any differentiation of the clay particles can occur. As shown in Figure 1c, d, h, and i, these techniques show very consistent results with little or no varition in the individual clay mineral contents with varying quantities of sample mounted.

DISCUSSION

According to Gibbs (1965), the structure of the on-slide clay film formed by settling of clay particles from suspension consists of an upper portion enriched in montmorillonite (17Å), and a lower portion in which illite (10Å) and kaolinite (7Å) are the dominant species (Fig. 3). This configuration results from the fact that the montmorillonite particles are significantly smaller (Grim, 1965) than the other clay mineral types. Hence, the settling velocity of montmorillonite (17Å) is lower than that of illite (10Å) or kaolinite (7Å).

The depth from which 50%, 75%, and 90% of the diffraction pattern for montmorillonite, illite, and kaolinite originates is calculated by Gibbs (1965), and diagrammed in Figure 3; the calculated depths are shown in Table 4.

Assuming an average density of 2.6 g/cm^3 for the clay film, the thickness of this film corresponding to the different on-slide concentrations can be calculated. The results are tabulated in Table 5. Comparison of Tables 4 and 5 clearly demonstrates that with a thick clay film, the diffraction pattern originates from the upper part of the film which is greatly enriched in montmorillonite and depleted in illite and kaolinite. As the on-slide concentration decreases, the thickness of the film decreases, and the diffraction pattern originates from a greater portion of the total film thickness. Thus, even if the structure of the clay film is the same, the observed montmorillonite content will decrease as compared to illite and kaolinite. This model accounts for the observed effect down to a certain minimum concentration, or minimum film thickness. At an on-slide concentration of between 1 and 2 mg/cm^2 (film thickness of 3.9 μ–7.7 μ) the diffraction pattern could be expected to originate from the total

TABLE 4.—*Depth from which 50, 75, and 90% of diffraction pattern originates. After Gibbs (1965)*

	50%	75%	90%
Montmorillonite	1.4μ	2.9μ	4.8μ
Illite	2.6μ	5.2μ	8.6μ
Kaolinite	3.6μ	7.4μ	11.9μ

TABLE 5.—*Calculated thickness of clay film with on slide concentration of clay minerals. Average density of clay film set to 2.6 g/cm³*

On-Slide Concentration of clay minerals:	0.004 mg/cm²	0.1 mg/cm²	0.5 mg/cm²	1 mg/cm²	5 mg/cm²	10 mg/cm²
Thickness of clay film:	0.02μ	0.4μ	1.9μ	3.9μ	19.2μ	38.5μ

thickness of the clay film. At, or below, these film thicknesses, then, it might be anticipated that accurate determinations of clay mineral content would be obtained. However, it is observed that with further decreases in on-slide concentration the effect of decreasing montmorillonite as compared to illite and kaolinite continues unabated. Indeed, montmorillonite disappears when the concentration is reduced to 0.004 mg/cm² in sample A. It is suggested that the explanation of this pattern is to be sought in the orientation of the different mineral particles in the clay film. Since it is the basal diffractions from montmorillonite, illite and kaolinite that are recorded, it is essential that the three types of mineral particles achieve the same order of preferred orientation. One should expect, however, that particles with the shape of large plates should end up on their basal orientation more often than particles with the shape of small plates. In a very thick clay film this might not be the case since small and large particles interfere with each other and disturb the perfect basal orientation to approximately the same extent for all types of mineral particles. But when the on-slide concentration approaches 0.004 mg/cm² and the thickness of the film is reduced to approximately 0.02 μ, the minerals occur as single particles on the glass slide. In this situation the larger particles can more easily achieve a basal orientation while the smaller particles (of montmorillonite) are more randomly oriented (perhaps filling interstices between the larger particles and are shielded from the X-ray beam at the low angles), and therefore, do not give a well-defined diffraction pattern.

CONCLUSION

Examination of four common mounting techniques for quantitative clay mineral X-ray diffraction analysis shows that those which require gravitational settling of particles from suspension give variable results, depending upon the quantity of sample deposited on the slide. The calculated montmorillonite (17Å) content decreases as the quantity of total mounted sample decreases. Illite (10Å) and kaolinite (7Å) both increase concomitantly, although at equal rates. The results of quantitative clay mineral analyses which utilize these mounting techniques are clearly suspect, particularly if the concentration of the mounting suspension or quantity (mg/cm²) of the mounted sample are not carefully monitored. In contrast, the two mounting techniques (suction on ceramic tile and smear on glass slide) which do not employ particle settling, show no variation with the quantity of sample mounted. These techniques should be used to the exclusion of those which require settling of particles from suspension.

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