SHORT TITLE

MASTER

EXTRACTABLE POTASSIUM IN ILLITE

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COMPLETE TITLE

EXTRACTABLE POTASSIUM IN GRUNDITE ILLITE:

II. EFFECTS OF PARTICLE SIZE AND GRINDING

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TABLE 1

Comparison of size-fractions separated from Grondite illite samples that were dispersed in water by mechanical agitation

Size- fraction (μ)	Total K (me/100g)	Extractable K			Total C (%)	Total N (ppm)
		NH ₄ OAC (me/100g)	NaTPB ^{1/}			
			(me/100g)	(%)		
Original	102	2.9	67.8	67	1.3	896
<50	103	2.9	70.4	68	0.9	854
<20	108	2.6	68.7	64	0.7	896
<10	110	2.2	70.0	64	0.7	896
< 2	123	3.8	81.4	66	0.6	1022
<0.2	133	3.6	68.2	51	0.7	1035
10-20	80.5	1.0	52.9	66	1.0	938
0.2-2	126	2.9	84.2	67	0.6	1035

^{1/} Maximum extractable

TABLE 2

K extracted from <2 μ illite samples by various chemical treatments and subsequent contact with NaTPB solutions

Chemical pretreatment ^{1/}	K extracted (me/100g)		
	Pre-treatment	NaTPB ^{2/}	Total
None	--	81.4	81.4
1N NaCl	4.8	72.1	76.9
H ₂ O ₂ (repeated)	5.4	68.1	73.5
NaOBr	5.6	68.2	73.8
Sodium citrate-dithionite	3.4	72.8	76.2
Sodium citrate-dithionite - H ₂ O ₂	6.6	69.3	75.9
Boiling 2% Na ₂ CO ₃	4.4	73.0	77.4
Boiling 0.5N NaOH	5.4	71.0	76.4
1N Citric acid	5.7	70.0	75.7
1N Oxalic acid	6.3	68.5	74.8
Boiling 1N Sodium citrate (repeated)	11.6	61.7	73.3
1N HCl	6.3	69.6	75.9
Boiling 6N HCl	121	2.1	123

^{1/} 0.5 g sample in 20 ml solutions, then leached with 1N NaCl

^{2/} Maximum extractable

TABLE 3

Comparison of size-fractions separated from Grundite illite samples that were dispersed by chemical treatments

Size-fraction (μ)	Total K (me/100g)	Extractable K			Total C (%)	Total N (ppm)
		NH ₄ OAC (me/100g)	NaTPB ^{1/} (me/100g)	(%)		
<10	108	1.6	70.6	65	0.3	770
< 2	119	2.8	77.0	65	0.2	832
2-10	53.8	0.6	35.1	65	0.7	476
0.2-2	102	2.0	82.2	81	0.2	882
0.08-0.2	132	3.5	98.6	75	0.2	1035
<0.08	128	4.3	61.4	48	0.2	980

^{1/} Maximum extractable

TABLE 4

Effect of wet-grinding <2 μ illite samples in NaCl or NaTPB solutions on the amount of nonextractable K and nonoxidizable N in the mineral

Grinding-Solution Treatment	K extracted		Non-extractable K (me/100g)	Non-oxidizable ^{2/} N (ppm)
	NaCl (me/100g)	NaTPB ^{1/} (me/100g)		
None	4.8	72.1	46.1	798
Pica mill-NaCl 1 hour	4.4	74.0	44.6	---
Agate mortar-NaCl 96 hours	5.5	71.5	46.0	---
Ultrasonic-NaCl 4 hours	8.9	68.1	46.0	719
24 hours	14.4	62.9	45.7	689
72 hours	19.5	57.6	45.9	708
Ultrasonic-NaTPB 4 hours	--	89.9	33.1	378
24 hours	--	109	14.0	224
72 hours	--	121	2.0	84

^{1/} Maximum extractable

^{2/} By NaOBr

TABLE 5

Effect of dry-grinding <2 μ illite samples on the amount of non-extractable K and nonoxidizable N in the mineral

Grinding Treatment	K extracted		Non-extractable K (me/100g)	Non-oxidizable ^{2/} N (ppm)
	NaCl (me/100g)	NaTPB ^{1/} (me/100g)		
None	4.8	72.1	46.1	798
Pica mill				
1 minute	6.3	74.6	42.1	---
10 minutes	19.6	71.0	32.4	---
60 minutes	44.9	57.7	20.4	---
Agate mortar				
6 hours	13.2	72.7	37.1	672
12 hours	17.3	72.1	33.6	602
24 hours	28.6	69.5	24.9	504
Agate mortar-quartz added				
4 hours	44.9	60.9	17.2	379
6 hours	53.5	60.0	9.5	244
8 hours	55.6	59.4	8.0	203

^{1/} Maximum extractable

^{2/} By NaOBr

FOOTNOTE

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FIGURE LEGENDS

- Fig. 1. K extracted from original and mechanically dispersed <20 , <2 , $10-20$, $0.2-2$, and $<0.2\mu$ fractions of Grundite illite that were placed in NaTPB solution for different periods.
- Fig. 2. K extracted from chemically dispersed $2-10$, $0.2-2$, $0.08-0.2$, and $<0.08\mu$ fractions of Grundite illite that were placed in NaTPB solution for different periods.
- Fig. 3. Extractable K and nonoxidizable N in samples of the original illite that were ground with quartz for different periods in an agate mortar.

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When solutions containing NaTPB failed to remove 32 percent of the K in a $<20\mu$ fraction of Grundite illite even though they extracted essentially all the K in $<50\mu$ biotite and muscovite samples, a detailed study of factors that might be responsible for the limited exchange of K in illite was initiated (15). With a $<2\mu$ Grundite illite fraction, various modifications in the NaTPB extraction procedure were made, but no more than 66 percent of the K in the mineral was replaced. As a result, attention was shifted from the extraction procedure to various characteristics of the illite sample that might affect the exchange of K. Reported here are the effects that have been observed in relation to the size of the illite particles.

The possibility that particle size might affect the exchangeability of interlayer K in illite seemed to be ruled out by some earlier determinations of NaTPB-extractable K in $<20\mu$ and $<2\mu$ fractions of Grundite illite (12). Subsequent comparisons of the maximum exchangeable K in other size-fractions of this illite and in ground mica samples, however, have made it clear that particle size can be one of the main factors governing the release of interlayer K (11). With dry-ground mica samples, variations in the mechanism, rate and degree of interlayer K exchange were observed when the mica particles were reduced in size to 5μ or less. Thus, similar effects of particle size can be anticipated with illites. Obviously, the absence of such effects in earlier illite experi-

ments needs to be explained, but even more important is the need for information about the specific nature of the particle-size effects prevailing in the fine-grained micaceous minerals that abound in nature. To obtain such information, various fractions of Grundite illite were studied in greater detail.

The incomplete exchange of K that occurred when small particles of ground mica were placed in NaTPB solutions (11) cannot be attributed to the extraction procedure because similar limitations in K exchange have been observed with small particles treated with dodecylammonium chloride at 70°C (8) and with BaCl₂ in an autoclave (10). However, the grinding required to prepare small mica particles could have caused alterations in the mineral or the particle edges and thereby been involved. The uncertain effects of grinding can be avoided by using size-fractions of naturally occurring, fine-grained, micaceous minerals, but the isolation of particles with a discrete size is still a problem. Chemical treatments were used in the separation of the Grundite size-fractions that were compared with dry-ground micas (11), but the effects of the chemical treatments on the exchangeability of interlayer K were not accounted for. Thus, in this investigation of illite particle-size effects, the changes in K exchangeability induced by both dispersive and grinding treatments were determined.

MATERIALS AND METHODS

Grundite illite was obtained from the Illinois Clay Products Company and dispersed by mechanical agitation in water or by chemical treatments. Details regarding these dispersive treatments are given with the relevant experiments. In either event, various size-fractions were separated by sedimentation and centrifugation, air-dried and then crushed in a porcelain mortar to pass a 60-mesh screen. Since fractions with the same size-limit designations were separated from illite samples receiving different dispersive treatments, the terms mechanically dispersed and chemically dispersed will be used to distinguish between them. The unfractionated illite will be referred to as the original material. Some illite samples were also ground before they were used. The various grinding procedures employed and the subsequent treatment of these samples are described with the experiments.

NH_4 -exchangeable and total K values were determined for each illite sample by leaching with neutral normal NH_4OAC and HF fusion, respectively. The general procedure of extracting K with solutions containing NaTPB was the same as that used previously with illite (11, 15). The amounts of K extracted by various contact periods with NaTPB solution were determined, but often only the maximum amounts of NaTPB-extractable K are reported. Total N determinations were made by a semimicro-Kjeldahl procedure (2). An HF

pretreatment was used with some of the N determinations, but proved not necessary. The accessibility of nitrogenous compounds in the samples to oxidation was determined with a hypobromite procedure similar to that described by Bremner (3), but with Na reagents in place of K reagents. Total C determinations were made by the dry combustion method described by Allison et al. (1).

RESULTS AND DISCUSSION

Mechanically Dispersed Size-Fractions

Table 1

Portions of the original illite were dispersed in distilled water by mechanical agitation (shaking) and fractionated without further treatment to minimize chemical or physical alterations in the mineral. Various characteristics of these size-fractions and of the original illite are given in Table 1. The total and NH_4 -exchangeable K values tend to be greater for the fractions with smaller upper size limits. Part of the differences in total K can be attributed to the presence of more quartz in the coarser fractions (verified by x-ray diffraction analysis), but the combination of total and NH_4 -exchangeable K data suggests that some fractionation of the micaceous mineral particles was achieved by this method of subdividing the illite. On the other hand, the mechanically dispersed fractions were surprisingly alike when their C, N and maximum exchangeable K contents were determined.

Differences in the amounts of NaTPB-extractable K were

observed, as might be expected from the differences in total K. Except for the $<0.2\mu$ fraction, however, the portion of the total K extractable from each sample was always close to 66 percent. Only the $<0.2\mu$ fraction, with 51 percent extractable K, gave any indication that there might be an effect of particle size on K exchange.

Figure 1

Since the mechanically dispersed illite fractions released comparable portions of their K, they were further compared by a determination of how they released their K as a function of time in NaTPB solutions (Fig. 1). The K release curves for all but the $<0.2\mu$ fraction were so alike only a band encompassing several of them has been shown. On the other hand, the $<0.2\mu$ curve was distinctive in that it emphasized the lower degree of exchange achieved with this one fraction. In terms of the rate with which the fractions were K depleted, however, even the $<0.2\mu$ fraction was comparable to the others. Most of the extractable K was replaced in 1 day, and the extraction was completed in seven days. Thus, these experiments with mechanically dispersed size-fractions confirmed earlier observations (12) that such fractions fail to provide much information about the effects of particle size on K exchange in illites.

Perhaps no particle-size effects were observed with the mechanically dispersed illite fractions because this means of subdividing the illite failed to break up aggregates in the sample.

Electron micrographs of the illite have shown that such aggregates can exist (7, 13), and their presence in the fractions employed in these experiments is supported by the presence of uniform amounts of C and N and by the observation of deviations in K exchange behavior in only the finest ($<0.2\mu$) fraction. To the degree that the agitation of illite in water did not disperse the material, the fractions would not provide a comparison of individual particle sizes and the results would not be indicative of the effects of particle size on illite K release. Nevertheless, these results have considerable value, because they emphasize the difficulties encountered in determinations of particle-size effects in naturally fine-grained minerals and they show that part of the K in illite particles is nonexchangeable even when there has been no grinding or chance of mineral alterations from chemical pre-treatments. Moreover, the uniformity of the values for the degree of K exchange shows the various illite aggregates must contain combinations of particle sizes that are comparable enough to obscure any effects the size of individual particles might have.

Chemically Dispersed Size-Fractions

Past experiments with chemically dispersed samples of Grundite illite have shown that this illite can be subdivided into fractions that differ in K release behavior (11). The interpretation of these results in terms of particle-size effects, however, is complicated by the possibility of side effects from

the chemical treatments. With illite, such treatments could produce uncertain effects through the removal of particle coatings, the dissolution or alteration of the mineral, etc. Thus, to isolate the effects of illite particle size, it was necessary to determine the extent to which the dispersive treatments are involved.

The procedure used in the dispersion of illite samples for earlier experiments (11) involved the sequential hydrogen peroxide, sodium citrate-dithionite and sodium carbonate treatments described by Jackson (4) and left each illite fraction in a Na-saturated state. Therefore, these and other treatments for the removal of organic or oxide coatings, the separation of particles, etc. were tested for their effect on the exchangeability of K in the illite. To do so, samples of the mechanically dispersed $<2\mu$ illite material described in Table 1 were subjected to the various treatments, leached with 1N NaCl to remove any K released by the treatment and to Na saturate the samples, and then degraded in NaTPB solutions. To delineate the effect the Na-saturated state might have on the extraction of K by NaTPB solutions, some $<2\mu$ illite samples were given no treatment, while others were only leached with NaCl before they were exposed to NaTPB. The amounts of K extracted by the chemical pretreatments and by the subsequent NaTPB treatments are given in Table 2.

Table 2

The boiling 6N HCl pretreatment released nearly all the K from the illite, but much of the mineral was destroyed in the process. Otherwise, the various chemical treatments did not alter the exchangeability of the K in this illite appreciably from that observed with NaCl-leached samples. By itself, the NaCl-leaching treatment extracted about 5 me K/100g and reduced the total extractable K to about 77 me/100g. Evidently, the saturation of illite samples with Na reduces the NaTPB-extractable K to a greater degree than can be accounted for by the K extracted during the saturation treatment and must be considered in the evaluation of the effects of other chemical pretreatments. Some variations in the NaCl-extracted K were induced by the various pretreatments, especially the successive use of boiling sodium citrate, but corresponding changes in the amount of K extracted by the subsequent NaTPB treatments kept the total extractable K relatively constant. Thus, we concluded that any organic materials or oxides that are removed by such chemical treatments cannot be responsible for the limited exchangeability of K in this illite. Moreover, the absence of any major change in the exchangeability of K in the illite samples subjected to these chemical treatments means such treatments can be used to disperse illite samples for further studies of particle-size effects.

Chemically dispersed size-fractions of Gründite illite were prepared by treating samples of the original illite with NaOAC

buffer (pH 5), H_2O_2 , sodium citrate-dithionite-bicarbonate, and boiling Na_2CO_3 solutions as described by Jackson (4) and then separating $<10\mu$, $<2\mu$, $0.2-2\mu$, $0.08-0.2\mu$, and $<0.08\mu$ particles by sedimentation and centrifugation. This procedure must have achieved a better separation of the illite particles, because the yield of fine fractions was much greater than when the illite was only agitated in water. In doing so, as shown in Table 3, most of the C in the illite was removed, but the N content was reduced surprisingly little. Moreover, this procedure must have caused little change in the exchangeability of K in the mineral, because the values for the percentage extractable K reported in Tables 1 and 3 for the $<2\mu$ and $<10\mu$ fractions are nearly the same. Still, the data in Table 3 show that this means of subdividing the illite made it possible to see that there is an effect of particle-size on the exchange of K in this illite. The magnitude of this effect is emphasized by less than half the K in the finest fraction being exchangeable.

As with ground micas (11), the maximum degree of K exchange in the clay-size fractions increased as the illite particle size increased. The presence of more feldspars in the coarser fractions, however, modified the magnitude of this increase in the percentage extractable K and led to a decrease when the particle size exceeded 2μ . By using the selective dissolution method of Kiely and Jackson (6), it was estimated that the $0.2-2\mu$ and $2-10\mu$ fractions contained 4 and 11 mg feldspar-K per 100g, respectively. If an adjustment

Table 3

for the nonexchangeable K of the feldspar in the 2-10 μ fraction is made, the percentage extractable K value for just the illite particles would be 82%. This is still much less exchange than was observed with ground mica particles of this size. Since the level of exchange in the 2-10 μ fraction was comparable to that observed with the <2 μ and <10 μ fractions or even the mechanically dispersed samples (Table 1), it is probable that some aggregates of small illite particles resisted dispersion, were included in the 2-10 μ separation, and accounted for the absence of the higher degrees of exchange anticipated.

Figure 2

The K-extraction curves for the chemically dispersed illite fractions (Fig. 2) show the effects of particle size on the K-exchange behavior of this mineral are not confined to the maximum degree of exchange. In general, the rate of K release increased as the particle size decreased. But, for some unknown reason, the finest fraction did not exhibit the highest rate of K release. A similar observation has been made with a fine clay fraction of Marshall soil that was only mechanically dispersed in water (14). Thus, this distinctive behavior of the very fine illite particles does not seem to be due to the chemical treatments employed in the separation of the fraction. The fine illite fractions are also distinctive in that they differ from similar ground-mica samples in having a much smaller portion of their K released during the initial layer-weathering phase. Obviously, there are many details about the exchange of K in illite particles that still need to be resolved.

Ground Samples

Since the effect of grinding mica particles to smaller size was known to be one of making more of the interlayer K nonexchangeable (11), there seemed little hope that the illite particles could be ground to overcome the limited K release they already exhibited. Nevertheless, illite samples were ground in various ways to determine what effects such treatments do have on aggregated and naturally fine-grained materials and to develop the possibility of a relationship existing between the N content and K-release properties of this mineral. As shown in Table 3, the illite samples retained most of their N when they were treated with H_2O_2 and even the finest size-fraction contained appreciable amounts of N. If the N compounds escape oxidation by being located in physically inaccessible interlayer positions, they could interfere with the exchange of interlayer K.

Portions of the <2 μ mechanically dispersed fraction described in Table 1 were ground by various wet and dry procedures. The wet grinding was conducted with separate 0.5 g samples in 10 ml 1N NaCl -- the dry grinding with larger samples of air-dry material that were subsequently divided for the various determinations. In either event, 0.5g samples of the ground material were washed with a total of 20 ml 1N NaCl to extract any K exposed by the grinding and to prepare Na-saturated samples that were subsequently analyzed

for NaTPB-extractable K and NaOBr-oxidizable N. In addition, samples of the original $<2\mu$ illite were degraded in NaTPB solutions while they were subjected to ultrasonics for periods comparable to those used with NaCl. The ultrasonic treatments were carried out with a Measuring and Scientific ultrasonic probe (20 kc., 60 watt) and stirred, water-cooled illite suspensions.

Table 4

A summary of the results obtained with selected wet-grinding procedures is given in Table 4. The NaCl-extractable K values provide a measure of the exposed K in each sample and thus of the degree of particle diminution achieved. With the pica mill, agate mortar and similar unreported treatments, little particle grinding occurred and the nonextractable K remained relatively unaltered. Ultrasonics did alter the illite samples in NaCl, increasing the NaCl-extractable K by 14.7 me per 100g in 3 days. However, the non-extractable K and nonoxidizable N contents of these samples were little affected -- showing the ultrasonic treatment of illite in NaCl only exposed K that was already extractable with NaTPB. Possibly, the effect of this ultrasonic treatment was largely limited to a disruption of the aggregates. At least, none of the wet-grinding procedures provided enough fracturing of illite particles to produce a significant change in the limited K-release behavior of the mineral. On the other hand, by using ultrasonics with illite samples in NaTPB solutions, progressively more of the K and N in the mineral was rendered exchangeable and oxidizable, respectively.

This effect of the ultrasonic-NaTPB treatment supports the idea that some relationship between the nonextractable K and nonoxidizable N in the illite exists, but the extent to which this effect was achieved by grinding individual particles is not known. As reported earlier (15), the extraction of essentially all the K in illite by this procedure does not cause appreciable destruction of the mineral structure. Thus, the increase in oxidizable N in illite samples receiving the ultrasonic-NaTPB treatment is more likely due to more of the interlayer K being replaced and an exposure of interlayer N compounds by the expansion of the mineral.

Table 5 The data in Table 5 are indicative of the effects of dry grinding observed with several procedures. While most of the procedures were effective in exposing more illite K to exchange, the rate and degree of grinding varied as might be expected from the results others (5, 9) have obtained with micas in ball mills. With the pica mill, grinding increased the NaCl-extractable K quickly, but temperatures greater than 200°C developed and the sample became progressively diluted with material from the container and balls of the grinder. With the agate mortar, high temperatures and sample dilutions were not a problem, but the illite did not undergo much grinding. On the other hand, just a few hours of grinding in the agate mortar was enough to increase the NaCl-extractable K by more than 50 me/100g if the illite were mixed with an equal amount

of 60-mesh quartz. Moreover, the decrease in nonextractable K and nonoxidizable N, observed with all dry-grinding procedures, was greatly enhanced by grinding illite-quartz mixtures. Therefore, the procedure of grinding illite with quartz in an agate mortar was adopted for a more detailed study of the degree of change that grinding can induce in the accessibility of K and N in this illite. The results of this study with samples of the original illite (described in Table 1) are given in Fig. 3.

A decrease in the NaTPB-extractable K (17 me per 100g) was observed when the illite was dry-ground. This decrease could mean that some of the interlayer K was rendered nonexchangeable by a reduction in particle size and that illite particles exhibit some of the same responses to grinding as those observed with micas. Since the NaCl-extractable K also increased, and by an amount greater than the change in NaTPB-extractable K, however, there is no way of being sure that grinding did produce this particle-size effect in the illite. It is just as possible that the decrease in NaTPB-extractable K occurred because some of this K was exposed by grinding and subsequently extracted by NaCl. In either event, the grinding treatment must have also converted some of the non-extractable K into NaCl- or NaTPB-extractable forms, because the total extractable K was increased. Thus, contrary to the expectations based on the behavior of dry-ground micas (11), the illite data show the limited K exchange exhibited by this mineral can be

largely overcome by grinding. Moreover, the response of illite to dry-grinding probably means there is a limit to the reduction in maximum K exchange that can be induced by decreasing the size of micaceous mineral particles. This limit will occur when further diminution of the particles exposes more K ions at the surface of the particles than are rendered nonexchangeable in the interlayers.

Grinding increased the total extractable K to a maximum of 91% and decreased the nonoxidizable N to a minimum of 24%. No other grinding procedure had this much effect and no greater change in the accessibility of the K and N could be induced by prolonging the grinding. The illite contained 102 me K per 100g and a total of 896 ppm N, of which 608 ppm was not oxidizable by NaOBr. Thus, dry-grinding failed to release 9 me K per 100g and 146 ppm N -- amounts greater than those left by ultrasonic-NaTPB treatments. Unlike the sonified samples, however, the illite samples that were ground enough to achieve this degree of K and N release exhibited no evidence of crystallinity in their x-ray diffraction patterns. That is, there was no direct evidence that enough illite particles persisted in the ground sample to account for the inaccessible K and N. Still, this much illite could easily escape detection by x-ray diffraction and is the most likely explanation for both K and N remaining in inaccessible positions.

A comparison of the various ground illite samples shows the nonoxidizable N changed whenever the nonextractable K changed and

by comparable degrees. The persistence of a close relationship between the amounts of inaccessible K and N was especially evident in the original illite that was progressively ground to obtain the data in Figure 3. Before grinding, this sample contained 34.6 me per 100g nonextractable K and 608 ppm nonoxidizable N. Samples ground for 2 hours contained 80 and 89% of these amounts of inaccessible K and N, respectively, and those ground for 24 hours contained 24% of both. Thus, there seems little doubt that some N in this illite is associated with the K in the interlayers of the mineral. Preliminary infrared analyses of the illite samples indicate that much of the N in the original material is in the form of NH_4 ions, but the information available on the nature of the compounds persisting in treated illite is less conclusive. The NH_4 ions should not interfere with the extraction of interlayer K by NaTPB solutions, because any NH_4 replaced by Na would be precipitated by the NaTPB. It is still possible that other N compounds in the interlayer are restricting the exchange of both K and NH_4 , but until such effects can be verified, the limited exchange of K and NH_4 (for subsequent oxidation) in ground or unground illite samples is best explained by the small particle-size effects already established with micas.

SUMMARY

To obtain more information about the K exchange behavior of naturally occurring, fine-grained micaceous minerals, and especially the reasons for part of the K in these minerals being nonexchangeable, samples of Grundite illite were subdivided on a particle-size basis or ground in various ways and characterized in regard to their NaTPB-extractable K. To avoid the possibility of chemical dispersive treatments causing changes in the K release behavior of the illite particles, some of the original illite was dispersed in water to obtain mechanically dispersed size-fractions. Several chemical treatments that are commonly used to disperse clay suspensions were tested for their effects on K release by illite samples and then used with the original illite to prepare chemically dispersed size-fractions. Both wet- and dry-grinding procedures were used and the effects of grinding were evaluated in terms of the changes induced in the nonoxidizable N and nonextractable K in the illite.

All but the finest ($<0.2\mu$) mechanically dispersed fractions released a maximum of about 66% of their K and yielded essentially the same K release versus time curves. Thus, this method of subdividing the illite failed to identify the existence of a particle-size effect comparable to that observed with ground mica. Still,

the data obtained with the mechanically dispersed fractions merit consideration because they emphasize the difficulties attending the isolation of particle-size effects in naturally fine-grained micaceous minerals, they show the occurrence of limited K exchange in micaceous minerals is not confined to ground or chemically dispersed samples, and they establish the general level of limited K exchange that should be used to assess the effects of particle size in this illite. Coupled with the uniformity of the total C and N values for these fractions, the K release data also led to the conclusion that all but the $<0.2\mu$ fraction were comprised of aggregates with similar combinations of particle sizes.

When samples of the $<2\mu$ mechanically dispersed illite fraction were subjected to various chemical treatments that would enhance the dispersion of the material, no changes in the maximum extractable K occurred. Thus, the K release data obtained with chemically dispersed size-fractions were interpreted as a measure of the effect the size of the indigenous particles in this illite has on K exchange. As with ground mica particles, the rate of K exchange increased and the degree of exchange decreased as the particle size decreased. The exchange of only 48% of the K in the $<0.08\mu$ illite fraction, however, means the limitations on K exchange imposed by particle size are far greater in illite than in ground mica. Also, unlike the ground micas, none of the illite size-fractions released all its K even though a correction was made for the presence of feldspars.

A comparison of various wet-grinding procedures failed to produce any method that would cause enough comminution of illite particles to modify the amounts of nonextractable K and nonoxidizable N in the mineral. Even samples sonified in NaCl solutions for 72 hours did not release more of their K and N. On the other hand, comparable ultrasonic treatments with samples in NaTPB solutions enhanced the exchange of interlayer K and exposed most of the N in the mineral to oxidation by NaOBr. A simultaneous decrease in the nonextractable K and nonoxidizable N was also achieved by dry-grinding the illite samples. As shown by the changes in NaCl-extractable K, however, the effects of dry-grinding stemmed from a decrease in particle size. This means a reduction in the size of the illite particles had a different effect from that observed with micas, in that more K becomes exchangeable instead of less. The maximum K extraction achieved with dry-grinding was 91%, whereas 98% of the K was replaced by the NaTPB-ultrasonic treatment. By the time this degree of K extraction was accomplished by dry-grinding, however, all x-ray diffraction evidence of crystallinity in the illite sample was lost.

All the illite fractions contained N that was not oxidizable by NaOBr. Any treatment of the illite that reduced the nonextractable K in the mineral also exposed more of this N to oxidation, but no illite sample was entirely freed of N or K. Since the

changes induced in nonextractable K and nonoxidizable N were simultaneous and related in degree, it may be concluded that the N is located in the interlayers with the K. There is no evidence that the presence of this interlayer N interferes with the exchange of the K. Instead, the inaccessibility of both K and N in contracted interlayers of the illite seems to be due to an effect of particle size.

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Smith & Scott

Fig 3
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