# EXCHANGEABILITY OF POTASSIUM IN HEATED FINE-GRAINED MICACEOUS MINERALS

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Abstract-Samples of several naturally fine-grained micaceous minerals were heated at 450°C for 24 hr (after the effects of other temperatures and heating periods were evaluated with the  $\langle 2 \mu m$  fraction of Grundite) and then characterized in terms of their release of K to NaCI-NaTPB (sodium tetraphenylboron) solutions and other potentially related properties.

This heat treatment produced a substantial increase in the amount of K that each mineral released when first placed in the NaCl-NaTPB solution (the greatest increase being 22 m-equiv K/IOO g in Marblehead illite). Depending upon the mineral heated, the subsequent rate of K release was increased, decreased or unchanged. Also, all the minerals except glauconite exhibited an increase (ranging from 4 to 38 m-equiv K/IOO g) in their maximum degree of K release if they were heated. Thus, it was established that the K release behavior of these minerals is not only subject to appreciable alteration by heat treatments but is altered in a manner that varies with the mineral. The nature of these alterations, however, did not clearly identify an involvement of the other mineral properties that were examined. An increase in  $NH_{4-}$  and Cs-exchangeable K occurred when these minerals were heated- presumably as a result of exfoliation. With Morris illite samples, this increase was nearly 28 m-equiv 100 g. Thus. heated samples of these minerals may be useful sinks for the removal of  $NH<sub>4</sub>$  and Cs in various wastes.

## INTRODUCTION

Information on the effects of heat treatments on micaceous minerals can help provide an understanding of the factors involved in interlayer cation exchange (Scott et al., 1972) and lead to improvements in the use of cation sorption for the removal of radioactive Cs from atomic wastes (Tamura and Jacobs, 1960, 1961). Particularly relevant are the changes in K release behavior known to occur when some of these minerals are heated.

Numerous reports have verified that changes in soluble and  $NH_4$ - exchangeable K levels can occur in soils that are dried or heated (Scott and Hanway, 1960). Also, the use of successive heat treatments to achieve a progressive release of K from illites and micas has been described (Kolterman and Truog, 1953; Legg and Axley, 1958). The extent to which the K release behavior of micaceous minerals can be altered by heat treatments was not apparent, however, until Smith and Scott (1963) heated samples of Grundite before they were extracted with NaCl-NaTPB (sodium tetraphenylboron) solutions. By heating this mineral at 450°C for 24 hr, the maximum extractable K was increased from 68 to 93 per cent (a change of 32 m-equiv K $/100$  g). Now from subsequent experiments with micas. we also

know that the effects of heat treatments on K exchangeability can vary widely from one mineral to another and can vary in regard to both their nature and degree.

When biotite was heated to oxidize  $Fe<sup>2+</sup>$  in the mineral, Robert (1971) observed a reduction in the amount of K that could be extracted by sodium cobaltinitrite. In a comparison of several coarse-grained mica samples, however, Scott *et* al. (1972) concluded it was mainly the rate of K exchange that was altered by heat treatments. With specific heat treatments, the extraction period for nealy all the K in  $<$  50  $\mu$ m muscovite particles was reduced from 2 yr to 1 week, whereas the period for 65 per cent K release in  $<$  50  $\mu$ m lepidomelane particles was increased from a few days to 2 yr. On the other hand, heat treatments induced little change in the exchangeability of K in phlogopite and altered both the rate and degree of K exchange in a synthetic fiuorphlogopite. In view of these complex responses of well-defined micas to heat and their interpretation in terms of  $Fe<sup>2+</sup>$  oxidation, dehydroxylation, and structural adjustments, the question arises as to what would happen if the heated micaceous minerals had the added features of small particle size and different degrees of mixed layering with expansible material. Part of the answer is provided by the data in this paper for heat-treated samples of several naturally occurring, fine-grained micaceous minerals

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#### MATERIALS AND METHODS

Samples of < 60-mesh Beavers Bend, Marblehead, Fithian and Morris illites and of glauconite (Monmouth County, New Jersey) and metabentonite (Tazewell, Virginia) were prepared with a minimum amount of hand crushing in a mortar.  $A < 200$ -mesh sample of Rock Island illite was obtained from H. Gaudette, University of New Hampshire, Durham, New Hampshire, and  $a < 2 \mu m$  fraction of Grundite (clay from Goose Lake area, Illinois supplied by Illinois Clay Products Co., Joliet, Illinois) was available from earlier studies by Smith and Scott (1963, 1966). All samples were air-dried.

The various heat treatments were carried out with 0·5 g (l 10°C oven-dry basis) air-dried samples in Pyrex Erlenmeyer flasks or platinum crucibles (for temperatures above 450°C) and a ventilated furnace controlled to  $\pm 10^{\circ}$ C. The samples were placed on a raised platform in the furnace, heated at specified temperatures for different periods and then cooled. The entire sample of heated or unheated mineral was then mixed with 1·026 g NaTPB and 10 ml 1·7 N NaCl-O'01 M EDTA solutions  $25^{\circ}$ C to determine the exchangeability of the K. Exchangeable K determinations were also carried out by shaking the entire  $0.5$  g sample with 10 ml 1 N solutions of NaCl, NH<sub>4</sub>OAc or CsCl and leaching with another 40 ml of the same solution.

The general procedure used in the extraction of K by NaCl-NaTPB solutions has been described by Smith and Scott (1966). Layer charge values were calculated by summing the total K and Na contents of Na-saturated samples.  $HF-HCl<sub>4</sub>$  digestions were used in the total K and Na determinations, and all solutions were analyzed for K and Na by flame emission. Nitrogen was determined by a semi-micro Kjeldahl procedure (Bremner, 1965). In some instances, an HF pretreatment was. used in the N determinations but never proved necessary. Ferrous iron contents were determined by the method described by Peters (1968).

All results have been expressed in terms of the ovendried (110 $\degree$ C for 48 hr) weight of the original samples that were selected for the various heat treatments and determinations.

#### RESULTS AND DISCUSSION

### *Heat treatments*

When coarse-grained mica samples were heated, the exchangeability of their interlayer K was changed by the length of the heating period as well as the temperature (Scott *et al.,* 1972). Thus, the initial heat treatments employed with fine-grained materials were varied in regard to temperature and duration. Using

the  $\lt 2\mu$ m Grundite sample and heating periods of 24 hr, we found that the amount of K extracted in 7 days by NaCI-NaTPB solutions was reduced slightly (from 81.5 to 79.7 m-equiv K/100 g) by heating at 110 $^{\circ}$ C, but was increased to 89.1, 92.0 and 100 m-equiv K/100 g by temperatures of 250, 350 and 400°C, respectively. The results obtained with other temperatures and heating periods are given in Table 1. Each of these 7-day, NaTPB-extractable K values represents the maximum degree of K exchange that could be achieved after the heat treatments. Samples heated at temperatures up to 750°C and for periods up to 48 hr were analyzed for total K and always contained 123 m-equiv/100 g.

The response of Grundite samples to different temperatures and periods of heating was similar to that of muscovite (Scott *et al.,* 1972) in that K exchange was depressed by low temperatures, increased appreciably by temperatures over *350°C* and greatly reduced by long periods of high temperatures. With Grundite, however, these effects of different heat treatments pertain to changes in maximum degree of exchange, whereas only the rate of exchange was altered in the coarse muscovite particles. Obviously, the heat treatments employed and the nature of the changes in K release behaviour need to be specified clearly in a comparison of the results obtained with different minerals.

An increase in K exchangeability occurred in the Grundite samples that were heated for 24 hr at a temperature of only 250°C. Further increases were observed as the temperature was raised to 450°C or the time of heating at 450°C was increased from 10 min to 24 hr. Evidently, the heat-induced reactions responsible for changes in K release in Grundite were initiated by lower temperatures than those required by muscovite, probably because the Grundite particles were smaller and susceptible to a lateral escape of interlayer water. The maximum effect of heat treatments was also achieved with a lower temperature and shorter heating period (650°C for 20 min) when this fine-grained mineral was used. Higher temperatures or longer heating periods at even 650°C produced a progressive decrease in the exchangeability of K. Presumably, this decrease was due to a progressive destruction of the mineral structure which Grim and Bradley (1940) concluded can begin at approximately  $700^{\circ}$ C.

### *K extraction curves*

To further characterize the effects of preheating on K exchange in Grundite, entire K extraction curves were obtained. Figure 1 shows the curves obtained with samples that were unheated, heated at 450°C for 24 hr or heated at 650°C for 30 min and then placed in NaTPB solutions for different periods. A comparison

Heating period	K extracted (m-equiv/100 g)*								
	$350^{\circ}$ C	$450^{\circ}$ C	550°C	$650^{\circ}$ C	$750^{\circ}$ C				
$10 \text{ min}$		101		112	115				
$20 \text{ min}$		103	103	118	116				
$30 \text{ min}$		105	104	118	116				
1 <sub>hr</sub>		107	108	115	112				
24 hr	92	113	113	104	42				
48 hr	92	113	112	98	20				

Table 1. Amounts of K extracted from  $\lt 2\mu$ m Grundite samples that were heated for different periods at various temperatures and placed in NaCI-NaTPB solutions for 7 days

\* Total and extractable K in unheated Grundite was 123 and 81·5 m-equiv *KjlOO* g, respectively.

of these curves shows various changes in K release behavior were induced by heating the mineral. Besides increasing the maximum amount of K extracted, heating increased the rate of K release and the amount of K released in the shortest extraction period. The combined effect of these changes in rate and degree of K exchange, however, led to no change in the time (approx. 1 week) required for maximum K exchange.

The initial release of K was increased by 20 mequiv/100 g when the samples were heated at  $450^{\circ}$ C and by another 45 m-equiv/l00 g when the heating temperature was increased to 650°C. Practical limitations to the minimum extraction period that can be used with NaTPB solutions (about 15 sec) make it impossible to use these curves to clearly identify the reasons for these changes in initial release. In contrast to ground mica, little of this initial release by unheated samples of  $<$  2  $\mu$ m Grundite is believed to be due to layer weathering (Ismail and Scott, 1972). However, the heat treatment exposed interlayer K by exfoliation (the  $NH_{4}$ exchangeable K was increased  $12$  m-equiv/ $100$  g by the 450°C treatment) and could have left more of the



Fig. 1. K extracted from  $\langle 2 \mu m \rangle$  Grundite samples that were heated at 450°C for 24 hr or 650°C for 30 min and placed in NaCI-NaTPB solutions for different periods.

mineral susceptible to an initial release of K by layer weathering in the NaTPB solution. Thus, only part of the increase in initial K release by heated Grundite can be attributed to the higher rate of edge weathering depicted by the rest of the curves.

To the extent that the initial release of K by heated samples was increased by exfoliation during the heat treatment and by subsequent layer weathering in the NaTPB solution, some consideration must be given to the fact that the maximum degree of  $K$  exchange was also increased. Experiments with Grundite and ground mica size-fractions have made it clear that an increase in immediate K release by layer weathering leads to a closely related decrease in maximum exchange in small particles (Scott, 1968). To account for this inverse relationship between the initial and maximum K release, it was suggested that a separation of some mineral layers left the K between adjacent contracted layers in a more strongly held position as proposed by Bassett (1959). In heated Grundite, this effect of open layers is evidently overshadowed by other effects of the heat treatment on the exchangeability of K in the remaining contracted position of the mineral. Indeed, as shown by the slope of the curves at equivalent degrees of K exchange (e.g. at 70 m-equiv/IOO g), the rate of subsequent K release by edge weathering was enhanced by the heat treatment.

The extraction curves in Fig. 1 show the amounts of K extracted by contact periods of less than 1 min. The inclusion of these data for short extraction periods gives added emphasis to the earlier conclusion that the relationship between K extracted. and the log of the contact period is curvilinear for Grundite, not linear as was observed with dilute NaTPB solutions, and with initial extraction periods in the order of 1 hr (Smith and Scott, 1963, 1966). The K extraction curves obtained with the heated samples retain the curvilinear form.

As stated for the data in Table 1 and now shown by the curves in Fig. 1, the maximum degree of K

exchange was not enhanced by extending the extraction period beyond 7 days. This means that no combination of heating temperature, heating period and K extraction period made it possible to replace all the K in Grundite. At best, a release of  $118$  m-equiv K/100 g (96 per cent) was achieved by heating samples at 650°C, but the heating period had to be restricted to a narrow range. On the other hand, by using a temperature of only 450°C to reduce the possibilities of mineral destruction, the samples could be heated for periods varying from 24 to 48 hr and still obtain an exchange of 113 m-equiv  $K/100$  g (92 per cent). Thus, a heat treatment of 450°C for 24 hr was selected as a standard for subsequent comparisons of other micaceous minerals.

K extraction curves were determined with heated (450°C for 24 hr) and unheated samples of all the micaceous minerals, but only the curves for the Beavers Bend and Marblehead illites and for glauconite are given in Fig. 2 to illustrate the various responses observed. With each of the minerals, as with Grundite, heating resulted in an increase in K extracted initially. Thereafter, the K in heated samples was extracted much faster (Beavers Bend), slower (glauconite) or at nearly the same rate (Marblehead). Increases in maxi-



Fig. 2. K extracted from samples of fine-grained micaceous minerals that were heated at 450°C for 24 hr and placed in NaCl-NaTPB solutions for different periods.

mum K exchange due to heating occurred in all minerals except glauconite, which exhibited no change. Obviously, the effects of heat treatments on the K release behavior of these minerals were much more varied than would be anticipated from Grundite and cannot be described by a comparison of results obtained with a single extraction period. **In** view of this varied response of the minerals to heat treatments, a further search for related changes in other characteristics of the heated minerals was undertaken.

## *Chemical properties*

Various properties of heated and unheated samples of the micaceous minerals are described in Table 2. As was reported for Grundite samples that were subjected to a variety of heat treatments, the total K content of the various minerals was not altered by the 450°C heat treatment. Changes in other characteristics, however, did occur.

The heat treatment increased the maximum amount of NaTPB-extractable K in all the minerals except glauconite, but there was some K in each mineral (up to 38 per cent of the K in Marblehead) that was still not exchangeable. Since the limited exchange of K in the unheated samples can be largely attributed to the small size of the particles (Scott, 1968), it may be concluded that one role of heating is that of reducing the small particle effects. As shown with Grundite, other temperatures and heating periods can make even more of the K in these minerals exchangeable, but some limitation on K exchange can be anticipated from feldspar impurities in these nonfractionated samples of naturally fine-grained micaceous minerals (Smith *et al.,*  1968). As shown by Raman and Jackson (1966), 4·1 per cent of the  $\langle 2 \mu m \rangle$  fraction of Marblehead consists of feldspar. The presence of even more feldspar in the complete Marblehead sample may be responsible for the particularly low NaTPB-extractable K value obtained with heated portions of this mineral.

Heating the minerals increased by severalfold the amounts of K that were extracted by leaching with NaCl,  $NH_{4}O$ Ac and CsCl solutions. Furthermore, the fixable cations,  $NH_4$  and Cs, were nearly as effective as Na in replacing K in the heated samples. Thus, the heat treatment must have altered the mineral particles in such a way as to expose interlayer  $K$ —presumably by an exfoliation of the minerals comparable to that observed with heated samples of hydrobiotite (Scott *et al.,* 1972). To account for a similar release of K by heated soils, Kolterman and Truog (1953) emphasized the critical role of prior ammonium saturation of samples. According to their explanation, heat released  $NH<sub>3</sub>$  from the NH<sub>4</sub> cations and this gas forced the clay

Heat treatment	Beavers Bend	Marblehead	Rock Island	Fithian	Morris	Glauconite	Metabentonite	$< 2 \mu m$ Grundite
Total K (m-equiv/100 g)								
None/450 $\mathrm{^{\circ}C}$	122	188	87	101	103	174	135	123
Max. NaTPB-Extractable K $(\%)$								
None	94	42	82	70	67	78	84	66
$450^{\circ}$ C	97	62	89	91	88	78	96	92
Exchangeable K (m-equiv/100 g)								
<b>NaCl</b>								
None	$1-6$	1.8	$1-7$	1.5	2.3	3.6	1.3	4.9
450°C	3.9	$10-4$	5.9	$12 - 0$	$30-3$	$13 - 0$	9.8	17.9
NH <sub>4</sub> OAc								
None	0.7	$1-0$	1.4	$0-7$	$1-0$	3.2	0.5	3.8
450°C	3.3	$10-2$	$3-4$	$11 - 8$	29.7	12.2	9 <sub>0</sub>	$16-2$
CsCl								
None	0.6	$1-0$	$1-0$	0.9	0.9	3.2	0.5	
450°C	2.7	9.6	2.8	$10-2$	$28 - 6$	$11-0$	6.9	
Layer charge (m-equiv/100 g)								
None	138	209	100	132	126	193	162	153
$450^{\circ}$ C	136	203	101	130	104	192	156	145
pH (in 1 N NaCl)								
None	60	7.8	6.8	$3 - 7$	2.6	6.4	$8-0$	7.2
450°C	5.9	9.5	5.3	4·0	2.9	5.8	7.7	$4-4$
Nitrogen (ppm)								
None	826	395	720	1176	785	126	756	1022
$450^{\circ}$ C	364	105	165	113	79	$\bf{0}$	168	42
550°C	10	$\mathbf 0$		25	10	$\theta$		

Table 2. Characteristics of micaceous minerals before and after being heated for 24 hr

Exchangeability of potassium in micaceous minerals

layers apart. Our results show that ammonium saturation is not a necessary condition for the occurrence of K release in heated micaceous minerals.

The increase in K replacement by Cs that was achieved by heating these minerals merits attention in terms of the disposal of atomic wastes; i.e. the sorption of Cs can be enhanced by heating the mineral. The Morris illite should be especially useful because a single heat treatment produced a 30-fold increase in Cs exchange of K  $(0.9-28.6 \text{ m-equiv}/100 \text{ g})$ . Further experiments have shown that even more Cs can be sorbed by these micaceous materials if the heating-Cs exchange sequence is repeated. At the same time, the heat treatment improves the porosity of the minerals and, as shown by Tamura and Jacobs (1961) with bentonite, the Cs selectivity of minerals can be enhanced by heating. Therefore, both the chemical and physical properties of the heated materials should be well suited for their use in the removal of Cs from various wastes.

The changes in layer charge and pH that occurred in the heated samples of micaceous minerals were too minor or inconsistent to account for the associated changes in K exchangeability. Similarly, the nitrogen data in Table 2 contradict an earlier suggestion (Smith and Scott, 1963) that nitrogen compounds might be responsible for the limited exchange of interlayer K in unheated illite samples. The simultaneous loss of nitrogen and increase in K release that occurred in heated Grundite led to this suggestion. Now, however, we find a complete removal of nitrogen produced no change in extractable K in glauconite and left the Marblehead samples with appreciable amounts of nonextractable K. Also, the release of K by heated and unheated samples of Beavers Bend illite was essentially complete, despite the presence of nitrogen in both samples. The rest of the minerals were more like Grundite in that heated samples exhibited changes in nitrogen and extractable K content, but no relationships between the amounts of residual nitrogen and nonextractable K exist. Thus, it seems unlikely that nitrogen compounds limit the exchange of K in any of these minerals. Moreover, these data show the nitrogen in these minerals is not as easily removed by heat treatments as might be expected, in that some samples retained nitrogen after being heated at 550°C for 24 hr.

Since the heat treatment altered the rate of K release in most of the micaceous minerals, changes in mineral characteristics other than those imposed by exfoliation must have occurred. Scott *et al.* (1972) have noted that changes in basal spacing and structural rearrangements from dehydroxylation of dioctahedral micas may be jnvolved in the changes in K release rate induced by heating ground mica samples. Berger (1965)

found no appreciable destruction of mineral structure occurred in Marblehead and Fithian illite at temperatures below approx. 930°C. As noted previously, early studies by Grim and Bradley (1940) indicated that no destruction of mineral structure begins in illites until a temperature of at least 700°C is reached. If any structural alterations did occur in the minerals heated at temperatures up to 650°C in this study, they were not evident from X-ray diffraction analyses. The X-ray patterns obtained with unheated and heated (450°C for 24 hr and 650°C for 2 hr) samples differed only in regard to a sharpening of the basal reflections upon heating. It is still possible that alterations in the structure of these minerals are induced by heat treatments, but their detection will likely stem from further work on heated micas and the use of more homogeneous fractions of these fine-grained materials.

Both Robert (1971) and Scott *et al.* (1972) have found the rate of K release can be reduced by the oxidation of iron in heated trioctahedral micas. Thus, the decrease in K release rate observed with heated glauconite could be anticipated and attributed to its high ferrous iron content  $(67 \text{ m-moles}/100 \text{ g})$ . On the other hand, the rates of K release by Beavers Bend illite and Grundite were not reduced by the heat treatments even though they contain 42 and 38 m-moles ferrous iron/loo g, respectively. Although the effects of iron oxidation may have been overshadowed by other changes in the heated samples of these minerals, these results could also mean that iron oxidation does not always impair the exchangeability of interlayer K.

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### **REFERENCES**

- Bassett, W. A. (1959) Origin of the vermiculite deposit at Libby, Montana: *Am. Mineralogist* 44,282-299.
- Berger, R. L. (1965) The effect of adsorbed ions on the structural derangement temperature of illite and phlogopite: *Diss. Abstr.* 26, 309.
- Bremner, J. M. (1965) Total nitrogen: *Agronomy* 9, 1149- 1178.
- Grim, R. E. and Bradley, W. F. (1940) Investigation of the effect of heat on the clay minerals illite and montmorillonite: *J. Am. Ceram. Soc.* 23, 242-248.'
- Ismail, F. T. and Scott, A. D. (1972) Temperature effects on interlayer potassium exchange in micaceous minerals: *Soil Sci. Soc. Am. Proc.* 36,506-510.
- Kolterman, D. W. and Truog, E. (1953) Determination of fixed soil potassium: *Soil Sci. Soc. Am. Proc.* 17, 347-351.
- Legg, J. O. and Axley, 1. H. (1958) Investigation of a thermal method for the determination of fixed potassium in soils: *Soil Sci. Soc. Am. Proc.* 22, 287-290.
- Peters, von Arnd. (1968) Ein neues Verfahren zur Bestimmung von Eisen (II) oxid in Mineralen und Gesteinen: *Neues Jahrbuch für Mineralogie Monatshefte Heft.* 3/4, 119- 125.
- Raman, K. V. and Jackson, M. L. (1966) Layer charge relations in clay minerals of micaceous soils and sediments: *Clays and Clay Minerals* **14,** 53-68.
- Robert, M. (1971) Etude experimentale de I'evolution des micas (biotites): *Ann. Agron.* 22, 43-93.
- Scott, A. D. (1968) Effect of particle size on interlayer potassium exchange in micas: *Trans. 9th Intern. Congr. Soil Sci. (Adelaide)* 2, 649-660.
- Scott, A. D. and Hanway, J. J. (1960) Factors influencing the change in exchangeable soil K observed on drying: *Trans. Intern. 7th Intern. Congr. Soil* Sci. *(Madison)* 3,72- 79.
- Scott, A. D., Ismail, F. T. and Locatis, R. R. (1972) Changes in interlayer potassium exchangeability induced by heating micas: *Preprints* 1972 *Intern. Clay Conf.* (*Madrid*) 2, 143- 158.
- Smith, S. 1. and Scott, A. D. (1963) Extraction of potassium from heated illite: *Agronomy Abstr.* 1963, 25.
- Smith. S. 1. and Scott. A. D. (1966) Extractahle potassium in Grundite illite<sup>1</sup> I. Method of extraction: Soil Sci. 102, 115-122.
- Smith, S. J., Clark, L. J. and Scott, A. D. (1968) Exchangeability of potassium in soils: *Trans. 9th Intern. Congr. Soil Sci. (Adelaide)* 2,661- 669.
- Tamura, T. and Jacobs, D. G. (1960) Structural implications in cesium sorption: *Hlth Phys.* 2, 391-398.
- Tamura. T. and Jacobs. D. G. (1961) Improving cesium selectivity of bentonites by heat treatment: *Hlch Phys. 5,*  149-154.

Résumé—Des échantillons de plusieurs minéraux micacés existant naturellement à l'état de grains fins ont été chauffés à 450°C pendant 24 h (après que les effets d'autres températures et temps de chauffage aient été testés avec la fraction < 2  $\mu$ m de la Grundite); ils ont ensuite été caractérisés par leur aptitude a Iiberer K dans des solutions de NaCI-NaTPB (sodium tetraphenylbore)et par d'autres proprietes re1iees en principe à la libération de K.

Le traitement thermique produit une augmentation substantielle de la quantité de K que chaque minerallibere quand i1 est, pour Ie premiere fois mis au contact de la solution NaCI- NaTPB (I'augmentation la plus forte etant de 22 m-equiv K/ I 00 g dans I'illite de Marblehead). Pour les mineraux chauffes, et selon leur nature, la vitesse de libération de K consécutive au chauffage, augmente, diminue ou reste inchangée. En outre, tous les minéraux sauf la glauconite montrent une augmentation (allant de 4 à 38 m-equiv K/ $(100 g)$ ) de la quantité maximum de K libéré s'ils ont été chauffés. Il est donc établi que le comportement de ces minéraux vis-à-vis de la libération de K ne subit pas seulement une modification appréciable du fait des traitements thermiques, mais est aussi modifié d'une manière qui varie avec le mineral. Toutefois, la nature de ces modifications ne permet pas d'identifier clairement une implication des autres propriétés du minéral qui ont été examinées.

Une augmentation de K échangeable contre  $NH<sub>4</sub>$  ou Cs est observée avec les minéraux chauffés, ce qui est probablement le résultat d'une exfoliation. Avec les échantillons de l'illite de Morris, cette augmentation est de 28 m-equiv/100 g environ. Ainsi, les échantillons chauffés de ces minéraux pourraient utilement servir de pièges à NH<sub>4</sub> et Cs présents dans divers déchets.

Kurzreferat-Proben verschiedener, von Natur aus feinkorniger, glimmerartiger Minerale wurden flir 24 h auf 45°C erhitzt (nachdem die Wirkungen anderer Temperaturen und Erhitzungszeiten mit der Fraktion  $<$  2  $\mu$ m von Grundit ermittelt worden waren) und anschließend hinsichtlich ihrer K-Freisetzung in NaCl-NaTPB(Na-Tetraphenylborat)-Losungen und anderer moglicherweise hierzu in Beziehung stehender Eigenschaften gekennzeichnet.

Die Erhitzung rief einen wesentilichen Anstieg in der K-Menge hervor, die jedes Mineral freisetzte, wenn es zum ersten Mal in die NaCl-NaTPB-Lösung gebracht wurde. (Der gößte Anstieg betrug 22 m-val/lOO g bei Marblehead-IIlit.) In Abhangigkeit von der Art des erhitzten Minerals wies die anschlieBende K-Freisetzungsrate eincn Anstieg auf, zeigte eine Abnahme oder blieb unverandert. Uberdies wiesen aile Minerale, mit Ausnahme von Glaukonit nach Erhitzung einen Anstieg der maximal freigesetzten K-Menge auf (der 4 bis 38 m-val K/100 g betrug). Auf diese Weise wurde festgestellt, daß das K-Freisetzungsverhalten dieser Minerale nieht nur einer erheblichen Veranderung durch Hitzebehandlung unterliegt, sondern auch in einer von der Mineralart abhangigen Weise variiert. Die Art dieser Veranderungen lieD jedoch eine Verkniipfung mit anderen untersuehten Mineraleigenschaften nicht deutlich erkennen.

Wenn die Minerale erhitzt wurden, erfolgte ein Anstieg des NH<sub>4</sub>- und Cs-austauschbaren K-vermutlich als Folge einer Aufblatterung. Sei Proben von Morris-lIlit betrug dieser Anstieg nahezu m-val/ IOO g. Erhitzte Proben dieser Minerale können demnach als brauchbares Adsorbens für die Entfernung von NH4 und Cs aus verschiedenen Abfallen angesehen werden.

Резюме - Несколько образцов мелкозернистых слюдистых минералов нагревали в течение суток при температуре 450°С (после определения по фракции <2  $\mu$ м грюндита эффектов других температур и других периодов нагрева), а затем характеризовали с точки зрения выделения К в NaCl-NaTPB (раствор тетрафенилбор-натрия) и по другим потенциально связанным свойствам.

Эта термообработка повела к значительному повышению количества К вылеляемого каждым минералом при первоначальном погружении в раствор NaCl-NaTPB (самое большое повышение в иллите Марблхэд = 22 мэкв К/100 г). В зависимости от нагреваемого минерала. результирующий коэффициент высвобождения повышался, понижался или оставался без изменения. При нагревании все минералы, за исключением глаконита, выявляли максимальное повышение выделения К (от 4 до 38 мэкв К/100 г). Таким образом установили, что поведение выделения К этими минералами не только заметно изменяется термообработкой, но также, что изменения различаются в зависимости от минерала. Однако, характер этих изменений ясно не показал до какой степени вовлечены другие исследуемые свойства минерала.

При нагреве этих минералов обменные К в NH<sub>4</sub>- и C<sub>5</sub>-повышались, очевидно, вследствие расслаивания. В образцах иллита Морриса это повышение равнялось приблизительно 28 мэкв/100 г. Таким образом, нагретые образцы этих минералов могут оказаться полезными поглотителями при удалении NH<sub>4</sub> и Cs из различных отходов.