RELATION OF POTASSIUM EXCHANGE AND FIXATION TO DEGREE OF WEATHERING AND ORGANIC MATTER CONTENT IN MICACEOUS CLAYS OF PODZOL SOILS*

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Abstract—The rates of K exchange of untreated and peroxide-treated micaceous clays from five Podzol soils of increasing degrees of weathering were determined using sodium tetraphenyl boron. In addition, the amounts of K fixed against NH₄ were measured. The Ae horizon clays of these soils contained mainly interstratified mica-vermiculite-montmorillonite whereas the C horizon clays contained mica of a more discrete nature.

As was expected, there was an inverse relationship between rates of K exchange and degrees of weathering of the Ae horizon clays. However, in the samples from each of these soils except in those of the most weathered one, the K exchange rate of the interstratified mica from the Ae horizon was higher than that of the less weathered, more discrete mica from the corresponding C horizon. The abundance of hydrated edges and layers exposing K exchange sites in the Ae horizon micas probably contributed to their higher rates of K exchange. Amounts of K fixed in the Ae horizon clays were not related to degrees of weathering.

Removal of organic matter from the Ae horizon clays by peroxide considerably increased both the rates of K exchanged and the amounts of K fixed. These increases were attributed to the elimination of a blocking effect of adsorbed organic matter on K exchange and fixation.

INTRODUCTION

Studies in the artificial weathering of micas show that their K may be exchanged with hydrated cations and that this results in a swelling mineral resembling vermiculite. During this process the rate of K exchange decreases as the front of the exchanged region approaches the center of the particle. Diffusion appears to be the rate-limiting step in this reaction (Mortland and Ellis, 1959; Rausell-Colom et al., 1965; Reed and Scott, 1962).

The natural weathering process apparently is not this uniform. Micas in soils generally become interstratified to varying degrees of randomness with hydrated layers. Also some of the hydrated layers may show montmorillonite-like characteristics (Kodama and Brydon, 1968; Lisitsa and Tikhonov, 1969; Sokolova and Shostak, 1969).

However, considering the results of the studies cited thus far, it seems reasonable to assume that it becomes more difficult to exchange K from mica in soil as weathering progresses. The validity of this assumption might be tested by comparing K exchange rates of micaceous clays obtained from soils of similar genesis but in advancing stages of weathering.

Another aspect that may be studied by using these micaceous soil clays is the effect on K exchange of material adsorbed on clay surfaces. Adsorption of hydrous aluminum oxide on outer and interlayer surfaces of weathered micaceous clays is well substantiated and has been shown to inhibit K release and fixation to varying degrees (Rich, 1960a; Rich, 1960b; Rich and Obenshain, 1955). Laboratory experiments have demonstrated also adsorption of soil humic compounds on outer and interlayer surfaces of expanding clays (Greenland, 1956; Kodama and Schnitzer, 1969; Schnitzer and Kodama, 1966). This process seems to occur at least in some soils as indicated by the presence in these soils of clay-organic complexes in which charge sites are blocked by organic matter (Dudas and Pawluk, 1970; Greenland, 1965; Syers et al., 1970). However, notwithstanding this evidence and the evidence obtained by Mortland (1961) who showed that certain organic compounds greatly inhibited the adsorption of K on vermiculite, the effect of organic matter on K exchange and fixation in soil micaceous clays has not been specifically studied.

In view of these considerations, this investiga-
tion was aimed at clarifying the effect of degree of weathering and of organic matter content on K exchange and fixation. Hydrated micaceous Podzol clays were used which varied chiefly in degree of weathering and organic matter content and which contained very small amounts of free aluminum oxide.

EXPERIMENTAL

The main results were obtained from samples taken from the Ae and C horizons of five Podzol soil series in New Brunswick. Chemical and structural analyses of the coarse and fine clays from portions of these samples had been made previously by Kodama and Brydon (1968) and pertinent data are shown in Table 1. The Poitras (Podzol) and Breton (Grey Luvisol) soils were included for purposes of comparison. The five Podzol soils from New Brunswick were arranged according to the kind and degree of weathering and organic matter content and which clays were used which varied chiefly in degree of weathering and of organic matter content on K exchange and fixation. Hydrated micaceous Podzol clays were used which varied chiefly in degree of weathering and organic matter content and which contained very small amounts of free aluminum oxide.

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Table 1. Clay mineral and chemical analysis of the 2–0·2 μ fraction†‡

| Soil type | Horizon | Sample No. | Chlorite | Mica | Kaolinite | M–Ch | V–Ch | Ch–S | M–V–S | M–V–Ch | TiO₂ (per cent) | TiO₂ Ae/C ratio | K₂O (per cent) | Carbon (after peroxide treatment) (per cent) |
|-----------|---------|------------|----------|------|-----------|------|------|------|-------|-------|---------------|----------------|---------------|----------------|-----------------------------------|
| Kedgewick | Ae      | SMJ1       | *        |      |           |      |      |      |       |       | 1·97          | 1·26           | 3·29           | 2·64                | 0·41                |
|           | C       | SMJ2       | ***      | *    | tr.       |      |      |      |       |       | 1·56          | 5·46           |               |                    |                    |
| Monquart  | Ae      | SMJ3       | *        |      |           |      |      |      |       |       | 2·12          | 1·85           | 2·81           | 3·24                | 0·63                |
|           | C       | SMJ4       | ***      | *    |           |      |      |      |       |       | 1·14          | 5·46           |               |                    |                    |
| Glacier   | Ae      | SMJ5       | *        |      |           |      |      |      |       |       | 3·00          | 1·92           | 2·72           | 3·13                | 0·97                |
|           | C       | SMJ6       | **       |      |           |      |      |      |       |       | 1·56          | 4·13           |               |                    |                    |
| Serpentine| Ae      | SMJ7       | *        |      |           |      |      |      |       |       | 3·39          | 2·17           | 2·94           | 5·15                | 0·55                |
|           | C       | SMJ8       | **       |      |           |      |      |      |       |       | 1·25          | 3·13           |               |                    |                    |
| Tuadook   | Ae      | SMJ9       | tr.      | *    |           |      |      |      |       |       | 1·25          | 3·13           |               |                    |                    |
|           | C       | SMJ10      | ***      | **  | *         |      |      |      |       |       | 1·73          | 3·17           |               |                    |                    |
| Poitras   | Ae      | SML2       | ***      | *    |           |      |      |      |       |       | 1·70          | 3·62           | 3·99           | 0·46                |                    |
|           | C       | SML13      | ***      | **  |           |      |      |      |       |       | 1·30          | 4·65           |               |                    |                    |
| Breton    | C       | SML12      | *        |      |           |      |      |      |       |       | 0·80          | 1·93           | 0·72           | 0·73                |                    |

***Abundant; **Moderate; *Minor. M – Mica; V – Vermiculite; Ch – Chlorite; S – Smectite; tr. – Trace.
†Clay mineral data and TiO₂ contents for the first 10 samples from Kodama and Brydon (1968). Data for TiO₂ in per cent of ignited weight of samples and for K₂O and carbon in per cent of air-dry weight of samples not treated with peroxide.
‡Clay mineral data for SML12 from Brydon et al. (1968). The author thanks Dr. J. E. Brydon for the use of the clay mineral and TiO₂ data for the SML2 and SML13 samples.
between 20 and 50 per cent of the organic matter was removed.

The amount of K fixed in the untreated Ae horizon clays did not increase with increased degrees of weathering (Table 2). On the contrary, no K was fixed in the most intensively weathered SMJ7 and SMJ9 clays prior to removal of their organic matter. The amounts of K fixed after removal of organic matter increased considerably in all the Ae horizon clays, particularly in the SMJ1, SMJ7 and SMJ9 clays. The SML2 clay, which had a large vermiculite component and contained 4 per cent organic carbon, showed the largest increase in K fixation after organic matter removal.

### Table 2. Fixation of K against NH₄ in meq/100 g

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Before peroxide treatment</th>
<th>After peroxide treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMJ1</td>
<td>3.8</td>
<td>12.5</td>
</tr>
<tr>
<td>SMJ3</td>
<td>2.8</td>
<td>7.7</td>
</tr>
<tr>
<td>SMJ5</td>
<td>7.7</td>
<td>12.8</td>
</tr>
<tr>
<td>SMJ7</td>
<td>0</td>
<td>11.5</td>
</tr>
<tr>
<td>SMJ9</td>
<td>-0.7</td>
<td>7.7</td>
</tr>
<tr>
<td>SML2</td>
<td>9.2</td>
<td>24.0</td>
</tr>
<tr>
<td>SML12</td>
<td>6.1</td>
<td>5.1</td>
</tr>
</tbody>
</table>

However, the interstratified SML 12 clay, which contained no organic carbon that could be removed by peroxide, showed no increase in K fixation after peroxide treatment. The C horizon clays fixed virtually no K by the fixation procedure followed.

To make the interpretation of the aforementioned results less equivocal, additional data were obtained on the effect of the peroxide treatment on the clays. The data in Fig. 4 show no difference in rates of K exchange before and after peroxide treatment of the interstratified SML12 clay which contained no removable organic matter. Neither did the amount of K fixed in this clay increase after this treatment (Table 2). Analysis of the supernatants showed that the peroxide treatment extracted less than 0.1 per cent Al and Fe and less than 0.03 per cent K from each clay. Since there was a possibility that particles remained aggregated in the untreated 2-0.2 μ clay and segregated during the following peroxide treatment producing additional small particles, some of the peroxide-treated clays were redispersed and the 2-0.2 μ fraction was again separated. There was no difference, however, between the rates of K exchange of the once- and twice fractionated clays.

The efficiency of the K fixation procedure was also investigated using an extracted SMJ1 sample in which the K content was reduced from 2.70
Fig. 2. Per cent of total K exchanged from the Ae and corresponding C horizon clays of Podzol soils. Both Ae and C horizon samples were treated with peroxide. Total K refers to K contents of peroxide-treated samples.

per cent to 0.70 per cent by extraction with 0.1N BaCl₂ at 100°C (Graf von Reichenbach and Rich, 1968). The K content after the K fixation procedure was 2.80 per cent, slightly higher than its original K content.

**DISCUSSION**

The inverse relationship between rates of K exchange and degrees of weathering was evident only in the comparison of the rates of K exchange of the Ae horizon clays. Smith *et al.* (1968) also observed that the rates and amounts of K replaced from micaceous clays, although obtained from soils of diverse genesis, decreased with increasing soil development. This inverse relationship did not apply to the comparison of Ae and corresponding C horizon clays. The lower rates of the C horizon clays in the latter comparison could not be attri-
organic matter removed by peroxide treatment did
remaining ones. However, increased amounts of
tained 1.5-2 times more organic matter than the
which decomposed in the range from 20 to 50
ning. From the data in Fig. 3, the organic matter
change of K for a hydrated cation in some mica
adsorbed on charge sites of interlayer
This "blocking" effect of organic matter on both
K release and fixation indicates the adsorption of
organic compounds on charge sites of interlayer
surfaces of micaceous clays. This adsorption
apparently is sufficiently strong to inhibit the diffu-
sion of K from and into the interlayer spaces. The
organic compounds in soil organic matter which
produce this inhibiting effect may well include some
of the nitrogen compounds shown by Mortland
(1961) to be very effective in inhibiting K adsor-
ption in vermiculite.

Several alternative interpretations which could
explain the effect of peroxide treatment on K
exchange and fixation were considered and found
inadequate. The increase in rate of K exchange and
extent of K fixation did not seem to be caused by
exfoliation of silicate layers resulting from the
peroxide treatment since this treatment did not
affect the K release and fixation of an interstratified
micaceous clay containing no organic matter.
Neither could this increase by explained by
removal of interlayer or otherwise absorbed hy-
drous oxides of aluminum or iron because only
small amounts of free aluminum or iron were
present initially (Kodama and Brydon, 1968) and
negligible amounts were extracted by the peroxide
treatment. Nor could the increase be attributed to
an increased number of small particles which could
have resulted from a dispersion of aggregates by
the peroxide treatment. Such dispersion, if present,
did not affect subsequent K release as was indica-
ted by refractionation of peroxide-treated samples.

Apparently only the highly charged layers in the
interstratified clays fixed K in the procedure used
since the amount of K fixed in one of these clays
exceeded only slightly the amount of K extracted
from it prior to the K fixation procedure. According
to diagnostic criteria based on X-ray diffraction
data, the mica components comprised about 40-55
per cent of the interstratified clays of the soils in
the weathering sequence used. If it is assumed that
the hydrated layers in these clays largely originated
from mica, the relatively small amounts of K fixed
suggest a considerable reduction in charge during
the weathering of mica in these soils.

The evidence obtained in this investigation shows
that the natural process of mica alteration,
such as occurs in Podzol soils, is much more
complicated than is indicated by laboratory
experiments on the alteration of pure micas. The
main features of this natural process may be
sketched as follows.

When mica weathers in Podzol soils, the ex-
change of K for a hydrated cation in some mica
layers is more rapid than in others resulting in an
interstratified structure. The charge is also reduced
following and perhaps during this exchange.
Hydrous oxides of aluminum and iron are adsor-
bond in expanded interlayers and on outer surfaces
but are eventually removed. Organic matter is
retained, however, and contains compounds
which are adsorbed on charge sites of interlayer
surfaces with sufficient energy to impede K
exchange and fixation. As weathering progresses
increasing amounts of organic matter are adsorbed
and eventually exchange and fixation reactions of
K are virtually blocked. The evidence suggests
that this weathering process may be delayed
initially until a sufficient number of mica layers and

buted to a higher content of potassium feldspars
in the C horizon clays because X-ray data (Kodama
and Brydon, 1968) indicated that the feldspar
minerals in these clays belonged to the plagioclase
series. The greater abundance of hydrated edges
and layers exposing K exchange sites in the Ae
horizon clays probably contributed to their higher
rates of K exchange. This explanation derives
support from the work of Newman and Brown
(1969). They showed that K exchange was
considerably delayed at ordered natural crystal
dges, whereas this delay was eliminated at
roughly-cut disrupted edges. This explanation is
also supported by unpublished results which show
that the rate of K exchanged from muscovite-type
layers of interstratified mica-montmorillonite was
much higher than that from disordered muscovite.
However, the presence of adsorbed hydrous oxides
of aluminum and iron in the C horizon clays cannot
be ruled out and, if present, they could also have
contributed to a retarded K exchange.

Increasing amounts of organic matter adsorbed
on clay surfaces evidently acted in conjunction
with increasing degree of weathering to reduce the rate
at which K was exchanged. The reduction in K
exchange caused by adsorbed organic matter was
more pronounced at increased degrees of weather-
ing. From the data in Fig. 3, the organic matter
which decomposed in the range from 20 to 50
per cent of the total carbon had the greatest effect
on the rate of K exchange. The data suggest also
that at high levels of organic matter K fixation in
these clays may be completely inhibited. Some K
was fixed in all the untreated Ae horizon clays
except in the SMJ7 and SMJ9 clays which con-
tained 1.5-2 times more organic matter than the
remaining ones. However, increased amounts of
organic matter removed by peroxide treatment did
not seem to be related to increased amounts of K
fixed. The SMJ1 clay had as much increase in K
fixation as the SMJ7 and SMJ9 clays but it had
contained only half as much organic carbon. Ap-
parently, in some of these clays the organic matter
was more effective in blocking highly charged
layers than in others.

This "blocking" effect of organic matter on both
K release and fixation indicates the adsorption of
organic compounds on charge sites of interlayer
surfaces of micaceous clays. This adsorption
apparently is sufficiently strong to inhibit the diffu-
sion of K from and into the interlayer spaces. The
organic compounds in soil organic matter which
produce this inhibiting effect may well include some
of the nitrogen compounds shown by Mortland
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edges have become hydrated to provide readily accessible K exchange sites.

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Résumé—On a déterminé, à l’aide du tétraphénylborate de sodium, les vitesses d’échange de K dans des argiles micacées, traitées et non traitées à l’eau oxygénée, provenant de cinq sols podzoliques ayant subi une altération naturelle à des degrés croissants. En plus, les quantités de K fixées ont été mesurées par rapport à NH₄. Les argiles de l’horizon Ae de ces sols contenaient principalement un interstratifié mica-verbatimiculite-montmorillonite, alors que les argiles de l’horizon C contenaient un mica de nature plus distincte.

Comme on pouvait l’espérer, il y a une relation inverse entre les vitesses d’échange du K et les degrés d’altération des argiles de l’horizon Ae. Toutefois, dans les échantillons provenant de chacun de ces sols, à l’exception de ceux relatifs au plus altéré, la vitesse d’échange du K du mica interstratifié de l’horizon Ae est plus élevée que celle du K du mica moins altéré et plus distinct, appartenant à horizon C correspondant. L’abondance de bords hydratés et de feuilletots dotés de sites d’échange de K dans les micas de l’horizon Ae contribue probablement à conférer à l’échange du K une vitesse plus élevée. Les quantités de K fixé dans les argiles de l’horizon Ae ne sont pas reliées au degré d’altération.
La destruction de la matière organique des argiles de l’horizon Ae par le peroxyde a considérablement augmenté et les vitesses d’échange de K et les quantités de K fixé. Ces augmentations ont été attribuées à l’élimination de l’effet de blocage que la matière organique adsorbée exerce sur l’échange et la fixation de K.


Резюме — С использованием натрий-тетрафенил-бора определена степень обмена ионов K⁺ для исходных и обработанных перекисью водорода слюдистых глин из пяти подзолистых почв. Кроме того определялось количество фиксированного K по отношению к NH₄. Глины горизonta Ae подобных почв содержали, главным образом, смешанно-слойный слюда-вермикулит-монтморillonит, в то время как глины горизонта C содержали слюду более дискретной природы.

Как и ожидалось, была установлена обратная зависимость между долей обменного K и степенью выветривания глин горизонта Ae; однако во всех образцах изученных почв, за исключением одного (наиболее выветрелого), степень обмена K в смешанно-слойной слюде из горизонта Ae была выше, чем в менее выветрелой, более дискретной слюде из горизонта C. Обилье в слюдах горизонта Ae гидратированных краев и слоёв с обнажёнными позициями обменного K, возможно, и обуславливает их более высокую степень обмена K. Количество K, фиксированного, в слюдах горизонта Ae, не зависит от степени выветривания.

Удаление органического вещества из глин горизонта Ae при обработке перекисью водорода приводило к значительному увеличению как степени обмена K, так и количества фиксированного K. Это увеличение способствовало ликвидации блокирующего влияния поглощенного органического материала на обмен и фиксацию K.