THERMAL STUDIES OF AMMONIUM FIXATION AND RELEASE IN CERTAIN CLAY MINERALS

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Abstract

The thermal decomposition of NH₄ ions adsorbed on kaolinite, illite, bentonite and vermiculite occurred over a wide range in temperature. The temperature of decomposition appeared to be influenced by the nature of the exchange site and by the entrapment of NH₄ ions in the lattice. The H ions that remained when NH₄ ions were decomposed interfered with this method of determining the amount of NH₄ held on the different exchange sites or fixed in the lattice of the clay materials.

Wyoming bentonite fixed 15 m.e. of NH₄ per 100 grams when the NH₄ saturated clay material was heated at 300° to 350° C. The loss of NH₃ from these fixed NH₄ ions produced an exothermic peak at 550°C in the differential thermal analysis curve for NH₄ bentonite.

The thermal decomposition of NH₄ saturated bentonite and a kaolinite clay has been investigated by Bottini (6, 7) and Cornet (9). They have shown that NH₃ is volatilized from these clays as the NH₄ ions are decomposed at high temperatures. Furthermore, from the relative rate of NH₃ loss at different temperatures, Cornet concluded that the site of the NH₄ ions on the clay determined the temperature at which they were decomposed. Working with NH₄ saturated bentonite, Cornet suggested that temperatures up to 125° C. decomposed NH₄ ions on the broken bond surfaces, while the rapid loss of NH₃ at 275° and 400° C. was due to NH₄ on exterior planar and interplanar surfaces, respectively.

In a study of vermiculite and its relation to biotite, Barshad (2) determined the weight loss due to NH₃ and water when NH₄ vermiculite was heated. Up to 255° C. the weight loss was due to water alone. Apparently the NH₄ ions on the vermiculite were not decomposed at this temperature. Between 255° and 500° C. a small amount of NH₃ was lost, whereas temperatures of 550° to 600° C. decomposed all of the NH₄ on the exchange.

It would appear from these investigations that NH₄ saturated clay minerals differ in the manner in which they lose NH₃ at elevated temperatures. Some of these differences are probably associated with the type of exchange sites holding the NH₄ ions on the clay. It is, however, also possible that differences arise because NH₄ ions are fixed in some clay minerals and not in others. The difference in thermal decomposition of NH₄ vermiculite and NH₄ bentonite, for instance, may be due to the fact that NH₄ ions are fixed in vermiculite but generally not in bentonite. If fixed

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NH₄ ions are decomposed at a characteristic temperature that is different from the exchangeable NH₄ ions, it is possible that thermal decomposition measurements could be used to determine fixed NH₄ in clays as well as to identify the presence of NH₄ fixing clay minerals. The objective of this study, therefore, was to determine whether a relationship existed between the thermal decomposition of adsorbed NH₄ and its fixation in clay minerals.

Differential thermal analyses are commonly used as one means of characterizing clay minerals. While each clay mineral group has in general a characteristic differential thermal curve, the individual curves obtained vary with the cation adsorbed on the clay. The differential thermal curves of NH₄ saturated clay minerals are of particular interest since the loss of NH₃ as well as water will influence the shape of the curve. It is evident from the differential thermal curves of vermiculite and bentonite obtained by Barshad (2, 3) that the effect of the adsorbed NH₄ varies with the clay mineral involved. Since these differences are probably related to the manner in which the clay minerals hold the NH₄ ions, differential thermal analyses were made in the present study to gain further information about the relationship between the thermal properties of adsorbed NH₄ and its fixation in the clay minerals. Differential thermal curves of the clays saturated with other ions were also obtained to further identify the clay minerals used in this study.

**Materials and Methods**

Samples of the two vermiculites investigated by Allison, et al. (1) were obtained from Dr. F. E. Allison for this study. One vermiculite was from Libby, Montana; the other, from Greenville, South Carolina. According to Allison, et al., both materials are actually vermiculite-biotite mixtures. Wyoming (Volclay) bentonite from the American Colloid Company and Goose Lake Grundite from the Illinois Clay Products Company were used as sources of montmorillonite and illite, respectively. Kaolinite of unknown origin was also used in this investigation.

The vermiculite flakes were about 0.25 inch in diameter. In some cases, therefore, the vermiculite was ground in a Christy-Norris Laboratory hammermill using a screen with round holes 1/16-inch in diameter. The other clay materials were used without previous fractionation except as noted in the individual experiments.

Fifty to 100 grams of the clay minerals was placed on a Buchner funnel and leached with 1000 ml. of 1 N NH₄Cl to saturate them with NH₄. They were washed with 70 per cent methanol until the leachate gave a negative test with Nessler reagent and then air dried. The dry NH₄ saturated clays were placed in a muffle furnace on a raised platform near
the thermocouple to be heated at different temperatures and for varying lengths of time. The temperature fluctuated within plus or minus 20° C. of the desired temperature.

To determine the amount of exchangeable and fixed NH₄ on the clays, both before and after the heat treatment, the systems were made alkaline with NaOH or KOH and the NH₃ distilled into a measured amount of 0.05 N HCl. The excess acid was titrated with a standard NaOH solution. Blank controls were included in each set of distillations. The NH₄ on the clay mineral displaced by K will be regarded as exchangeable, while that displaced by Na but not by K will be regarded as fixed in this investigation. In some cases the total NH₄ in vermiculite was determined by first digesting the sample in concentrated H₂SO₄.

Differential thermal analyses were made with automatic recording equipment. The sample holders and covers were made of 18-8 chrome-nickel steel. Pt—Pt (10% Rh) thermocouples were used to measure the differential temperature. The furnace temperature was measured with a chromel-alumel thermocouple in the center of the sample block. Powdered alumina was used as the inert material. The temperature was increased at the rate of 10° C. per minute.

**Time of Heating**

A study was first made to determine how long the NH₄ clay minerals should be heated at any one temperature. There is no evidence in the literature to indicate the stability of the adsorbed NH₄ to prolonged heating. It was, therefore, entirely possible that all of the NH₄ could be decomposed even at a relatively low temperature if the NH₄ clay mineral were heated long enough.

To determine the effect of time of heating, one gram samples of NH₄ saturated vermiculite, bentonite and illite were heated at a few specified temperatures for different periods of time. The NH₄ remaining on the clay mineral after the heating period was determined by distillation in 200 ml. of 1 N NaOH for 1 hour. In some cases, duplicate samples were distilled in 200 ml. of 1 N KOH for 1 hour.

_Bentonite_. The NH₄ saturated bentonite contained 74 m.e. NH₄ per 100 grams prior to heating. All of this NH₄ was displaced by distillation in either NaOH or KOH. That is, there was no fixed NH₄ in the initial NH₄ bentonite.

The heated bentonite was distilled only in NaOH. In each case the NaOH displaced all of the NH₄ on the bentonite. The results shown in Fig. 1 therefore indicate the total amount of NH₄ remaining on the bentonite after it was heated at different temperatures for different periods of time. It is apparent from these results that there was a rapid initial loss
of NH₃ at any one temperature followed by a slow but consistent loss as the heating period was extended.

Since NH₃ on the bentonite continues to be decomposed as the heating time is increased, it may be concluded that the fractions of NH₃ held on the different exchange sites cannot be sharply distinguished by this method. This does not preclude the possibility that the decomposition temperature of the NH₃ ions varies with the exchange site occupied. In fact, the temperature dependence of the rapid initial loss of NH₃ would suggest that the NH₃ ions on the bentonite do vary in their decomposition temperature. The difficulty in distinguishing between the different NH₃ exchange sites is probably due to the H ions that remain on the exchange sites when the NH₃ is driven off. These H ions may interchange with exchangeable NH₃ ions on other sites. By this process, NH₃ ions that would normally not be decomposed at the temperature employed may be transferred to sites where they can be decomposed. Thus, the process involved

![Fig. 1. NH₃ released from Wyoming bentonite by a one hour distillation in 200 ml. of 1 N NaOH after the NH₃ saturated bentonite has been heated at different temperatures for varying lengths of time.](image-url)
in these prolonged heating experiments is probably not merely a volatilization of \( \text{NH}_3 \) from the \( \text{NH}_4^+ \) ions on certain exchange sites at a specific temperature but one of \( \text{H} - \text{NH}_4 \) exchange as well.

Evidence that \( \text{H} \) ions are left on the bentonite when \( \text{NH}_4 \) bentonite is heated was obtained by Cook (8), who prepared a \( \text{H} \) saturated bentonite by heating \( \text{NH}_4 \) bentonite at 450\(^\circ\) C. for 48 hours. In the present study, the pH of the \( \text{NH}_4 \) bentonite was determined before and after heating at 400\(^\circ\) C. for 24 hours. The pH determinations were made with a glass electrode and a 1:5 bentonite to water ratio. The pH of the unheated sample was 7.3 and of the heated sample was 4.0.

**Vermiculite.** Unground Montana vermiculite which had been exfoliated with \( \text{H}_2\text{O}_2 \) prior to \( \text{NH}_4 \) saturation was used in this experiment. The \( \text{NH}_4 \) saturated vermiculite contained 83 m.e. of \( \text{NH}_4 \) per 100 grams. Distillation for 1 hour in 200 ml. of 1 \( \text{N} \) \( \text{NaOH} \) released 69 m.e. of \( \text{NH}_4 \) per 100 grams, whereas a similar distillation with \( \text{KOH} \) released only 3 m.e. of \( \text{NH}_4 \) per 100 grams. Data reported elsewhere\(^3\) show that a longer distillation with \( \text{NaOH} \) would release all of the \( \text{NH}_4 \) but the \( \text{KOH} \) would release no more if the time of distillation were increased. Thus, according to the procedure of Barshad (4), the vermiculite contained 80 m.e. of fixed \( \text{NH}_4 \) per 100 grams.

When the \( \text{NH}_4 \) vermiculite was heated at temperatures up to 400\(^\circ\) C. and for as long as 80 hours, there was little or no loss of \( \text{NH}_3 \) as shown in Fig. 2. Apparently, temperatures greater than 400\(^\circ\) C. are needed to decompose the \( \text{NH}_4 \) on vermiculite. These results, therefore, cannot be used to evaluate the effect of time of heating. That is, it is not known if there would be a gradual loss of \( \text{NH}_3 \) with time once the decomposition temperature of at least part of the adsorbed \( \text{NH}_4 \) is exceeded.

The results of this study do, however, show that the relative ease of \( \text{NH}_4 \) displacement by \( \text{Na} \) is influenced by the temperature at which the samples were previously heated. With temperatures up to 250\(^\circ\) C., a one hour \( \text{NaOH} \) distillation continued to replace about 69 out of the 83 m.e. of \( \text{NH}_4 \) on the vermiculite. When the samples were heated at 300\(^\circ\) or 350\(^\circ\) C., however, more of the \( \text{NH}_4 \) on the vermiculite was displaced by \( \text{NaOH} \). Although the vermiculite used in this experiment was exfoliated with \( \text{H}_2\text{O}_2 \) before it was \( \text{NH}_4 \) saturated, it exfoliated even more when it was heated at 300\(^\circ\) C. or higher. The increase of \( \text{NH}_4 \) displacement by \( \text{NaOH} \) is, apparently, the result of this exfoliation. Since \( \text{NH}_4 \) was not lost at these temperatures (see the constancy of the total \( \text{NH}_4 \) values in Fig. 6 also) the exfoliation observed must have been due to the volatilization

\(^3\) Hanway, J. J., Scott, A. D., and Stanford, G., Replaceability of ammonium fixed in clay minerals as influenced by ammonium and potassium in the extracting solution. Submitted for publication.
and loss of water alone. It should be noted that the amount of NH₄ replaced by KOH distillation was not influenced by this exfoliation. That is, the NH₄ would still be considered as being fixed.

Samples heated at 400° C. did not release as much NH₄ to NaOH in one hour as those heated at 300° C. even though exfoliation occurred in both cases. As the heating temperature was increased from 350° C. to 400° C., it is possible that K was released from the biotite present in the sample. Kolterman and Truog (10) have shown that heating NH₄ biotite to 500° C. does release K. Such a release of K in the present study would account for the decrease in NH₄ displacement since Hanway, et al., have shown that very small amounts of K interfere with the release of fixed NH₄ by NaOH. The fact that the samples heated at 400° C. released the same amount of NH₄ as those heated at 250° C. is probably coincidental.

Results from a similar experiment with unground South Carolina...
vermiculite are given in Fig. 3. This vermiculite sample was not exfoliated with \( \text{H}_2\text{O}_2 \). The results are quite similar to those obtained with the Montana vermiculite. In this case there is a more pronounced decrease in the \( \text{NH}_4 \) displaced by Na as the time of heating at 400° C. was increased. This decrease is probably not due to a loss of \( \text{NH}_3 \) since the total \( \text{NH}_4 \) data given in Fig. 7 shows that there is no loss of \( \text{NH}_3 \) after heating for 24 hours at 400° C. The decrease is more likely due to a gradual release of K from the biotite which renders the fixed \( \text{NH}_4 \) less and less easily replaced by Na.

**Illite.** Prior to heating, the \( \text{NH}_4 \) saturated illite used in this study contained 26 m.e. of adsorbed \( \text{NH}_4 \) per 100 grams which could be displaced by distillation in \( \text{NaOH} \). Distillation in \( \text{KOH} \) displaced all but 1 m.e. of this adsorbed \( \text{NH}_4 \). The heated illite was distilled only in \( \text{NaOH} \).

The effect of heating the \( \text{NH}_4 \) illite at different temperatures for varying lengths of time is shown in Fig. 4. These results are similar to those obtained with bentonite in that \( \text{NH}_3 \) was lost rapidly at first and then grad-

![Graph showing NH₄ released from vermiculite by distillation](image-url)
usually as the heating time was extended. However, essentially all of the 
NH$_4$ on the illite was decomposed by heating at 300° C., while a consider-
able portion of the NH$_4$ remained on the bentonite even after pro-
longed heating at 400° C. This difference must be associated with the 
interlayer NH$_4$ ions that are present in the bentonite but not in the 
illite. It will be shown later that some of these interlayer NH$_4$ ions in 
bentonite are fixed when the clay mineral is heated to about 350° C. and 
that these fixed NH$_4$ ions in bentonite resist decomposition at tempe-
ratures below 400° C. There was little or no NH$_4$ fixation in the illite. It is,

\[ \text{Fig. 4. NH}_4 \text{ released from illite by a one hour distillation in 200 ml. of 1 N NaOH} \]
\[ \text{after the NH}_4 \text{saturated illite had been heated at different temperatures for varying lengths} \]
\[ \text{of time.} \]

Therefore, apparent from the illite results that prolonged heating at 300° 
C. will decompose most of the adsorbed NH$_4$ as long as it is exchangeable.

**Temperature of Heating**

To determine the relationship between the decomposition of NH$_4$ on 
various clay minerals and the temperature of heating, one or two gram 
samples of NH$_4$ saturated minerals were heated for 24 hours. This time of 
heating was selected because it was beyond the period in which the 
initial rapid loss of NH$_3$ occurred and should provide for reasonably re-
producible results. The total NH$_4$ remaining on the clay minerals was 
determined by boiling a sample for 1 hour in concentrated H$_2$SO$_4$, making 
the digest alkaline with NaOH and distilling. NH$_4$ released by NaOH 
and KOH was determined by distilling a sample in 200 ml. of 1 N solu-
tions of the hydroxides for one hour.

**Bentonite.** The amount of NH$_4$ released from the bentonite by NaOH
distillation was the same in all cases as that released by the H₂SO₄ digestion; therefore, in Fig. 5 a curve for the release to NaOH is not given. The curve showing the total NH₄ retained by the bentonite at various temperatures is similar to those obtained by other workers (5, 6, 7). Little NH₃ was lost at temperatures up to 200° C. The loss of NH₃ increased rapidly as the temperature increased from 200° to 300° C. and again from 350° to 450° C. with a decreased rate of NH₃ loss as the temperature increased from 300° to 350° C. Very little NH₄ remained on the bentonite after heating at 500° C. for 24 hours.

Barshad (3) has proposed that adsorbed NH₄ not replaced by distillation in KOH may be considered to be fixed. After heating at temperatures up to 200° C., KOH released all but 2 m.e. of the NH₄ on the bentonite. However, after heating at temperatures above this, and especially at temperatures from 300° to 400° C., a considerable portion of the NH₄ on the mineral was fixed; i.e., it was not replaced by KOH. As much as 15 m.e. of NH₄ per 100 grams was fixed at these higher temperatures.
Since the bentonite sample used in this study was not fractionated, the question arose as to whether the NH₄ fixation which occurred represented fixation by a normally expanding lattice mineral like montmorillonite or was due to the presence of a degraded micaceous mineral such as illite in the bentonite. In this case, since the essentially non-expanding micaceous materials would tend to exist in larger particle sizes, the <.2 micron fraction of the bentonite should be relatively free of these materials. A suspension of the Volclay bentonite, which is normally Na saturated, was therefore run through a Sharples super centrifuge to separate out some of the <.2 micron fraction. This fraction was NH₄ saturated by passing the suspension through an NH₄ saturated Amberlite IR-100 resin exchange column.

The NH₄ released by NaOH and KOH distillation from this NH₄ saturated <.2 micron fraction following different heating treatments is shown in Table 1. There was no fixed NH₄ in the unheated samples or in the sample dried at 110° C. However, just as in the original unfractionated bentonite sample, there was 15 m.e. of NH₄ per 100 grams fixed in the <.2 micron clay material after it was heated at 350° C. for 24 hours.

<table>
<thead>
<tr>
<th>Heating temperature</th>
<th>Time of heating, hrs.</th>
<th>m.e. NH₄ released per 100 grams of bentonite by:</th>
<th>m.e. NH₄ fixed per 100 grams of bentonite (NaOH—KOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unheated</td>
<td>0</td>
<td>126</td>
<td>0</td>
</tr>
<tr>
<td>110° C.</td>
<td>24</td>
<td>118</td>
<td>0</td>
</tr>
<tr>
<td>350° C.</td>
<td>24</td>
<td>38.8</td>
<td>23.6</td>
</tr>
</tbody>
</table>

The distillation was continued for 4 hours to assure complete release of all the NH₄ that would be released, but very little was released after the first hour. It was observed that the NH₄ clay, after drying and heating at 350° C. consisted of large flakes. These flakes broke up and the clay was completely dispersed in the NaOH solution whereas the large flakes persisted in the KOH solution. These results suggest that NH₄ is fixed in montmorillonite at this higher temperature because the contracted lattice resists re-expansion by KOH.

_Vermiculite_. The vermiculites lost no NH₃ at temperatures up to 400° C. as shown in Figs. 6 and 7. At temperatures above 500° C. the Montana vermiculite lost large amounts of NH₃ but still retained 9 m.e. of NH₄ per 100 grams after heating at 600° C. for 24 hours. The South Carolina vermiculite started to lose NH₃ at a slightly lower temperature, and after heating at 550° C. it contained essentially no NH₄.
After heating at temperatures up to 250° C., NaOH distillation failed to replace 2 to 3 m.e. of the total NH₄ per 100 grams during a one-hour distillation. However, heating at 300° C. resulted in essentially complete release of the NH₄ by NaOH. As discussed earlier, the exfoliation of vermiculite at 300° C. definitely resulted in the NH₄ being more easily replaced by NaOH. After heating at temperatures greater than 400° C., a one-hour distillation in NaOH failed to release considerable quantities of the NH₄ present. This reduction in the amount released by Na was probably due to a release of K at these high temperatures from the biotite present in the sample. This conclusion was substantiated by the observation that prolonged distillation, which has been shown to be effective when small amounts of K were present (10), resulted in complete release of the NH₄. Furthermore, removal of the potassium by precipitation resulted in a complete replacement of the NH₄ by Na in one hour.

The KOH distillation removed very little NH₄ from the vermiculite,
but it continued to release some NH₄ even when the samples were heated at 500° C. There was no increase in the release of NH₄ by KOH even though on heating at temperatures of 300° or above the vermiculite exfoliated, with an expansion of two to three times its original volume. This expansion of the lattice obviously did not make the NH₄ ions more easily replaced by K.

**Illite.** The NH₄ saturated illite used in this study released 20 m.e. of NH₄ when it was distilled in NaOH. When it was digested in concentrated H₂SO₄ for 1 hour and then distilled in NaOH it released a total of 24 m.e. of NH₄. The difference in NH₄ released is probably due to the presence of organic matter since the original untreated illite contained nitrogen equivalent to 4.7 m.e. of NH₄ per 100 grams as determined by Kjeldahl analysis. The NH₄ displaced by distillation in NaOH alone is probably a good measure of the NH₄ adsorbed on the illite. In any case, both the total NH₄ and NaOH released NH₄ values given in Fig. 8 show the same general change in the NH₄ retained at different temperatures. Up to 200° C., there was a slow but gradual loss of NH₄, a more rapid loss between 200° and 350° C., and by 400° C. essentially all of the NH₄ was decomposed.

The amount of NH₄ released by KOH was consistently 1 to 2 m.e. per 100 grams less than that released by NaOH. Thus, there was little NH₄
fixed in this illite, and the amount fixed was not influenced by heating at higher temperatures. The relative absence of NH₄ fixation is probably due to the fact that the illite received no pretreatment, such as electrodialysis, that would remove fixed K. Thus, all positions capable of fixation were already occupied by K ions.

![Graph showing fixation and release of ammonium by illite as influenced by heating for 24 hours at different temperatures.](image)

**Fig. 8.** Fixation and release of ammonium by illite as influenced by heating for 24 hours at different temperatures.

*Kaolinite.* The NH₄ saturated kaolinite contained 7.5 m.e. of NH₄ per 100 grams. NaOH distillation, KOH distillation and H₂SO₄ digestion prior to alkaline distillation all released the same amount of NH₄ from kaolinite. Therefore, only the total NH₄ values have been used in Fig. 9 to show the effect of heating NH₄ kaolinite. From these results, it appears that the NH₄ on kaolinite is gradually decomposed as the temperature is increased from 50° to 400° C.

![Graph showing release of ammonium by kaolinite as influenced by heating for 24 hours at different temperatures.](image)

**Fig. 9.** Release of ammonium by kaolinite as influenced by heating for 24 hours at different temperatures.
Comparison of different minerals. The percentage of the total NH$_4$ lost by each of the minerals at different temperatures is given in Fig. 10. In general each of the minerals loses NH$_3$ over a wide range of temperatures. One of the biggest differences between minerals is that illite, kaolinite and bentonite begin to lose NH$_3$ at 100° C., while vermiculite loses little or no NH$_3$ until 400° C. Illite and kaolinite lose all of their NH$_3$ by 400° C.; thus their curves do not overlap the vermiculite curve. The NH$_4$ bentonite thermal decomposition curve, however, overlaps both the illite and vermiculite curves. These differences appear to be primarily determined by the presence of fixed NH$_4$.

Illite and kaolinite with NH$_4$ primarily on external surfaces and in an exchangeable location readily lose NH$_3$ by thermal decomposition. The illite curve conforms with the suggestion of Cornet (9) that NH$_4$ on broken bond surfaces is decomposed by 125° C., while the maximum evolution of NH$_3$ from exterior planar surfaces occurs at 275° C. The NH$_4$ on kaolinite, which is presumably all on broken bond surfaces, however, was not entirely decomposed by 125° C. Instead, there was a gradual loss

Fig. 10. Percentage of the total NH$_4$ lost from different minerals on heating for 24 hours at different temperatures.
of NH₃ up to 400° C. with only a slight indication of a decrease in slope of the curve between 100° and 200° C. It should also be noted that this kaolinite curve is very different from the curve Bottini (7) obtained with a kaolinite clay.

The inflections in the bentonite curve showing a more rapid loss of NH₃ at temperatures of about 275° C. and 400° C. are similar to those observed by Cornet (9). The inflection at 275° C. is probably associated with the loss of NH₃ from planar surfaces as Cornet has suggested, since illite also shows an inflection at this temperature. The results of this investigation, however, indicate that the fixation of NH₄ on bentonite caused the decrease in the slope of the total NH₃ curve between 300° and 350° C., which gave rise to another distinct inflection at 400° C. The exchangeable NH₄ ions, on the other hand, continued to decrease at a fairly constant rate over the temperature range of 300° to 400° C. It may be concluded that the interplanar exchangeable NH₄ ions on bentonite are not more resistant to thermal decomposition than the exterior planar ions. It is expected that in the absence of NH₃ fixation the curve for the decrease in total NH₃ on bentonite would be similar to that of illite. In fact, a plot of the decrease in exchangeable NH₄ only does show very little indication of separate inflections at 275° and 400° C.

It is apparent from Fig. 5 that the fixed NH₃ ions resisted thermal decomposition until the temperature exceeded 400° C. The NH₃ loss at higher temperatures was, however, partly due to exchangeable NH₄ ions. Since the exchangeable NH₃ ions were not entirely decomposed before the fixed NH₃ ions started to decompose, the fixed and exchangeable NH₃ on bentonite cannot be distinguished by this method. It is entirely possible that the observed exchangeable NH₄ at these higher temperatures become exchangeable because of a H displacement of the fixed NH₃ during the cooling period. This point is being investigated at the present time.

The NH₃ in vermiculite resists decomposition until 400° C. The high temperature of decomposition is probably due to the fact that essentially all of the NH₃ on vermiculite is fixed. A comparison of the vermiculite and bentonite curves shows that most of the fixed NH₃ in vermiculite required a higher temperature for decomposition than fixed NH₃ in bentonite. This observation is in line with the ease with which NH₃ is fixed in the two minerals. While vermiculite will fix NH₃ under moist conditions, NH₃ bentonite must be dehydrated at 300° to 350° C. before the lattice is sufficiently contracted to fix the NH₃.

In general it may be concluded from these results that NH₃ held on sites where it is fixed required a higher decomposition temperature than NH₃ ions on sites where they were not fixed. There was, however, no case where heating at one temperature resulted in the loss of NH₃ from
the exchangeable NH₃ leaving just the fixed NH₄ on the clay. The temperature of decomposition, therefore, cannot be used to distinguish sharply between fixed and exchangeable NH₄.

**Differential Thermal Analysis**

The differential thermal curves obtained for the various clay minerals are given in Figs. 11, 12, 13 and 14. The curves obtained with the natural material; that is, the first curve in each figure, are quite typical for the mineral concerned. It is apparent from Fig. 11 that adsorbed NH₄ had no effect on the kaolinite curve.

The large ill-defined exothermic peak with a maximum at 400° C. in the illite curve, Fig. 12, is not usually observed. This peak is probably due to the presence of organic matter as indicated by the nitrogen content of the untreated illite. This exothermic peak detracts from the usefulness of the differential thermal curve in the thermal study of NH₄ on the clay. Curve 3 in Fig. 11 indicates that the NH₄ does influence the curve, either by its own decomposition, or by its effect on the impurity giving rise to the peak.

The curves for the natural (Na saturated) and K saturated bentonite in Fig. 13 are characteristic of those generally obtained for montmorillonite clay. The two endothermic troughs were not affected by any of the

![Differential Thermal Curves](image-url)
Fig. 12. Influence of adsorbed cation on the differential thermal curve for illite.

Fig. 13. Influence of adsorbed cation on the differential thermal curve for Wyoming (Volclay) bentonite.
other treatments except that shown by curve 5. In this case, the differential thermal analysis was made soon after the bentonite had been heated at 350° C. and the clay mineral apparently had not had time to become rehydrated. Since the bentonite was not protected from the atmosphere during the intervening period, it apparently does not exhibit the rapid rehydration Barshad (2) observed with vermiculite.

Saturating the bentonite with NH₄ resulted in the production of an exothermic peak at about 550° C. This was observed with both the unfractoned and the <.2 micron material. Curves obtained for an NH₄ saturated Mississippi bentonite were similar except that the exothermic peak occurred at 425° C. These results differ from those of Barshad (3) in that only one exothermic peak was found, whereas the NH₄ bentonites he studied showed two peaks, one at 360° C. and another at 470° C.

It is evident from curves 5, 6 and 7 that the NH₄ fixed in bentonite at 300° to 350° C. is responsible for the 550° C. exothermic peak in the differential thermal curve. The peak was still evident in curve 5 for NH₄ bentonite that had been previously heated at 350° C. for 24 hours even though the sample retained only 31 of the original 80 m.e. of NH₄ per 100 grams after the preheating. On the other hand, when a K saturated bentonite was heated at 350° C. for 24 hours and then leached with NH₄Cl to saturate the clay with NH₄, the differential thermal curve exhibited no exothermic peak. Preheating the K bentonite at 350° C. apparently fixed K ions in those sites capable of fixing NH₄ ions. As a result the 66 m.e. of NH₄ per 100 grams adsorbed by this sample of clay prior to the differential thermal analysis were exchangeable ions that were decomposed without influencing the differential thermal curve. Curve 7 was obtained with bentonite that had been previously heated at 350° C. for 24 hours to fix NH₄ ions and then saturated with NH₄. In this case the sample was found to contain 66 m.e. of exchangeable NH₄ per 100 grams.

The exothermic peak in the bentonite differential thermal curves occurred in all cases where fixed NH₄ was present. If the NH₄ ions were blocked from the fixing sites by prior fixation of K, the curve exhibited no exothermic effects from NH₄ ions on the bentonite. Apparently any exothermic effect due to the loss of NH₃ from the exchangeable NH₄ ions is counteracted by a concurrent loss of water. On the other hand, the fixed NH₄ ions are decomposed and NH₃ lost without a concurrent loss of water, since an exothermic peak occurs. This indicates that the exchangeable NH₄ ions in bentonite are closely associated with water molecules while the fixed NH₄ ions are not.

The differential thermal curves obtained for Montana vermiculite, Fig. 14, correspond with those obtained by Barshad (2). In the curve for
the natural vermiculite there are low temperature endothermic troughs characteristic of Ca or Mg on the exchange complex. When the Ca and Mg were replaced by NH₄ ions, these low temperature troughs were eliminated. In this regard, vermiculite is different from bentonite which exhibits a low temperature endothermic trough even with NH₄ on the exchange complex. Apparently there is much more water associated with the exchangeable NH₄ ions in bentonite which gives rise to this endothermic effect as it is lost.

According to Barshad (2), each NH₄ ion in vermiculite is associated with one molecule of water. Furthermore, he has shown that the NH₄ lost from vermiculite by heating is accompanied by an equivalent loss of water. Any exothermic effects from the loss of NH₃ are apparently counteracted by the endothermic effect of the concurrent water loss since the NH₄ vermiculite differential thermal curve has the appearance of an anhydrous material.

**Conclusions**

The NH₄ ions on the kaolinite and illite used in this study were largely exchangeable. These exchangeable NH₄ ions started to decompose at temperatures below 100° C. and were completely decomposed by heating for 24 hours at 400° C. On the other hand, fixed NH₄ ions on vermiculite were stable until nearly 400° C. and required 24 hours of heating at 600° C. to decompose them entirely. The thermal decomposition curve for the NH₄ ions on bentonite was unique because some of the NH₄ ions which were initially exchangeable were fixed when the clay was heated at 300° to 350° C. Like kaolinite and illite the exchangeable NH₄ ions on bentonite started to decompose below 100° C., and like vermiculite the fixed NH₄ did not decompose until the temperature exceeded 400° C.
From these results it may be concluded that fixed NH₄ ions are not as readily decomposed as the exchangeable ions.

The thermal decomposition curve for the NH₄ adsorbed on illite supports Cornet's (9) suggestion that the exchange site of the NH₄ ions influences the temperature at which they are decomposed. In the case of NH₄ bentonite, however, the two distinct inflections in the curve between 200° and 500° C. does not occur because of the decomposition of NH₄ ions on different exchange sites. Instead, the two inflections occur because there is a decrease in the amount of NH₃ lost as NH₄ ions are fixed in the bentonite when this clay material is heated at 300° to 350° C.

While the fixed NH₄ ions appears to resist thermal decomposition more than the exchangeable NH₄ ions, no sharp distinction could be made between the two forms by the method used. In bentonite, some exchangeable NH₄ remained on the clay up to 500° C. where the fixed NH₄ was also decomposed. Likewise, a sharp distinction between the fractions of exchangeable NH₄ ions held on different sites could not be made because there was a slow but consistent loss of NH₃ when NH₄ saturated illite or bentonite was heated at one temperature for an extended period of time. The difficulty in both cases was that H ions remained when the NH₄ ions were decomposed. By exchange these H ions caused NH₄ ions that were normally not decomposed at the temperature employed to be transferred to sites where they were decomposed.

An exothermic peak occurred at 550° C. in the differential thermal analysis curve for NH₄ bentonite. This peak was due to the loss of NH₃ from the NH₄ ions fixed in bentonite at 300° to 350° C. The fixed NH₄ ions in vermiculite on the other hand produced no exothermic effects. It is apparent that the fixed NH₄ ions in bentonite do not have water associated with them like they do in vermiculite.

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