ABSTRACT

The clay mineralogy of a soil profile developed in a New England glacial till has been studied to a depth of 55 in. Degraded soil micas, probably produced by weathering, have been chloritized by both iron and aluminum hydroxide complexes. Aluminum and iron determinations and X-ray analyses indicate that iron chloritization has played the greater role. Citrate-extractable chlorite exists to a depth of 55 in. X-ray and heat stability data indicate that the chlorite is better developed or crystallized near the surface. X-ray and glycol retention data suggest that intense weathering at the surface has reduced the surface charge density of some of the degraded micas.

INTRODUCTION

During acid weathering, considerable interlayer potassium may be removed from micas in the soil. These degraded minerals generally expand appreciably upon glycolation but collapse back to a non-expanding mica structure after treatment with KCl solutions. The original purpose of this investigation was to study the effects of potassium treatment and the accompanying expulsion of interlayer water upon the engineering properties of a degraded soil clay. It was found that treatment of the surface soil (0-16 in.) with 1 N KCl solution for 1 day reduced the cation-exchange capacity by 25 percent. However, 14-day KCl treatment increased the exchange capacity to slightly above the original value. Soil from a depth of 55 in. gave a 20 percent increase in exchange capacity after 1-day KCl treatment. This increase in exchange capacity, which was thought to be related to the removal of adsorbed aluminum or iron, or both, led to a more detailed examination of the mineralogy of the soil profile.

The study has shown that the degraded soil micas or vermiculites have been chloritized by Fe and Al complexes. The study of chloritization presented here has two features not previously reported: (1) Chloritization was confirmed to a depth of 55 in., which is much deeper than previously reported, and (2) the interlayer material producing the chloritization contains much more iron than aluminum.
MATERIALS AND METHODS

The soil profile under consideration occurs in the steep side slope (approximately 55 degrees) near the crest of a drumlin in East Boston. The profile, which is typical of the Brown Podzolic Group, was studied mineralogically to a depth of 55 in. Although well above the water table, the dense nature of the till apparently prevents good drainage, as extensive mottling caused by the precipitation of iron oxides was observed around 24 in. Fissures in the soil as deep as 55 in. also contained coatings of precipitated iron oxides or hydroxides. The pH of the soil water varied from about 4 at the surface to 4.7 at 55 in. According to Tamura, Hanna and Shearin (1959) the pH of Brown Podzolic soils is rarely less than 4.

The X-ray work described herein was performed using both a Philips diffractometer with copper radiation generated at 40 kV and 15 mA, and a powder camera using chromium radiation. The glycol retentions were run by the procedure described by Martin (1955). X-ray spectrographic procedures were used to determine the cation-exchange capacity, total potassium, and extractable aluminum and iron.

The cation-exchange capacity determinations were run on clays homoionic in barium (5 washes in 1N BaCl₂ solution over a period of 24 hr), with the salt concentration washed down to 10⁻³M before air drying and X-raying. The barium and potassium contents were determined by comparison with standards.

Aluminum and iron were extracted by the sodium citrate procedure of Tamura (1958). No attempt was made to remove the free iron oxides before the citrate treatments. The extracted aluminum and iron were determined spectrographically by dipping filter strips in the solution extracts or their concentrates, X-raying the air-dried filter strips, and comparing the unknowns with standards prepared in the same manner.

A separate treatment for free iron oxide removal was made employing the extraction procedure of Mitchell and Mackenzie (1954). The iron concentration in the extract was determined colorimetrically using ortho-phenanthroline.

ANALYTICAL RESULTS

The analytical results are reported for the <1 μ clay. The X-ray results are presented first, followed by the results of the chemical work.

X-Ray Analyses

All 25 lines recorded on film from X-ray powder samples are attributable to mica and chlorite and a small amount of quartz. Changes in the hydration state between air dry and water wet or glycolated samples indicate that a swelling mineral is present. Both dioctahedral and trioctahedral layer silicates are present, as indicated by two 060 reflections.

Figure 1 shows changes in the X-ray diffraction traces produced by variations in the hydration state and the presence of different exchangeable
Citrate extracted and unextracted samples, homoionic in barium and potassium, in glycolated and air-dried states, are shown in the figure. In general four citrate extractions at pH 7.3 and 100°C were performed to remove the interlayer aluminum and iron complexes.

Glycolation of unextracted, air-dried Ba samples produced very little effect although the 14 Å peaks for the samples at 27 and 55 in. appear to contain some slightly expansible mineral. The effect of glycolation on the air-dried K samples was also insignificant. Comparison of the unextracted Ba and K samples shows that considerable collapse has resulted from the KCl treatment, particularly in the 4 lower samples. The reduced size of the 14 Å peak is
accompanied by an increase in the 10 Å peak and a pronounced 14–10 Å background. This behavior suggests that a vermiculitic component is present in the soil. The sample from 8 in. showed very little collapse upon K saturation, suggesting the presence of chlorite rather than vermiculite. Later tests show that this material is actually a low charge, chloritized vermiculite.

Pronounced changes in X-ray characteristics accompanied the sodium citrate extraction. The Ba sample showed pronounced expansion from about 14 Å to 16.5 Å upon glycolation suggesting the presence of vermiculite (Walker, 1957, p. 160). KCl treatment of the extracted clays resulted in complete collapse of the expansible phase in both the air dry and glycolated states. After collapse only a very tiny residual 14 Å peak remained accompanied by a strong 7 Å peak and a very strong 10 Å peak. The strength of the 7 Å peak relative to the 14 Å peak suggests that iron chlorite is an abundant constituent of this extracted clay.

Comparing the K clays before and after citrate extraction, one sees that the 14 Å phase is stronger than the 7 Å phase at all depths before extraction and the opposite after extraction. Some chlorite has been removed from all samples by the citrate extraction, greatly reducing the size of the 14 Å peak. It also appears as though the 14 Å phase decreases with depth in the unextracted K clay. In the extracted K clays, the 14 Å and 7 Å peaks appear to

Figure 2.—X-ray (CuK₂) diffractometer traces for heat treatments on < 1μ clay at indicated temperatures for 30 min.
weaken greatly with depth. This may be due to a reduced content of iron
chlorite, or poorer crystallinity with depth, or both. Increasing the number
of citrate extractions from 4 to 16 on the 55 in. sample gave no appreciable
change in the X-ray pattern.

In Fig. 2, the heat stability of the chloritized clay is shown for unextracted
samples from depths of 8 and 55 in. For the 8-in. sample there is a sequence
of events which is typical of chlorites except for a 12.3 Å phase, representing,
perhaps, an interstratified complex. At 350°C most of the 14.2 Å phase had
vanished still leaving a fairly strong 7.1 Å peak. At 500°C, the 14.2 Å peak
had shifted to 13.8 Å and increased greatly in intensity at the expense of a
much weakened 7.1 Å peak. At 600°C, the 13.8 Å peak had further intensified
and the 7.1 Å peak disappeared. It should be noted that an extracted sample
from 8 in. gave identical traces at 350°, 500°, and 600°; thus chlorite existing
at 25°C was collapsed completely by the 350°C heat treatment.

The sample from 55 in. gave similar results except that a good 13.8 Å peak
did not appear upon heating. The 12.3 Å peak is considered to be an interlayer
complex consisting of iron chlorite and mica. The diffraction trace at 350°C
is identical with diffraction traces of this same clay after citrate extraction
and K saturation. The extractable 14 Å phase again appears to be unstable
even at 350°C.

A comparison of the samples from 8 to 55 in. indicates some differences
in the heat stability of the 7 Å peaks. At 500°C, the 7 Å peak is present in the
8-in. sample and absent from the 55-in. sample, suggesting, therefore, a
greater heat stability of the iron chlorite in the 8-in. sample, possibly due to
better crystallinity.

Chemical Analyses

The results of the glycol retentions, exchange capacity determinations,
potassium analyses, and iron and aluminum determinations are presented
under three separate headings below. The data are tabulated in Table 1.

Unextracted clay.—The term unextracted clay refers to barium-saturated
clay samples which were not treated with sodium citrate. K₂O analyses on
the clays before and after barium saturation gave identical results. The
percent K₂O in the clay showed no particular depth function, remaining at
about 3.1 percent from 0 to 55 in. The cation-exchange capacity also showed
no regular change although the highest value of 35 meq/100 g occurred at the
surface. The glycol retentions also showed no regular change although the
lowest value occurred in the surface sample where chloritization is best
developed.

Citrate extracted clay.—The effect of sodium citrate extraction was pro-
nounced. The cation-exchange capacity rose in all samples by 9 to 20 meq/
100 g. The greatest increase occurred in the sample from 18 in. in which the
C.E.C. rose from 21 to 41 meq/100 g. It should also be noted that the C.E.C.
of these extracted clays increases fairly regularly towards the surface from
about 34 to 50 meq/100 g.
Table 1.—Analytical Data for the <1 μ Clay from a New England Till Soil

<table>
<thead>
<tr>
<th>Sample depth (in.)</th>
<th>K₂O (%)</th>
<th>Cation-exchange capacity (meq/100 g)</th>
<th>Glycol retention (mg/g)</th>
<th>Free iron oxide (meq Fe³⁺/100 g)</th>
<th>In solution (meq/100 g)</th>
<th>Cation-exchange capacity (meq/100 g)</th>
<th>Glycol retention (mg/g)</th>
<th>Ba</th>
<th>K</th>
</tr>
</thead>
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<tr>
<td>8</td>
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<td>35</td>
<td>65</td>
<td>196</td>
<td>285†</td>
<td>23</td>
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<td>169</td>
<td>16</td>
<td>n.d.§</td>
<td>41</td>
<td>82</td>
<td>n.d.</td>
</tr>
<tr>
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<td>28</td>
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<td>165</td>
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<td>43</td>
</tr>
<tr>
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<td>78</td>
<td>218</td>
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</tr>
<tr>
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<td>215</td>
<td>43</td>
<td>21</td>
<td>35</td>
<td>74</td>
<td>39</td>
</tr>
</tbody>
</table>

* Fractionated barium clay, unextracted.
† Clay after treatment with sodium citrate; 4 extractions except for 8-in. sample where 8 extractions were used.
‡ Removed in first 4 extractions; second 4 extractions removed an additional 215 meq Fe³⁺/100 g.
§ n.d., not determined.
The glycol retention decreased in all but the surface clay as a result of extraction, and although the decrease amounts to only 4 or 5 mg/g, it is consistent and significant. These results are very interesting since an increase was expected when the Fe and Al complexes were removed. The reason for these changes is described later. A column showing the decrease in glycol retention upon K saturation is also given in Table 1. In the lower three samples (27, 43 and 55 in.), the glycol retention decreased by 35 to 38 meq/100 g. In the surface sample (8 in.) it dropped by only 21 meq/100 g. This difference is believed to be related to a lesser charge deficiency or greater permanent chloritization in the surface clay as discussed later.

Aluminum and iron determinations.—The free iron oxide content expressed in meq of Fe$^{3+}$ per 100 g of clay varies from 165 to 218 meq/100 g and is more or less constant with depth. This free iron was easily removed, 95 percent coming out in the first extract. The resulting clay showed no tendency to swell upon glycolation. This is in agreement with Tamura (1958), who also found that the removal of free iron oxides caused no swelling whereas citrate extraction did.

The iron removed by eight citrate extractions of the surface clay (8 in.) amounted to 500 meq of Fe$^{3+}$/100 g of clay, of which 285 meq/100 g was removed in the first four extractions. The total aluminum extracted from this sample amounted to 23 meq of Al$^{3+}$/100 g of clay and was 99 percent removed by the first four extractions. The large amount of citrate-extractable iron suggests that iron has taken part in the chloritization, particularly in view of the fact that removal of the free iron oxides produced no swelling whereas removal of citrate-extractable iron allowed swelling. Certainly, iron chloritization is consistent with the relative strengths of the 14 and 7 Å chlorite peaks.

Four citrate extracts of the 55-in. sample removed 21 meq of Al$^{3+}$/100 g of clay, suggesting that the extractable aluminum remains fairly constant with depth. The Fe$^{3+}$ recorded for the lower samples was obtained from four citrate extracts only. At the surface, iron in the first four extracts exceeded the free iron removed, whereas at depth it amounted to about one-fifth of the free iron.

DISCUSSION

Using the increase in C.E.C. after citrate extraction as a measure of chloritization, it would appear that there is as much citrate-extractable chlorite at 55 in. as at 8 in. Whether this citrate-extractable chlorite was due to direct weathering or was inherited as parent material is not known. Since both the heat stability and strength of the 14 and 7 Å peaks are greater near the surface where the intensity of weathering should be greater, weathering is believed to be responsible for the improved order in the interlayer material at the surface, giving rise to a better-crystallized chlorite.

The glycol retention data also reflect the variations in chloritization. For the unextracted samples, the lowest value occurred in the surface clay where
the chloritization appeared to be best developed. For the four deeper samples the glycol retention was higher, possibly because the discontinuous Fe and Al hydroxide sheets held the layers apart so glycol could enter. After citrate extraction, the glycol retention of the four deeper samples went down about 5 mg/g of clay while that of the surface clay went up 5 mg/g. The glycol test specimens were then X-rayed to see if this anomalous behavior could be explained. It was found that only the surface clay existed in an expanded state, strongly suggesting that the surface clay had a lower charge density than the four deeper samples. Upon saturation with glycol, all the extracted samples showed expansion properties.

Glycol values on K-saturated, citrate-extracted samples showed the greatest decrease for the four deeper samples. These results suggest that the potassium did not collapse the surface clay as effectively as the deeper samples. A lower charge deficiency of the surface clay would explain the difference in glycol retention.

The X-ray and glycol retention data on the extracted clays indicate a lower charge density for the clay near the surface, yet the C.E.C. of the unextracted clays increased greatly at surface while the glycol retention decreased. In a glacial till such as this one, it seems reasonable to conclude that the clay mineralogy is the same throughout except as affected by weathering. The K₂O content appears to be about the same throughout so the removal of interlayers of potassium does not seem to be responsible for the differences in properties with depth. The most reasonable explanation is probably related to the kind and amount of chloritization and its relation to the charge deficiency.

The following explanation, although possibly not the only one, is consistent with all the data. Near the surface, some of the mica layers tend to a lower charge density either by (a) oxidation of octahedral Fe²⁺ to Fe³⁺ as suggested by Ellis and Mortland (1959) as a factor in weathering interlayer K from biotite, or (b) replacement of octahedral Fe²⁺ by Al³⁺, the reverse of the reaction suggested by Hower (1961) for increased charge density during glauconite formation. These layers are possibly so weakly charged that they do not become strongly chloritized and the hydroxyl complexes are exchangeable by other cations. This would increase the exchange capacity and should increase the glycol retention. Probably the low charge density layers do adsorb more glycol, but this adsorption is more than offset by the lowered glycol retention resulting from the marked improvement in the chlorite in the layers retaining a high charge density.

The peculiar effects of the initial KCl treatments can now be explained. The exchangeable aluminum and iron complexes were probably fairly easily exchanged by the potassium, which itself was not fixed because the charge density was too low. The exchange capacity therefore rose rather than decreased with the KCl treatments. Other authors also have found that potassium is effective in replacing adsorbed aluminum (and possibly iron), e.g. Lin and Coleman (1960) and Coleman, Weed and McCracken (1959).

Chloritized clay mineral complexes have been described previously by a
number of authors (Brown, 1953; Rich and Obenshain, 1955; Tamura, 1956, 1958; Klages and White, 1957; Sawhney, 1958, 1960; Rich, 1958, 1960; Tamura, Hanna and Shearin, 1959; Nelson, 1960; and Brydon, Clark and Osborne, 1961). In some cases the chloritized complex was formed from montmorillonitic soils (Tamura, 1958; Tamura, Hanna and Shearin, 1959; and Brydon, Clark and Osborne, 1961). In other cases (e.g. Rich and Obenshain, 1955; Rich, 1958; Klages and White, 1957; Tamura, 1956) weathered, potassium-deficient micas, illites, or vermiculites were chloritized into a non-expanding, non-collapsing complex. In all cases, chloritization occurs in the upper part of the soil profile where aluminum and iron may become fairly soluble in the low-pH water surrounding the clay minerals. Adsorbed hydrogen or hydronium, or both, probably produce a pH value close to the clay minerals that is considerably lower than the ground-water pH. Hydrogen clays are known to alter spontaneously to hydrogen-aluminum clays (Low, 1955; Mathers, Weed and Coleman, 1955; Carroll and Starkey, 1960; Coleman and Craig, 1961). Chloritization in all the above cases was attributed to interlayer aluminum, although occasionally the role of iron in the process was casually mentioned. In contrast, the work described in this paper indicates that iron plays the dominant role in chloritization of this particular soil.

CONCLUSIONS

The conclusions derived from this study are listed as follows: (1) Citrate-extractable chlorite is present in the soil profile to a depth of 55 in. (2) The citrate-extractable chlorite is very high in iron. Indeed, iron hydroxide complexes may cause most of the chloritization in this clay. (3) There appears to be a reduction in charge density of the clays near the surface as a result of weathering. (4) The chlorite, both extractable and unextractable, is better crystallized near the surface. The extractable chlorite breaks down under heat treatment as low as 350°C. The unextractable chlorite is stable to higher temperature in the surface clay than in the clay at 55 in. (5) Potassium seems to be quite effective in the partial removal of adsorbed aluminum and iron complexes, but did not fix because the charge deficiency was too low.

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