A SWELLING DIOCTAHEDRAL CLAY MINERAL OF A VERMICULITE-SMECTITE TYPE IN THE WEATHERING HORIZONS OF PODZOLS

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ABSTRACT

In Scandinavian podzols a swelling dioctahedral mineral, probably derived from dioctahedral mica and iron-rich chlorite, has been found in the clay (<2μ) fractions from A2-horizons. This mineral, or group of minerals, is shown by X-ray examination and differential thermal analysis to be of a vermiculite-smectite type, thus making the differentiation between vermiculite and smectite still more problematical. The pretreatment of the samples and choice of interlayer cations is shown to be of great significance for the identification of soil clay minerals.

INTRODUCTION

In a study of the clay minerals in podzol profiles in Fennoscandia (Gjem, 1960) smectite was found to be a common clay mineral in the clay fraction of the A2-horizon. In some profiles, however, it was observed that clay minerals which had originally given a lattice spacing of 18Å with glycerol, failed to expand beyond 14Å when peroxidized and saturated with Na+ (instead of Ca2+) prior to X-ray examination. These results called for a more detailed study of the effect of sample pretreatment and of interlayer cations on the swelling properties of clay minerals in Scandinavian soils.

EXPERIMENTAL

Materials. Samples were taken from two podzol profiles: one (No. 363) from Sogn, Norway, and the other (No. 373) from Järveneset, V. Norrland, Sweden. The latter contains a higher proportion of the swelling mineral in the clay fraction from the A2-horizon, and contamination with interglacially-formed clay minerals (frequently revealed by X-ray examination of C-horizon samples) is very small or absent. When no profile is specifically mentioned, therefore, the results given are based on the profile from Järveneset.

The two profiles were both typical iron podzols, the thickness of the bleached layer being about 8 cm. A mechanical analysis carried out after dispersing with a 0.01 M solution of tetrasodium pyrophosphate gave the values in Table 1.

Methods. The various size fractions were separated by repeated sedimentation, flocculated with calcium chloride, washed with water, and dried. The clay samples (<2μ) were deferrated by the dithionite-
citrate method of Mehra and Jackson (1960). Some samples were
deferrified directly (untreated samples), others were kept at 60°C
overnight with distilled water prior to deferrification (heat-treated
samples), and others were deferrified after heating overnight at 60°C
with a 10 per cent. hydrogen peroxide solution to destroy organic
matter (peroxidized samples).
Saturation of the samples with different cations was performed
using molar solutions of chlorides of the respective cations. The
suspensions were heated on the water bath for about 3 hours at 90°C,
centrifuged and washed twice with the salt solution. Excess salt was
removed by washing with distilled water. The residues in the centri-
fuge tubes were dispersed in water, sedimented on glass slides, and
dried at room temperature. Glycerol-saturated samples were pre-
pared by adding enough glycerol to the suspension to give specimens
visibly wet with glycerol after drying at room temperature. This
method should ensure full hydration before the glycerol complex is
formed. Glycerol-treated samples were also prepared from the dry
clays by adding the glycerol to the dry specimens on the slides.
For glycol treatment, dry samples were placed in a vacuum de-
siccator over ethylene glycol for different periods of time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage in range</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2000-60μ</td>
<td>60-20μ</td>
</tr>
<tr>
<td>363 A2</td>
<td>71.8</td>
<td>20.0</td>
</tr>
<tr>
<td>C</td>
<td>89.9</td>
<td>5.0</td>
</tr>
<tr>
<td>373 A2</td>
<td>42.5</td>
<td>28.5</td>
</tr>
<tr>
<td>C</td>
<td>55.8</td>
<td>16.7</td>
</tr>
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</table>

Unoriented specimens were made from air-dried samples by the
method described by Hathaway (1955).

X-ray examination was performed with a Philips X-ray diffracto-
meter using Cu radiation and a nickel filter. The scanning speed was
2° 2θ per minute.

The differential thermal investigations were carried out at Norges
gotekniske Institutt with the ‘Geonor’ Differential Thermal Ap-
paratus. The samples were equilibrated at 90 per cent. relative
humidity and diluted 1:1 with Al2O3; the heating rate was 10°C/min.

DIFFRACTION PATTERNS OF UNORIENTED SAMPLES

Powder diffraction patterns of unoriented samples from the A2
horizon show four reflections in the region 1.43-1.56Å—at 1.435Å,
1.45Å, 1.50Å and 1.54Å. Their relative intensities as indicated by
the peak heights are given in Table 2. A pure quartz sample was
included for comparison.

The intensity relationship of the line at 1.45Å to the line at 1.54Å
in the soil samples is in accordance with that in the quartz sample
TABLE 2—Relative observed X-ray diffraction intensities in the region 1.43-1.56 Å for quartz and samples from the A₂-horizon.

<table>
<thead>
<tr>
<th>Spacing (Å)</th>
<th>Samples from A₂ horizon</th>
<th>Quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;2μ</td>
<td>2-6μ</td>
</tr>
<tr>
<td>1.435</td>
<td>63</td>
<td>34</td>
</tr>
<tr>
<td>1.45</td>
<td>14</td>
<td>27</td>
</tr>
<tr>
<td>1.50</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>1.54</td>
<td>55</td>
<td>100</td>
</tr>
</tbody>
</table>

and since the intensities of the two lines increase in the coarser fractions, the 1.54Å line is attributed entirely to quartz. The 1.50Å line must be due to a mineral of the dioctahedral mica group, 060 reflections for which fall in the range 1.48-1.52Å (Walker, 1950). For dioctahedral vermiculite, Brown (1953) has shown the 060 reflection to be at 1.499Å. The line at 1.435Å (Table 2) may be the 1316,2018 reflection of vermiculite (Walker, 1951); however, no data are available for the dioctahedral form.

**Fig. 1**—X-ray diffractometer traces for clay samples from the A₂-horizon, peroxidized before saturation with: a—Mg²⁺, b—Ca²⁺, c—Li⁺, d and e—Na⁺, f—K⁺. Scale factor and time constant are given on each curve.
Table 3—Basal spacings of clay samples treated in different ways and saturated with various cations (in Å).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pretreatment</th>
<th>Treatment</th>
<th>Li+</th>
<th>Na+</th>
<th>K+</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>363 A₂</td>
<td>Deferrified</td>
<td>Air dry</td>
<td>12.1</td>
<td>12.4</td>
<td>12.4</td>
<td>13.12</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glycerol</td>
<td>17.7</td>
<td>14.0</td>
<td>13.4</td>
<td>17.4</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glycol</td>
<td>16.7</td>
<td>16.7, 13.6</td>
<td>13.4</td>
<td>16.7</td>
<td>—</td>
</tr>
<tr>
<td>373 A₂</td>
<td>Deferried</td>
<td>Air dry</td>
<td>12.3</td>
<td>12.3</td>
<td>12.8</td>
<td>12.3</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>105°C*</td>
<td>10.5</td>
<td>10.8</td>
<td>10.6</td>
<td>11.5-10.7</td>
<td>13.4, 11.8</td>
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<tr>
<td></td>
<td></td>
<td>Glycerol</td>
<td>17.7</td>
<td>18.4</td>
<td>14.0</td>
<td>18.4</td>
<td>17.7</td>
</tr>
<tr>
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<td>Glycol</td>
<td>16.7</td>
<td>16.7, 13.5</td>
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<tr>
<td>373 A₂</td>
<td>Deferried</td>
<td>Air dry</td>
<td>12.1</td>
<td>12.1</td>
<td>12.4-10.5</td>
<td>11.8</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>105°C*</td>
<td>13.4</td>
<td>—</td>
<td>10.2</td>
<td>13.4</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O overnight</td>
<td>13.2, 11.8</td>
<td>10.0</td>
<td>10.0</td>
<td>13.4, 11.8</td>
<td>—</td>
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<tr>
<td></td>
<td></td>
<td>at 60°C (Heat-treated)</td>
<td>14.7</td>
<td>17.0, 15.2</td>
<td>13.6</td>
<td>17.7</td>
<td>17.7</td>
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<tr>
<td></td>
<td></td>
<td>Glycerol</td>
<td>16.7</td>
<td>13.4</td>
<td>13.6, 10.0</td>
<td>16.6</td>
<td>16.7</td>
</tr>
<tr>
<td>373 A₂</td>
<td>Deferried</td>
<td>Air dry</td>
<td>14.0</td>
<td>11.9</td>
<td>(11.1)†, 10.0</td>
<td>11.3</td>
<td>14.0, 11.9</td>
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<tr>
<td></td>
<td></td>
<td>1050°C*</td>
<td>14.5</td>
<td>11.5</td>
<td>10.0</td>
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<td>14.0, 11.9</td>
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<tr>
<td></td>
<td></td>
<td>H₂O₂ overnight</td>
<td>13.6</td>
<td>10.6</td>
<td>10.0</td>
<td>—</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>at 60°C (Peroxidized)</td>
<td>14.7</td>
<td>(17.4), 14.0 (12.3)</td>
<td>13.6-10.0</td>
<td>17.5</td>
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<td></td>
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<td>Glycerol</td>
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<td>13.2, (11.9)</td>
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<td>16.7</td>
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<tr>
<td></td>
<td></td>
<td>Glycol</td>
<td></td>
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</table>

* After glycol treatment.  † Brackets indicate shoulders or additional peaks to the main diffraction peak.
Diffraction Patterns or Oriented Samples

Air-dry Samples. Oriented samples of the clay fraction from the A$_2$-horizon saturated with Li$^+$, Na$^+$, Ca$^{2+}$, and Mg$^{2+}$ and dried in the laboratory atmosphere (24°C, 20 per cent. relative humidity) give reflections which are in the 12-14Å region, but vary somewhat for different preparations (Table 3, Fig. 1). The peaks are sometimes broad, and double peaks often occur, indicating a mixture of minerals, some with single and some with double sheets of interlayer water molecules. Moreover, phases occur with basal spacings at about 11·3Å and 11·9Å for air-dry samples saturated with Ca$^{2+}$ and Na$^+$, respectively; similar partially hydrated phases have been reported for both vermiculite and smectite (Barshad, 1949; Jackson et al., 1952; Walker, 1956, 1958). According to Barshad (1949) these small spacings may be explained by the manner of packing of the water molecules between the oxygen sheets of the lattice, this packing being loose and discontinuous at low states of hydration.

Pretreatment of the K-saturated sample with hydrogen peroxide caused the layers to collapse to about 9·9Å (Fig. 1f). This is in agreement with the results of Brown (1953) who observed that diocta-

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**Fig. 2**—X-ray diffractometer traces for glycol-treated clay samples from A$_2$- and C-horizons, after different pretreatments: \(a\)—A$_2$-sample, untreated and saturated with Na$^+$; \(b\)—A$_2$-sample, peroxidized and saturated with Na$^+$; \(c\)—C-sample, peroxidized and saturated with Ca$^{2+}$; \(d\), \(e\), and \(f\)—A$_2$-samples, peroxidized and saturated with Li$^+$, Ca$^{2+}$ and K$^+$, respectively. Scale factor and time constant are given on each curve.
hedral vermiculite collapsed more readily after being peroxidized. Treatment of the sample with water overnight at 60°C resulted in partial collapse of the layers to give diffraction peaks at 12.4Å, 11.6Å and 10.5Å. A collapse to 10Å is, however, not generally limited to vermiculites, since according to Brown and Jackson (1958) a smectite with high layer charge can show a similar partial collapse to 10Å on K-saturation.

Heating the samples to 600°C for ½ hour caused the lattice to contract to 10Å, giving rise also to a more intense 5Å reflection.

**Glycol-treated Samples.** The pretreatment of the sample before saturating with Na⁺ and K⁺ influenced the glycol sorption (Table 3, Fig. 2). An untreated Na-saturated sample gave, after two days over ethylene glycol, a strong 13.4Å peak with a weaker one at about 16.7Å. After ten days the 16.7Å peak had increased at the expense of the 13.4Å reflection, indicating a change from single to double sheets of glycol molecules (Fig. 2a). The relative intensities of the two lines did not change with further ethylene-glycol treatment. A broad 001 peak between 24Å and 27Å indicates alternation of 10 +14Å and 10 +17Å spacings. Both the heat-treated and peroxidized Na-saturated samples failed to show any expansion beyond 13.4Å; these treatments therefore influence the swelling characteristics of the lattice (Fig. 2b). The untreated K-saturated sample expanded to 13.6Å when glycol-saturated, while the heat-treated sample gave reflections in the 10-13.2Å region. The corresponding peroxidized sample showed only the contracted spacing of 10Å (Fig. 2f), and could not be made to expand on treatment with Ca²⁺ and glycol, suggesting K-fixation.

The pretreatment of the sample had no apparent influence on the glycol sorption with Li⁺, Ca²⁺, and Mg²⁺ in the interlayer positions, and lattices with double sheets of glycol molecules developed within three hours in a glycol atmosphere (Fig. 2d and e). The spacings of 16.6-16.8Å for the glycol-treated samples are higher than the maximum reported basal spacings for vermiculite (Walker, 1958), suggesting that the mineral is near to smectite.

Heating to 105°C overnight after glycol treatment caused collapse of the lattice, giving spacings in the 11.8-10.5Å range, but the pretreatment was also of importance. Heat-treated and peroxidized samples gave higher spacings with glycol than untreated samples (except for K-saturated samples). This also applied when the samples were heated to 150°C after glycol treatment (Table 3). The glycol-complex spacing of 14.0Å for the Li- and Mg-saturated samples heated at 105°C is in accordance with the value given by Kunze (1955) for Mg-saturated smectite.

**Glycerol-treated Samples.** As for the glycol complexes, the pretreatment of the sample influenced the formation of glycerol complexes. The samples deferrified only prior to treatment with the different cations showed expansion with glycerol (Table 3). With interlayer K⁺ a diffraction peak at about 14.0Å developed—a value
only slightly lower than those quoted for single sheet glycerol-vermiculite (Walker, 1958) or single sheet glycerol-smectite complexes (Barshad, 1960). Samples saturated with Li\(^+\), Na\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\) showed basal spacings of about 18\(\AA\) with a nearly integral series of higher orders.

![X-ray diffractometer traces of glycerol-treated clay samples from A\(_e\)-horizon, peroxidized and saturated with different cations: a—glycerol added to wet Li-saturated sample; b—glycerol added to glycol-treated Ca-saturated sample; c—glycerol added to wet Mg-saturated sample; d—glycerol added to air-dry Ca-saturated sample; e—glycerol added to wet Na-saturated sample; f—same as c, after 14 days drying in air; g—glycerol added to wet K-saturated sample; h—glycerol added to wet Ca-saturated sample. Scale factor and time constant are given on each curve.](image)

Pretreatment of the sample with water at 60\(^\circ\)C overnight prior to saturation with Li\(^+\) impeded the development of complexes with double sheets of glycerol, only one small peak in addition to that 14.7\(\AA\) being observed. For the Na-saturated sample a sharp peak at 15.2\(\AA\) appeared together with a 17\(\AA\) reflection. The relative heights of the two peaks, however, did not seem to be constant for
different preparations. The peroxidized Na-saturated sample gave a diffraction maximum at about 14Å with smaller peaks at 12·3Å and 17·4Å (Fig. 3c), whereas with K+ in the interlayer positions basal spacings at 13·6Å, 12·1Å, and 11·3Å appeared together with a 10Å spacing (Fig. 3g). Samples saturated with Ca2+ and Mg2+ gave double sheet glycerol complexes (Fig. 3c and h). A marked reflection at about 9·3Å is thought to be the third order of the basal reflection at about 28Å, which may be attributed to a regular interstratification of 10Å and 18Å lattice spacings. For samples not treated with glycerol the first order reflection was observed at about 24Å. Regularly alternating interstratified smectite-illites with spacings of 28-29Å have already been reported by Jackson et al. (1952) from desert soils in China, and by Whittig and Jackson (1955) from soils of Northern Wisconsin.

The original state of hydration of the vermiculite lattice is important in determining the reaction with glycerol and samples with single sheets of interlayer water molecules give single sheet glycerol complexes (Walker, 1958). Air-dry samples saturated with Ca2+ and Mg2+ containing mainly single sheets of interlayer water were therefore treated with glycerol on slides and left in the atmosphere for two days before diffractometer measurements. With Ca2+ in the interlayer positions the diffraction pattern showed a splitting of the original 12Å peak to give marked reflections at 17·7Å and 10Å and a small reflection at about 14Å (Fig. 3d). These results are in accordance with those for a swelling mineral interstratified with illite (Brown and MacEwan, 1950; Heystek, 1955). With Mg2+ in the interlayer positions the sample did not expand beyond 14Å even when glycerol was added to samples containing double sheets of interlayer water. This result excludes, therefore, the possible presence of a true smectite in the sample (Walker, 1958). However, when glycerol was added to a glycol-treated Mg-saturated sample, the spacing at 16·7Å showed a shift to 18·4Å, and that at about 9·3Å was greatly enhanced: this also applied to the Ca-saturated sample (Fig. 3b). Although the Ca-glycerol complex 18Å phase remained stable in the laboratory atmosphere, the Mg-glycerol complex showed a slow shift towards lower spacings, and in one week a 14·5-17·4Å band had developed (Fig. 3f).

It seems reasonable from these X-ray investigations to consider the mineral in this soil clay to be of a swelling dioctahedral vermiculite-smectite type, interstratified to some extent with illite.

**Differential Thermal Analysis**

The differential thermal curves for the peroxidized, deferrified clay fraction of the A2-horizon saturated with K+, Ca2+, and Mg2+, and for the clay fraction from the C-horizon saturated with Ca2+ are given in Fig. 4.

The sample from the C-horizon shows endothermic peaks at 115°C and 615°C and a small endothermic effect about 320°C. Although X-ray data (Fig. 2c) indicate that the clay contains about 20 per cent.
chlorite, the differential thermal curve shows only a small exothermic effect at about 900°C. The 615°C peak may be attributed to chlorite but it could equally be indicative of mica (sericite).

The Mg-saturated clay from the A₂-horizon shows a low-temperature peak system of the vermiculite type (Barshad, 1948; Walker and Cole, 1957) with endothermic peaks at about 110°C, 152°C and 295°C. The broad endothermic peak at about 630°C may result from interstratified illite or chlorite (interleaved brucite layers), which are extremely difficult to recognize by X-ray examination (Cole and Hosking, 1957). The endothermic peak at about 915°C is followed by a slight exothermic effect at about 960°C. These temperatures are somewhat higher than those recorded for trioctahedral vermiculite and are similar to those given by montmorillonite.

The K-saturated sample, in accordance with its collapsed lattice, gives only very small low-temperature endothermic effects, as demonstrated by Barshad (1948) for trioctahedral vermiculites. The endothermic peak at about 650°C is approximately the same magnitude as that given by the Mg-saturated clay. The absence of the endothermic-exothermic effect at 900°C is noteworthy and gives the curve an appearance reminiscent of that for the C-horizon clay.

The Ca-saturated clay from the A₂-horizon has a differential thermal curve similar to those for montmorillonites (Greene-Kelly, 1957), but it must be remembered that the low-temperature peak system of a smectite is broadly similar to that of a Ca-saturated vermiculite (Walker and Cole, 1957). The loss of sorbed water, as indicated by a sharp large endothermic peak at 110°C and a smaller peak at 215°C, occurs at a temperature lower than that for typical smectites. Instances of water being lost at about these temperatures have, however, been observed for montmorillonites (Greene-Kelly, 1957). The collapse of the minerals at temperatures below 200°C (as seen from the X-ray diffraction patterns) is indicated by the differential thermal curve. The dehydroxylation reaction occurs at about
the same temperature (635°C) as for the other samples, but the magnitude of the endothermic effect is increased; this may be a further indication of the smectitic character of the mineral. The high temperature endothermic effect begins at 850°C with a peak at about 900°C and is followed immediately by a slight exothermic peak—features which are also associated with montmorillonite.

**Conclusions**

The above results confirm the observations of Roy and Romo (1955) and Walker (1956, 1958) that much confusion may arise in the differentiation of clays of the smectite and vermiculite groups on the basis of their X-ray diffraction patterns without taking into consideration the interlayer cations present. This also applies to the differential thermal curves of these minerals. It is further shown that the dioctahedral swelling mineral present in the soil clays examined might be classed as a smectite when saturated with Ca²⁺. However, the X-ray diffraction patterns of the mineral when peroxidized or pretreated with water at 60°C and saturated with Li⁺, Na⁺ and K⁺, and its thermal characteristics when saturated with Mg²⁺ and K⁺ indicate that it belongs to the vermiculite group of clay minerals. From these results it is reasonable to conclude that there is a gradation between dioctahedral vermiculite and dioctahedral smectite in the soil and that definite group names should be applied with caution.

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**References**

Barshad, I., 1948. _Amer. Min._, 33, 655.

Barshad, I., 1949. _Amer. Min._, 34, 675.


