SWELLING CHLORITE IN A SOIL OF THE DOMINICAN REPUBLIC

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Abstract—A 1–0·2 μm fraction from a soil in the Dominican Republic was studied by X-ray diffraction combined with solvation, cation saturation, and heat treatments. I.R., thermal (DTA, TGA) and chemical analyses were also made. This soil is saline and alkaline and its mineral composition is greatly influenced by the lacustrine parent material and poor drainage.

In addition to swelling chlorite, illite, kaolinite, carbonates and quartz are present in the 1–0·2 μm fraction. The swelling chlorite expanded to over 18 Å when Mg saturated and solvated with glycerol or water. Lower spacings with other cations and ethylene glycol were observed. 1 N HCl treatment partially removed the interlayer hydroxides in the chlorite and 6 N HCl destroyed the mineral. The mineral gave a reflection close to 14 Å up through 600°C but collapsed at higher temperatures to 10·2 Å.

INTRODUCTION

One of the principal clay minerals in a soil from the Dominican Republic is believed to be a swelling chlorite. Several major types of swelling chlorite have been described in the past. One type is illustrated by the first descriptions of a swelling chlorite by Honeyborne (1951) and by Stephen and MacEwan (1951). This mineral appears to be a chlorite which can take on a monomolecular layer of glycerol adjacent to the hydroxide sheet in the interlayer. The second type of swelling chlorite, also first described by Stephen and MacEwan, consists of alternate layers of swelling chlorite and chlorite, a regularly interstratified mineral. These two types are also described by Brindley (1961). Martin-Vivaldi and MacEwan (1957) studied clays which had both a regular and irregular mixture of chlorite and a swelling chlorite. Lippmann (1954) proposed the name corrensite for the regular type. A third type was proposed by Shimoda (1970) who described an irregular chlorite-swelling chlorite from the Hanaoka mine in Japan.

The major mineral described in the present study appears to be similar to one described by Honeyborne (1951), that is swelling chlorite without interstratification by chlorite. Chlorite as a separate phase as well as illite, kaolinite, quartz and calcite also are present in the sample.

MATERIALS AND METHODS

The sample was from the Barahona Sugar Mill Plantation in south-eastern Dominican Republic. The specific sample was taken 17·7 km from the sea between the mountain ranges Sierra de Neyba and Sierra de Baroruco. The soil is influenced by saline conditions since it is part of the Lake Enriquillo basin.

The soil has developed in lacustrine deposits. The climate of the plantation is considered arid even though the average (1937–69) rainfall is 53 cm. The plantation is irrigated. The entire profile exhibited swelling chlorite to some extent but the best developed swelling chlorite was noted in the 61–91 cm zone and the clay reported in this study was removed from this zone.

The clay fractions were separated by centrifugation using dilute NaOH at pH 9·5 as a dispersant.

The clay was saturated with various cations by adding 1 N chloride solutions, mixing and then centrifuging. This procedure was repeated five times. Excess salts were removed with water. Suspensions containing 225 mg of clay were filtered through unglazed ceramic tile (Rich, 1969). They were glycerol or ethylene glycol solvated by passing 5 ml of 20 per cent solutions of these reagents through the clay. In the case of the ethylene glycol solvated clays, the slides were placed in an ethylene glycol atmosphere until X-ray diffraction patterns were obtained to prevent ethylene glycol evaporation. The vapor pressure of glycerol is so low that this precaution was not necessary for glycerol solvated clays. X-ray diffraction patterns of the K-saturated slide that was air dried and heated at 100, 200, 300, 400, 500, 600, 700 and 800°C were obtained by placing it immediately, after heating, in a steel chamber, with a Saran window, placed over the slide holder. This chamber was flushed with dry air that had been passed through granular anhydrous $CaSO_4$ and then $Mg(ClO_4)_2$. These precautions were taken to prevent rehydration of the clay during the X-ray analysis. The General Electric X-ray diffraction unit (XRD-5) was adjusted to give Cu Kα X-rays at 40 kV and 20 mA. The slit system was 1° for the exit slit, MR for the soller slit, and 0·2° for the entrance slit. In most cases the goniometer was run at 0·2°/min with an 8 sec time constant. Other runs were at 2°/min with a 2 sec time constant.

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The (060) determination was made by the method of
Rich (1957). The differential thermal analyses were
made in an Inconel metal block heated at the rate of
12·5°C/min. Al_2O_3 was the inert material used. Ther-
mogravimetric analysis was run by heating a 0·3000 g
sample in a platinum crucible with lid for 2 hr, cooling
the sample over P_2O_5, and weighing. The increment of
temperature was 100° or 50°C up to 1000°C. I.R.
analyses were made with a Beckman IR-8 instrument.
The clay sample (1·5 mg) was mixed with KBr (1 g)
using a Wig-L-Bug and 0·35 g of this mixture was
pressed into a disk for the analyses.

The analyses for soluble salts present in the whole
soil were made by mixing 10 g of soil with 20 ml of
H_2O. The conductivity was measured and then the
solution phase was removed by centrifugation and
analysed for Ca, Mg, Na, and K by atomic absorption
analyses. In the case of NH_4OAc extraction for ex-
changeable cations, 100 ml of N NH_4OAc was passed
through the soil sample which was first leached with
H_2O. Analyses were made by atomic absorption. The
pH was determined in a 1:1 soil–water mixture using
a glass electrode. The particle size analysis was made
by the pipette method.

Chemical analyses were made of the Mg-saturated
sample and after treatment with 1 N or 6 N HCl to
remove chlorite and carbonates. The method outlined
by Bernas (1968) was used for the analyses. FeO was
determined by the method of Reichen and Fahey
(1962). The cation exchange capacity was determined
by a modified method of Rich (1961). The sample was
Mg-saturated and the Mg was displaced by 1 N $BaCl_2$.

The acid treatment was made by adding 1 g of clay
to 100 ml of either 1 N or 6 N HCl and shaking the
suspension overnight. For the total elemental analysis
the soil was digested in 1 N NaOAc, adjusted to pH
4·8 with HOAc, to remove carbonates.

RESULTS

Properties of the soil

The particle size distribution is given in Table 1.
Based on the clay content, our sample was derived

Table 1. Particle size analysis

Sample No.	Soil depth cm	>50 μm	2–50 μm %	<2 μm
1058	0–30	21·4	51·9	26·7
1059	30–61	21·9	47·4	30·7
1060	61–91	12·7	43·4	43·9

Table 3. Exchangeable cations (E) following H_2O extrac-
tion (Table 2)

Sample No.	Ca	Mg	K	Na	Total cations E	E + H*
			m-equiv/100 g			
1058	27·80	5·15	1·80	0·86	35·61	36·83
1059	25·60	8·30	1·73	1·18	36·81	37·69
1060	32·40	8·90	1·45	3·03	45·78	49·87

* See Table 2.

from a B horizon of the soil. The clay content increased
with depth.

In Table 2 the water soluble salts, with the exception
of Na and K salts, generally increased toward the sur-
face. The results suggest an upward movement of salts
by evaporation at the surface. It is also noted that the
pH of all 3 samples is high and that the pH increased
with depth. In Table 3 it is noted that the exchangeable
cations increased with depth following the greater clay
content and exchange capacity as the depth increased.

Swelling properties of the 1–0·2 μm clay

The swelling properties of the clay were affected by
the cation with which the clay was saturated, the liquid
with which the clay was solvated, and the time the clay
was in an ethylene glycol atmosphere.

In Fig. 1 it is noted that a portion of the Mg–chlorite
expanded to 18·0 Å in the case of glycerol solvation
and to 18·6 Å in the case of H_2O solvation in which
cases the samples were visibly wet.

When the clay was Mg-saturated, there was less
expansion of the clay when it was ethylene glycol sol-
vated than when it was glycerol solvated. The X-ray
diffraction patterns for the ethylene glycol solvated
clays, saturated with Ca and Sr, are shown in Fig. 2.
Slow spectrogoniometer and chart speed were necess-
ary to resolve the chlorite component. When the fast
speed mode was used (Fig. 3), the chlorite component
was not apparent except as suggested by the asymmet-
ric peak. Slight differences are noted between the Ca-
and Sr-saturated clays.

The effect of time seems to aid in segregating the
chlorite from the swelling chlorite component when
the clay was Sr-saturated. Over a 2-week period the
peaks shifted from 16·2 and 15·2 Å to 16·8 and 14·7 Å.
Apparently the individual particles became more
homogeneous with time. The particles which displayed
a large proportion of layers containing glycol in-
creased this proportion, whereas those particles con-
taining a large proportion of non-swelling chlorite in-
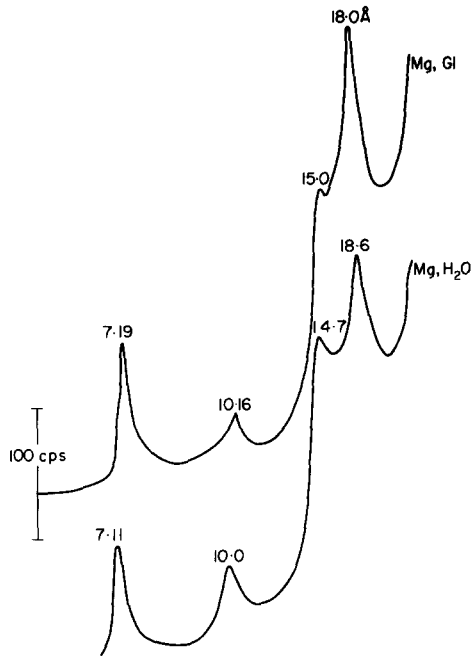creased the proportion of these layers.

Table 2. Water soluble cations, conductivity of the extract from a 2:1 water soil mixture and pH of the soil

Sample No.	Depth cm	pH	Conductivity μmhos	Ca	Cations in solution (H) Mg	Na	K
					m-equiv/100 g		
1058	0–30	7·63	732	0·59	0·21	0·30	0·12
1059	30–61	7·97	498	0·24	0·16	0·38	0·10
1060	61–91	8·13	690	0·15	0·12	1·40	0·42

Fig. 1. Swelling properties of the 1–0·2 μm clay as indicated by X-ray diffraction patterns of Mg-saturated samples solvated with glycerol and with water.

The (060) measurement was at 1·53 Å, placing the principal mineral(s) in the trioctahedral group.

Effects of K-saturation and heating on the stability of the swelling chlorite

Figure 4 gives the X-ray diffraction patterns for the K-saturated clay heated at 100°C increments to 800°C. At 100°C the swelling chlorite maintained a strong 15 Å peak. Vermiculite and montmorillonite would have approached 10 and 12 Å respectively under these conditions. There was a gradual shifting of the 15 Å
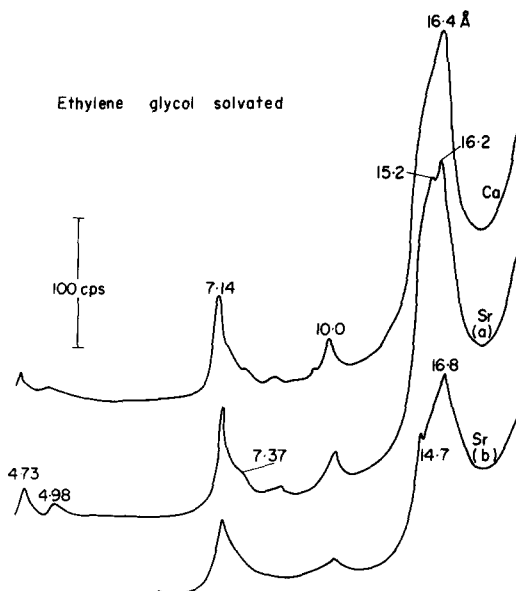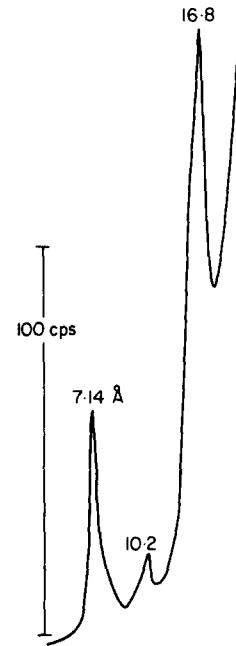

Fig. 3. The effect of fast spectrogoniometer and chart speeds on the resolution of the X-ray diffraction pattern of Sr-saturated and ethylene glycol solvated. The spectrogoniometer speed was 2°/min. Compare with Fig. 2 [Sr (b)] where the speed was 0·2°/min.

peak to 14·1 Å at 600°C and an increase in intensity is noted for that temperature, in agreement with the paper by Bradley (1953). The increase in intensity is due to ejection of material from the interlayer space. At higher temperatures there was sufficient material lost from the interlayer space so that a 14 Å spacing was no longer supported and there was collapse of the chlorite to 10·2 Å to add to the intensity of the illite peak.
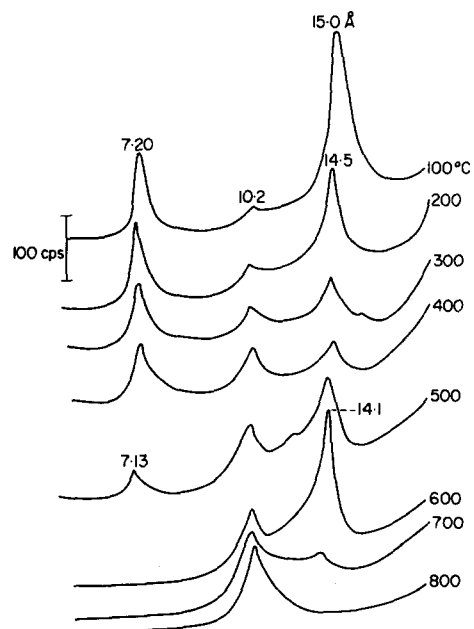

Fig. 2. The effect of cation saturation and time on the swelling properties of the 1–0·2 μm clay. (a) Sr saturated and 12 hr in an ethylene glycol atmosphere (b) Sr saturated and 14 days in an ethylene glycol atmosphere.

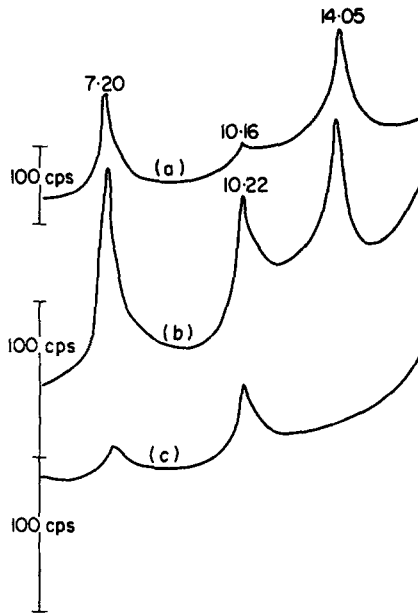Fig. 4. Effect of temperature on the X-ray diffraction pattern of the K-saturated 1–0·2 μm clay.

Fig. 5. Effect of HCl treatment on X-ray diffraction patterns of K-saturated 1–0·2 μm clay heated at 200°C. (a) No HCl treatment; (b) 1 N HCl treatment; (c) 6 N HCl treatment.

Effect of acid treatment on the properties of the 1·0–0·2 *μm clay*

Chlorite is destroyed by treatment with a strong acid (Brindley, 1961). The effects of 1 N and 6 N HCl treatment are shown in Fig. 5. The 1 N HCl apparently removed some of the interlayer material as indicated by an increase in the 10 Å peak and a decrease in the 14 Å peak intensity. The use of 6 N HCl caused the 14 Å peak to disappear but there was a slight decrease in the 10 Å peak intensity compared to that in the 1 N HCl treated clay. Apparently, in addition to removing interlayer material, a large portion of the whole chlorite component was destroyed by the 6 N HCl treatment and the treatment partially destroyed the illite.
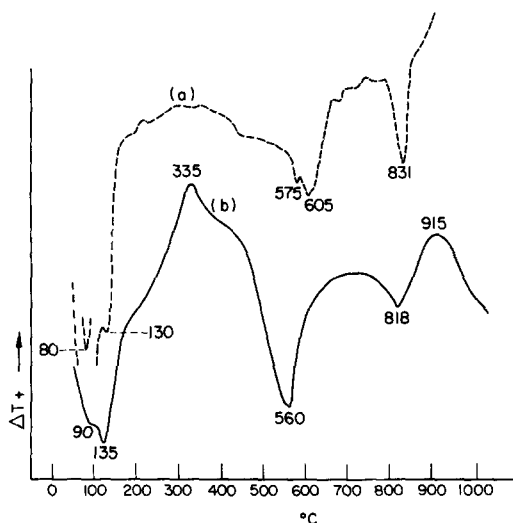
The retention of the 7 Å peak indicates that kaolinite was present. If trioctahedral 7 Å minerals made up this fraction entirely, one would expect the 7 Å peak to disappear (Brindley, 1961). Its lowered intensity may be due to the absence of the second order chlorite reflection and/or a partial destruction of the 7 Å mineral.

Effect of HCl *treatment on the* DTA *pattern*

In Fig. 6 are shown the DTA patterns for the 1–0·2 μm fraction not acid treated and the pattern for same clay treated with 1 N HCl. Both samples were Mg-saturated and equilibrated over a $Mg(NO_3)_2$ slurry which has a relative humidity of 56 per cent. The shifting of the loss-of-water endotherms to a lower temperature for the HCl-treated clay suggests less impedence by Fe, Mg, Al, OH interlayer groups which are partially removed by the HCl treatment.

The shifting of the OH-loss-endotherms to a higher temperature suggests more collapse at the edges of the particles where interlayer hydroxides probably were removed first. The collapse probably impeded the diffusion of H_2O from the breakdown of OH groups in the "mica" portion of the chlorite.

The presence of a strong endotherm at 831°C is typical of chlorite and since carbonates were removed by the HCl treatment this endotherm cannot be attributed to loss of CO_2 from carbonates.

The effect of HCl *treatment on the* TGA *pattern*

The TGA patterns in Fig. 7 are based on the 100°C weight of the clay. The acid-treated clay probably held more interlayer water than the non-acid-treated clay and this probably accounts for the weight loss between 100 and 400°C. It is noted that in the region of the first OH loss, 400–600°C, the acid treated samples (a) lost this water at a higher temperature than the clay not acid-treated.

In the zone of the second OH loss, 700–800°C, the clay not treated with HCl had more interlayer Fe, Mg, Al, OH groups from which to lose OH groups as H_2O and this is an explanation of the greater weight loss in this region by the clay not treated with HCl. The cause of the weight loss near 980°C by this acid treated clay is unknown. A summary of the peaks for DTA and inflections for TGA analyses is given in Table 4.
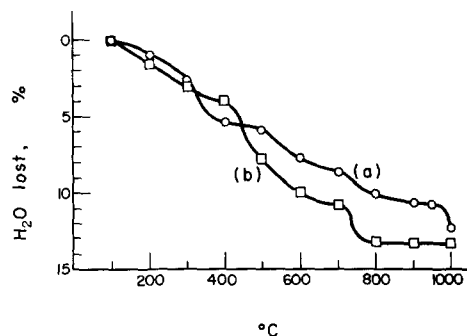

Fig. 6. Effect of 1 N HCl treatment on DTA patterns of the Mg-saturated 1–0·2 μm clay, (a) HCl (1 N) treated (b) not treated with HCl.
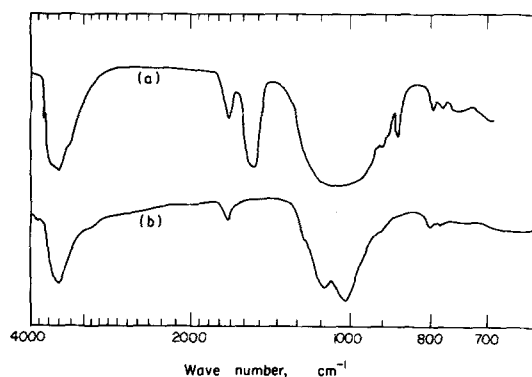

Fig. 7. Effect of 1 N HCl treatment on TGA patterns of the Mg-saturated 1–0·2 μm clay. (a) HCl (1 N) treated (b) not treated with HCl.

Table 4. Temperature of DTA peaks and TGA inflections for thermal reactions
in Mg-saturated clay

Reaction	Pretreatment			
	None		N HCl	
	DTA	*TGA*	*DTA*	*TGA*
H$_2$O loss	90, 135°C	—	80, 130°C	—
OH loss (1st)	560	425	575, 605	340, 460
OH loss (2nd)	818	740	831	750

Wave number, cm^{-1}

Fig. 8. Effect of 1 N HCl treatment on i.r. pattern of Mg-saturated 1–0·2 μm clay. (a) not treated with HCl (b) treated with 1 N HCl.

The effect of HCl treatment on the i.r. analyses

The i.r. analyses (Fig. 8) are useful in that they confirm the presence of carbonates in the sample not treated with acid. The absorption bands at 1400 and 870 cm^{-1} indicate carbonates. These peaks are absent after 1 N HCl treatment of the clay. The presence of quartz is indicated by the double peaks near 800 cm^{-1}. Kaolinite is indicated by the peak near 915 cm^{-1}.

Chemical properties of the clay

The cation exchange capacity (CEC) of the clay was 33·0 m-equiv/100 g. This indicates that there are a substantial number of cations in the swelling chlorite to solvate polar molecules and cause expansion of the mineral. The swelling chlorite probably had a higher CEC than 33·0 m-equiv/100 g because of the presence of minerals with low CEC, e.g., quartz, mica, kaolinite, and carbonates.

The cations removed by 1 N and 6 N HCl from the 1–0·2 μm clay are given in Table 5. Fe, Mg, and Ca were the major elements removed by the acid treatment. The X-ray powder diffraction analysis indicated that the interlayer material was partially removed by the 1 N HCl treatment. The color of the clay was gray in color indicating that the content of free iron oxides is low and therefore it is concluded that the dissolved Fe came largely from the interlayer position. Mg and Al are also frequent components of the hydroxide layer and it is concluded that Fe, Mg, and Al were the main cation constituents of the hydroxide layer of the swelling chlorite. A portion of the Mg (0·35 per cent) is present as an exchangeable cation. The Ca, Na, and K probably are present in illite and in the carbonates.

Table 5. Percentage of 1–0·2 μm clay removed as certain elements by HCl treatments

Element	Normality of HCl	
	1 N	6 N
	% of clay	
Na	0·028	0·040
K	0·125	0·553
Ca	0·480	2·20
Mg	0·926	2·45
Al	0·0231	0·418
Fe	4·81	6·05

Carbonates were removed from the soil prior to separation of 1–0·2 μm clay for total elemental analysis. The high amount of SiO$_2$ is attributed to the presence of quartz. The high amounts of Fe and Mg support the finding that the chlorite is trioctahedral. The fact that the total is not 100 per cent is attributed to error and to the fact that other elements probably are present in small amounts.

Table 6. Elemental analysis of Mg-saturated 1–0·2 μm fraction based on 1000°C weight

Component	%
Na$_2$O	1·41
K$_2$O	1·83
MgO	5·42
CaO	1·01
MnO	0·31
Al$_2$O$_3$	19·07
FeO	9·76
Fe$_2$O$_3$	4·03
TiO$_2$	1·28
SiO$_4$	52·98
Total	97·10

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