EXPERIMENTAL ALTERATION OF A CHLORITE INTO A REGULARLY INTERSTRATIFIED CHLORITE-VERMICULITE BY CHEMICAL OXIDATION

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Abstract—A IIb orthochlorite (brunsvigite), from the chloritic metabasalt in the Middletown Valley of Maryland, was altered to a regularly interstratified chlorite–vermiculite after four months reaction in saturated bromine water on the steambath. The artificial weathering product resembles the regularly interstratified chlorite–vermiculite in a soil in Adams County, Pennsylvania, that has developed in greenstone similar to the chloritic metabasalt in the Middletown Valley of Maryland. The results of this and previous investigations on artificial and natural weathering of chlorites indicate that oxidation of structural Fe^{2+} is an important reaction in the alteration of chlorites into vermiculitic products. The results also show that IIb orthochlorites, apparently structurally similar but having different Fe^{2+} contents may react differently under the same weathering conditions. For example the acid oxidation treatment altered a IIb chlorite (diabantite) directly into a vermiculite, whereas the same treatment altered another IIb chlorite (brunsvigite) into a regularly interstratified chlorite–vermiculite. Detailed investigations of the chlorite structures are probably necessary to determine whether or not these alteration processes are structurally controlled.

INTRODUCTION

The occurrence of vermiculite or chlorite–vermiculite as a natural weathering product of chlorite has been cited repeatedly in the literature (Bradley and Weaver, 1956; Johnson, 1964; Makumbi and Herbillon, 1972; Post and Janke, 1974; Obunbadejo and Quigley, 1974; Herbillon and Makumbi, 1975; Coffman and Fanning, 1975). For IIb chlorite, which is by far the most frequently occurring polytype in nature, Hayes (1970) has proposed the following weathering sequence: IIb chlorite → regularly interstratified chlorite–vermiculite → randomly interstratified chlorite–vermiculite → Ia vermiculite. Coffman and Fanning (1975) proposed essentially the same sequence for the weathering of IIb chlorite in Maryland soils developed in chloritic metabasalt but added the weathering of vermiculite → kaolinite. They also pointed out that hydroxy–aluminum interlayers may form in the vermiculite. Herbillon and Makumbi (1975) added the weathering of vermiculite → nontrite → kaolinite to the weathering sequence of Hayes (1970) to represent the weathering of chlorite in soils developed on greenschist to the Gangila region of Zaire.

Unlike the artificial alteration of mica to vermiculite, the artificial alteration of true unoxidized chlorite to vermiculite has not been successful (Gaillère *et al.*, 1954; Fanning, 1964; Ross 1969). Recently, however, Ross and Kodama (1973) have shown that heating up to 600°C to dehydroxylate the interlayer hydroxide sheet followed by acid treatment resulted in selec-

tive removal of this sheet and vermiculite formation. This indicated that the interlayer hydroxide sheet must be structurally disrupted before it can be selectively dissolved. Ross and Kodama (1973) suggested that in pedogenic weathering this structural disruption might be induced by oxidation of Fe^{2+}. From results of experiments on further alteration of a naturally oxidized chlorite to vermiculite, Makumbi and Herbillon (1972) also concluded that irreversible oxidation of Fe^{2+} plays an important role in this alteration process. They stressed that vermiculitization is induced only when the oxidized iron is dissolved and removed from the hydroxide interlayer. The importance of oxidation was supported by experiments (Ross, 1975) which showed that a IIb unoxidized chlorite, high in Fe^{2+}, (diabantite) altered within three weeks to discrete vermiculite in saturated bromine water on the steambath. In a solution of the same acidity without bromine the diabantite remained unaltered. Furthermore, a chlorite low in Fe^{2+}, (sheridanite) in saturated bromine water failed to show significant vermiculitization, even after six months reaction. Although in nature interstratified chlorite–vermiculite is the most commonly observed chlorite weathering product, no interstratified chlorite–vermiculite was observed in the experimental alteration of diabantite to vermiculite.

This paper deals with the effect of chemical oxidation in the laboratory on an orthochlorite (IIb polytype) of intermediate Fe^{2+} content. This chlorite is the major constituent of the chloritic metabasalt or greenstone underlying the soils in the Middletown Valley, Md. (Coffman and Fanning, 1975) and in Adams County, Pa., (Johnson, 1964). According to

these authors, the vermiculite in some of the soils in the Middletown Valley and the chlorite–vermiculite in the Highfield soil in Adams County are weathering products of the chlorite in the greenstone. This chlorite, although less oxidized, is also similar in structure and composition to the chlorite in the Gangila greenschist studied by Makumbi and Herbillon (1972) and Herbillon and Makumbi (1975). Therefore, in addition to learning about the effect of chemical oxidation on chlorites of intermediate Fe^{2+} content, it was anticipated that this study might clarify the weathering reactions of chlorites to vermiculites in soils.

MATERIALS AND METHODS

The chlorite sample (5–20 μm) was supplied through the courtesy of Dr. D. S. Fanning, University of Maryland. It was obtained from the chloritic metabasalt in the Middletown Valley of Maryland, and it is part of the rock sample No. 71, described by Coffman and Fanning (1975). The chlorite is trioctahedral with an (060) spacing of 1.544 Å and it has the IIb polytype structure. Additional data on this chlorite are given here in Tables 1 and 2 and in Figs. 1 and 2. A sample from the Highfield soil, containing the regularly interstratified chlorite–vermiculite described by Johnson (1964), was supplied through the courtesy of Dr. L. J. Johnson, Pennsylvania State University.

For chemical oxidation, three replicate samples of 300 mg each of the original chlorite were placed in 50 ml pyrex glass vials. After adding 20 ml of saturated bromine water, the vials were tightly closed with nylon-lined screw caps and placed in a steambath.

The alteration of the chlorite in one of the vials was monitored by X-ray powder diffraction. Every few weeks some of the chlorite suspension was taken from this vial, the bromine boiled off, the residue washed and sedimented on a glass slide for X-ray powder diffraction. When after four months no further alteration was observed, the bromine was boiled off all the samples. The pH of the chlorite–bromine suspension decreased from 2.7 initially to 2.0 at the end of the reaction. The residues were treated twice with sodium dithionite to remove free iron and aluminum hydrous oxides (Mehra and Jackson, 1960). The samples were then saturated with Ca or Mg by washing with 1N $CaCl_2$ or $MgCl_2$ solutions.

For analysis of cations, other than Si, samples of the original and of the altered dithionite-treated chlorite were digested in $HF/HClO_4$ solution; for analysis of Si the samples were fused with Na_2CO_3 (Jackson, 1956). Except for Si, which was measured colorimetrically (Weaver and Jackson, 1967), the structural and exchange cations were measured by atomic absorption spectrophotometry. Ferrous iron was determined by the method of Reichen and Fahey (1962).

Thermogravimetric analysis (TGA) curves of the original and altered dithionite-treated samples, initially equilibrated at 25°C and 30% r.h., were recorded with a Cahn thermogravimetric balance. Differential thermogravimetric analysis (DTGA) curves were plotted manually.

X-ray powder diffraction patterns were obtained from 22 mg samples basally oriented on 25 mm by 37 mm glass slides. A Phillips instrument with Fe-filtered, Co radiation ($\lambda = 1.7902$ Å) was used. Diffraction intensities were evaluated by measuring peak areas with a planimeter.

RESULTS

X-ray powder diffraction. Figure 1 shows diffraction patterns of the chlorite before and after alteration. The original chlorite is pure except for a small amount of feldspar (Fig. 1a). After four months reaction the chlorite has become regularly interstratified with expanding layers as shown by the long spacing with integral higher orders (Fig. 1b, c). This alteration product appears relatively stable as there was little or no change in the X-ray powder diffraction patterns even after one year reaction. The first order spacings occur at 32.2 Å with Ca and glycerol and at 29.0 Å with Mg and glycerol. This difference in expansion with Ca and Mg resembles that of low-charge vermiculites, such as Kenya vermiculite. The first order spacings shift to 23.0 Å after heating at 600°C (Fig. 1d). The small reflections at 14.26 Å from the Ca and glycerol saturated sample and at 13.68 Å from the heated sample indicate some remaining discrete chlorite.

Chemical analysis. Table 1 shows the compositions of the original and altered chlorite and the formulas calculated from these data. The CaO, Na_2O and K_2O in the original chlorite sample are probably due to the presence of feldspars. The composition of the altered material, which includes some discrete chlorite and some silica residue, is markedly different. There is a decrease in the Al_2O_3 and MgO content, reflecting the removal of alternate interlayer hydroxide sheets. There is an increase in SiO_2 which is probably due to SiO_2 residue of chlorite dissolved during the acid oxidation treatment. The amount of SiO_2 residue was estimated from the formula calculation of the chlorite–vermiculite by assuming that the tetrahedral Si to Al ration had not changed during alteration. It shows that about one-third of the chlorite had dissolved. In addition, X-ray diffraction measurements show that the altered material still contains approximately 23% discrete chlorite. During dissolution nearly half of the original FeO has oxidized and the CEC has increased from 1.5 m-equiv./100 g to 46.0 m-equiv./100 g.

The formula of the original chlorite was calculated after excluding the CaO, Na_2O and K_2O from its composition. This chlorite is a brunsvigite, according to the classification of Foster (1962). The formula of the regularly interstratified chlorite–vermiculite in the
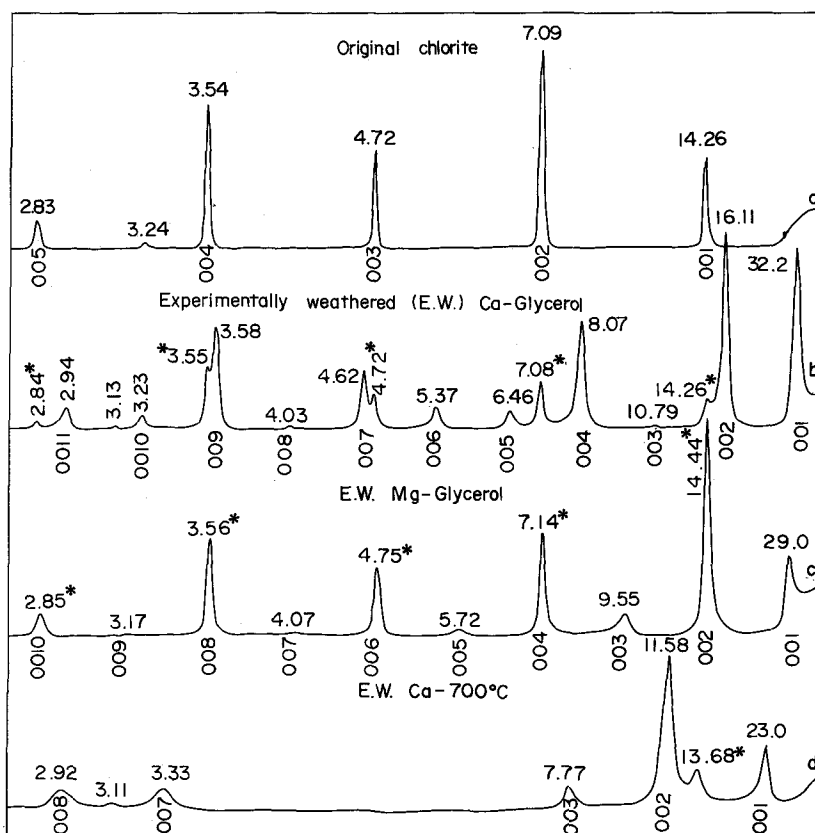
Fig. 1. Smoothed X-ray powder diffraction patterns of the original chlorite and the regularly interstratified chlorite–vermiculite formed by the artificial weathering of the chlorite in the laboratory. Spacings in Angstrom units. *Reflections (separate from other reflections or included in them) due to discrete chlorite.

Table 1. Chemical analysis and formulas of original and experimentally altered chlorite

	Chlorite before alteration (%)	Chlorite after alteration* (%)
SiO_2 (combined)	27.85	28.13
SiO_2 (free-amorphous)	—	9.3‡
Al_2O_3	18.78	14.70
FeO	13.07	8.21
Fe_2O_3	2.95	6.76
MgO	21.24	15.50
CaO	2.80	2.40
Na_2O	0.10	0.37
K_2O	0.12	0.43
H_2O (200°C)	—	5.20
H_2O (1000°C)†	10.49	15.01
C.E.C. (m-equiv./100 g air-dry wt)	1.5	46.0

$(Al_{1.19}Fe^{3+}_{0.23}Fe^{2+}_{1.14}Mg_{3.29}\square_{0.15})(Si_{2.89}Al_{1.11})O_{10}(OH)_8$
Chlorite

$(Al_{0.65}Fe^{3+}_{0.65}Fe^{2+}_{0.63}Mg_{2.28}\square_{0.29})(Si_{2.89}Al_{1.11})O_{10}(OH)_5$
$(Ca_{0.19})+0.38$
Chlorite–vermiculite

* Sample contains approximately 23% discrete chlorite.
† Weight loss at 1000°C adjusted to account for weight gain due to oxidation of FeO.
‡ Estimated from the formula calculation by assuming the same tetrahedral Si to Al ratio as for the original chlorite.

altered material was calculated after eliminating the chemical content of 23% discrete chlorite. According to its formula the chlorite–vermiculite component in the altered material has a CEC of 75 m-equiv./100 g. Thus the charge on the expanding layers is in the lower range of vermiculites. A comparison of the formulas shows an increase of vacancies from 0.15 in the 6 octahedral sites of the original chlorite to 0.29 in the 4.5 octahedral sites of the chlorite–vermiculite.

Thermal analysis. The TGA and DTGA curves for the original chlorite (Fig. 2a) show the characteristic major weight loss between 500°C and 750°C due to dehydroxylation of the interlayer hydroxide sheet and the smaller weight loss between 800 and 900°C due to dehydroxylation of the octahedral sheet of the 2:1 layer. The curves for the altered chlorite (Fig. 2b) show an additional weight loss of 5.2% of the initial sample weight below 200°C. This is attributed to loss of interlayer water which is released in two steps. About 80% of the total amount is lost below 100°C; the remaining 20% is lost between 100 and 200°C. There is a small weight loss between 300 and 450°C which is probably due to loss of water from some partially hydrated interlayer hydroxide sheets. As expected, the weight loss resulting from dehydroxylation of the interlayer hydroxide sheets in the altered
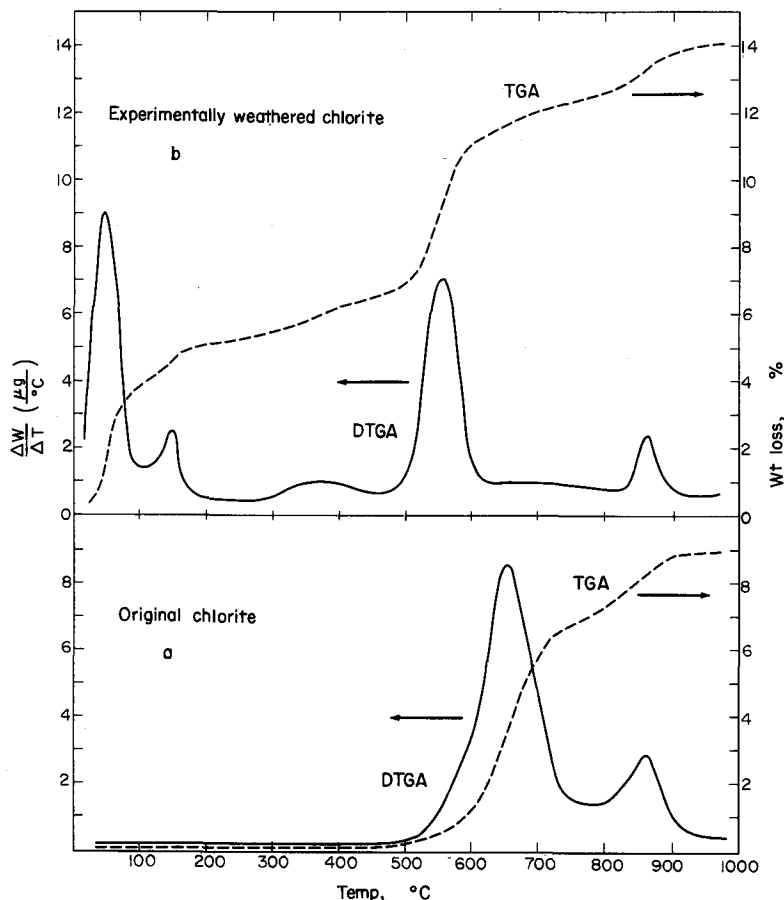
Fig. 2. Thermogravimetric analysis (TGA) curves and differential thermogravimetric analysis (DTGA) curves of the original chlorite and the regularly interstratified chlorite–vermiculite formed by the artificial weathering of chlorite in the laboratory.

chlorite is considerably smaller than the corresponding weight loss of the original chlorite. It also starts at 500°C but is completed at 620°C as compared with 750°C for the completion of this reaction in the original chlorite. The octahedral sheet of the 2:1 layer in the altered chlorite dehydroxylates within the same temperature range (800–900°C) as that of the original chlorite. The weight losses at the temperatures shown in the DTGA curve of the altered chlorite agree closely with those of the regularly interstratified chlorite–vermiculite shown by Bradley and Weaver (1956) and with those of the regularly interstratified chlorite–vermiculite described by Johnson (1964).

Structural analysis. X-ray powder diffraction data of the original chlorite and the chlorite–vermiculite are shown in Table 2. The asymmetry (defined as the number of heavy octahedral atoms (Fe) in the 2:1 layer minus those in the interlayer hydroxide sheet) of the original chlorite was calculated from its intensities shown in Table 2 using Petruk's curve (1964). In this method the degree of asymmetry is determined from the ratio $I_{003}I_{005}$. According to Petruk's curve the asymmetry of the chlorite is 0.6. After converting I_{obs} of the original chlorite in Table 2 to structure

amplitudes (F), the asymmetry of the chlorite was also evaluated using the structure amplitudes in the Brindley and Gillery tables (1956). According to their method the asymmetry of the chlorite is 0.4. Because of the uncertainties inherent in these methods (Bailey, 1972), this agreement is probably as good as can be expected.

The structure of the interstratified mineral was further investigated by Fourier analysis of the basal reflection intensities which provides information about electron density distributions along (001). Because a relatively small amount of the material was well dispersed on a glass slide, a nearly perfect basal orientation was assumed. After correcting for the intensity contributions belonging to the discrete chlorite, the observed (00l) reflection intensities were corrected for absorption, Lorentz and polarization factors. They were then converted into observed structure factors $(1F1_{obs})$ and normalized to calculated structure factors. Both random powder and single-crystal Lorentz polarization factors were used to compute $(1F1_{obs})$. As was expected from the basal orientation of the specimen, the use of single-crystal Lorentz polarization factor gave the best agreement with

Table 2. X-ray powder diffraction data for the experimentally-formed regularly interstratified chlorite–vermiculite (Ca + glycerol) and the original chlorite

		Chlorite–vermiculite					Original chlorite		
l	d(Å)	$D(001)$ (Å)	I_{obs} (*)(†)	$1F1_{obs}$	F_{calc} (‡)		d(Å)	$d(001)$ (Å)	I_{obs} (*)
1	32.24	32.24	30270	160	−169		14.26	14.26	3018
2	16.11	32.22	24340	205	−197		7.09	14.18	8321
3	10.79	32.37	299	28	46		4.724	14.17	4142
4	8.07	32.38	10920	196	168		3.544	14.18	6449
5	6.46	32.32	1475	82	−80		2.833	14.17	1596
6	5.37	32.24	1510	92	64		2.361	14.17	62
7	4.623	32.36	5640	192	−202		2.025	14.18	396
8	4.028	32.22	204	40	−32		1.775	14.20	23
9	3.584	32.26	11147	327	−304		1.574	14.17	143
10	3.233	32.33	780	94	78		1.418	14.18	356
11	2.936	32.30	2968	197	240		1.289	14.18	11
12	2.695	32.35	664	100	−114		1.180	14.16	218
13	2.484	32.29	75	36	4		—	—	—
14	2.309	32.33	370	87	−7		1.012	14.17	208
15	2.154	32.31	119	54	17				
16	2.023	32.36	720	141	178				
17	1.895	32.22	56	44	4				
18	1.794	32.29	66	49	−40				
19	1.699	32.28	19	29	−18				
20	1.614	32.28	29	39	−34				
21	1.540	32.34	155	93	92				
22	1.469	32.32	93	78	155				
23	1.407	32.35	448	181	−214				
24	—	—	—	—	61				
25	1.293	32.32	113	101	131				
26	—	—	—	—	41				
27	1.197	32.31	293	178	−196				
28	1.156	32.37	116	114	140				
29	—	—	—	—	−8				
30	—	—	—	—	−45				
31	—	—	—	—	−115				
32	1.011	32.35	208	156	91				

Mean $d(001) = 32.30$ Å; Mean $d(001) = 14.18$ Å.
* In an arbitrary scale.
† Overlapping intensities of discrete chlorite excluded.
‡ Calculations based on the model shown in Table 3.

calculated structure factors (F_{calc}). The agreement was further improved by correcting ($1F1_{obs}$) with an arbitrary temperature factor by multiplying with reciprocals of exp ($-2B \sin^2\theta/\lambda^2$), using $B = 3.7$ Å^2 (Johns and Sen Gupta, 1967). Calculated structure factors (F_{calc}) were computed for an idealized one-dimensional model of the regularly interstratified chlorite–vermiculite structure using atomic coordinates modi-

Table 3. Structural model and parameters for the experimentally formed regularly interstratified chlorite-vermiculite

	Composition	Z(Å)
Interlayer cation	0.76 Ca	0.00
Glycerol molecules	$\{$ 0.75 $(CH_2)_2 \cdot CH \cdot (OH)_3$	1.71
	0.75 $(CH_2)_2 \cdot CH \cdot (OH)_3$	2.54
Silicate layer	6 O	5.83
	2.9 Si, 1.1 Al	6.39
	6 O	7.95
	6 $(Fe^{2+}, Fe^{3+}, Al, Mg, \square)$	9.06
	4 O, 2 OH	10.17
	2.9 Si, 1.1 Al	11.73
	4 O, 2 OH	12.29
	6 OH	15.04
Interlayer hydroxide sheet	6$(Fe^{2+}, Fe^{3+}, Al, Mg)$ 6 OH	16.15 $(=c/2*)$

* Centre of symmetry for the 32.30 Å unit cell.

fied from those for chlorite (Pauling, 1930) by including Ca and glycerol alternate interlayers instead of interlayer hydroxide sheets. The parameters for the glycerated interlayers were derived from those for glycerated montmorillonite (Hamilton, 1967). Scattering factors for all atoms involved, except for O^{-2}, were obtained by analytical approximation using coefficients given in *International Tables for X-ray Crystallography* (Vol 4, 1974); the atomic scattering factor for O^{-2} was obtained with the analytical expression by Tokonami (1965). The heavy atom (Fe) content was distributed between the octahedral sheets using the asymmetry value of 0.6 calculated for the original chlorite. Different distributions were tried but gave poorer agreement between observed and calculated structure factors. The spacings and intensities of basal reflections and the structure factors of the chlorite–vermiculite are listed in Table 2 along with the spacings and intensity data of the original chlorite.

A one-dimensional Fourier synthesis was made using the $1F1_{obs}$ values and signs of the calculated structure factors (F_{calc}). For comparison a one-dimensional Fourier synthesis curve was also made using the values and signs of F_{calc}. The resulting electron density distribution curves are shown in Fig. 3. The Fourier synthesis curves clearly indicate that interlayer Ca, associated with glycerol molecules, and interlayer hydroxide sheets alternate between 2:1 layers in agreement with the chlorite–vermiculite mixed-layer structure. However, the Fourier curve computed from the $1F1_{obs}$ values shows a difference in electron density between the tetrahedral sheets, with the tetrahedral sheet next to the expansible interlayer having a higher electron density than the sheet next to the interlayer hydroxide sheet. This abnormality is absent in the Fourier curve computed from the F_{calc} values. Neither was it observed in the Fourier synthesis curve computed from the $1F1_{obs}$ values of the original chlorite (not given here). It is suggested that, if this abnormality is not due to errors in processing the intensity data, it may indicate the presence of some non-exchanged ions (likely Fe^{3+} and Al^{3+}) lodged near the hydroxyls in the hexagonal holes of the tetrahedral sheets facing the expansible interlayer. These ions may have become blocked there during their ejection from the interlayer and the 2:1 layer octahedral sheets.

COMPARISON OF THE EXPERIMENTALLY WEATHERED CHLORITE–VERMICULITE WITH A NATURALLY WEATHERED CHLORITE–VERMICULITE

In Fig. 4 X-ray powder diffraction patterns of the chlorite–vermiculite formed in the laboratory are compared with diffraction patterns of a chlorite–vermiculite formed in a Highfield soil in Adams County Pennsylvania. This soil has developed on greenstone similar to the rock containing the chlorite used in this study. It is likely, therefore, that the initial chlorites producing the artificially and naturally weathered

products were similar. The diffraction patterns of the artificially and the naturally weathered products at 95% r.h. (Fig. 4d, e) are nearly identical. The greater expansion with Ca and glycerol of the artificial product, however, indicates that its expansible layers are more montmorillonitic than those of the natural product (Fig. 4a, c). In addition to quartz, feldspar, and a kaolinite mineral (Fig. 4c, e), there is also some discrete chlorite in the naturally weathered material (Fig. 4g). In his study of the 2–5 μm fraction of this material, Johnson (1964) allocated 65% to chlorite–vermiculite, 25–30% to metahalloysite and 5–10% to mica and albite. He determined a CEC of 57 m-equiv/100 g. The CEC of the medium silt fraction (5–20 μm) of the same material determined in our laboratory was 36.3 m-equiv/100 g. This difference in CEC may be due to a lower degree of chlorite–vermiculite formation in the medium silt fraction than in the fine silt fraction (Johnson, 1964).

DISCUSSION

Previous chemical oxidation experiments (Ross, 1975), showed that a chlorite high in Fe^{2+} content (diabantite) altered directly to vermiculite within a few weeks, whereas a chlorite low in Fe^{2+} content (sheridanite) failed to alter to vermiculite after more than six months reaction. The present chemical oxidation experiments show that a chlorite of intermediate Fe^{2+} content (brunsvigite) from chloritic metabasalt or greenstone in Maryland, alters to a regularly interstratified chlorite–vermiculite within a few months. The experimental weathering product closely
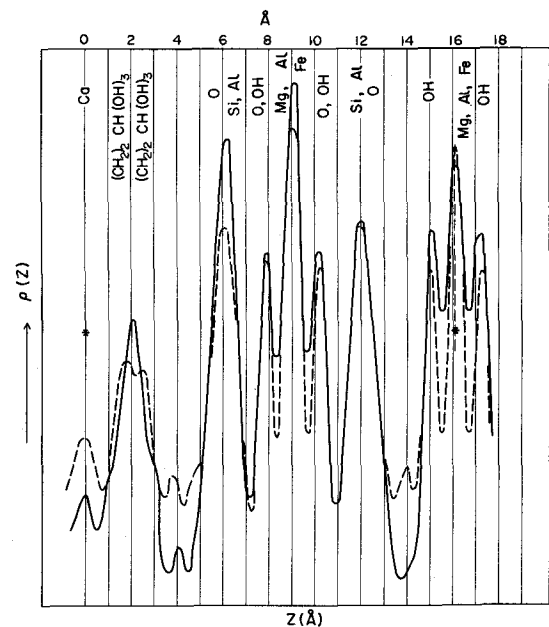

Fig. 3. One-dimensional Fourier synthesis curve of the regularly interstratified chlorite–vermiculite formed by the artificial weathering of the chlorite in the laboratory. Solid curve computed from observed structure factors; broken curve computed from calculated structure factors according to the structural model in Table 3.
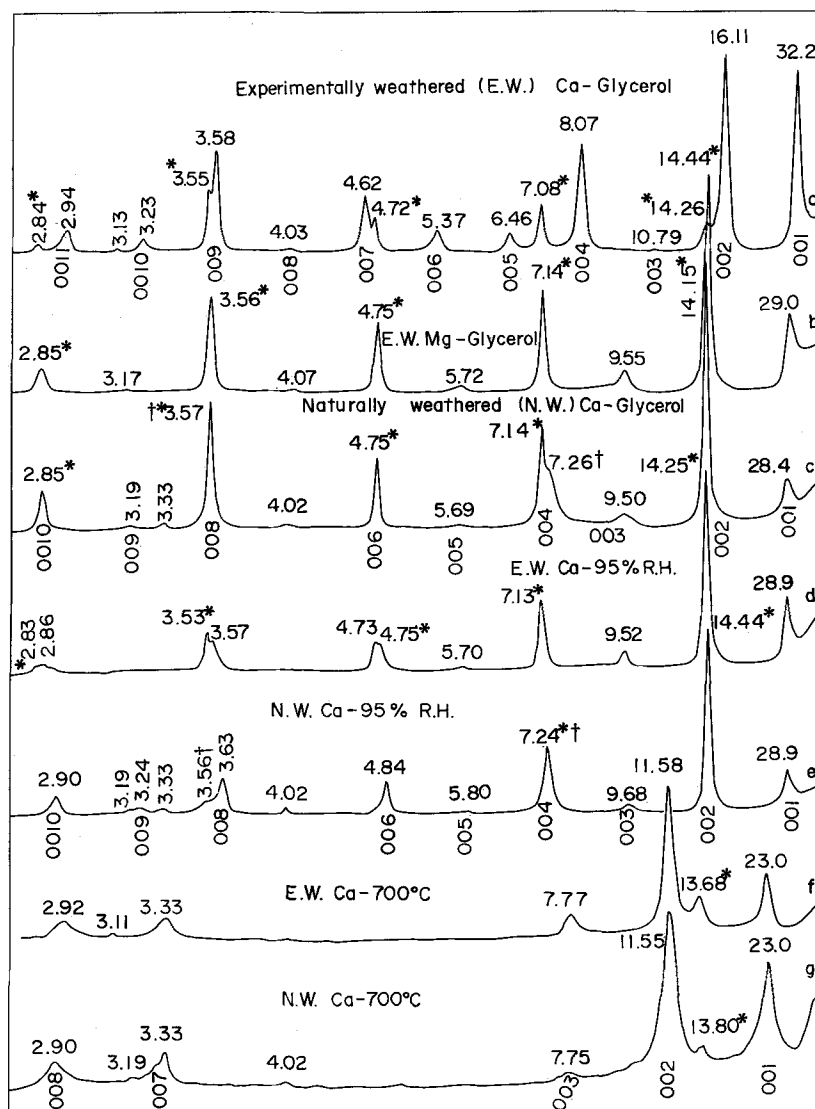
Fig. 4. Smoothed X-ray powder diffraction patterns comparing regularly interstratified chlorite-vermiculite formed by the artificial weathering of chlorite in the laboratory and by the natural weathering of chlorite in the Highfield soil in Adams Co., Pa. Spacings in Angstrom units. *Reflections (separate from other reflections or included in them) due to discrete chlorite. †Reflections (separate from other reflections or included in them) due to kaolinite.

resembles the regularly interstratified chlorite–vermiculite in a Pennsylvania soil developed on greenstone similar to the greenstone in Maryland (Johnson, 1964).

Investigations on the experimental weathering of chlorites (Makumbi and Herbillon, 1972; Ross, 1975; this study) and on the natural weathering of chlorites (Post and Janke, 1973; Herbillon and Makumbi, 1975; Coffman and Fanning, 1975) indicate that oxidation of Fe^{2+} is an important mechanism in the transformation of chlorite to vermiculite. During weathering much of the Fe^{2+} in the original chlorite becomes oxidized and some of it is lost from the structure. This loss of iron and other octahedral cations is evident from the increase in octahedral vacancies of oxidized chlorites and their vermiculi-

tized weathering products and from the accumulation of free iron oxides (Herbillon and Makumbi, 1975; this study).

No direct evidence is available and therefore only speculations can be offered to account for the mechanisms controlling the formation of a regularly interstratified chlorite–vermiculite from a chlorite, having the IIb structural unit, which is a one-layer polytype structure. Because the evidence indicates that vermiculite formation is induced by Fe^{2+} oxidation, a somewhat higher Fe^{2+} content in alternate interlayer hydroxide sheets may result in their preferential removal. Another possibility is that the tetrahedral sheets facing alternate hydroxide sheets have higher Al for Si substitution and higher negative charge which may also lead to preferential removal

of alternate interlayer hydroxide sheets. Bailey (1975) has suggested the possibility of such asymmetric distributions of negative charge in 2:1 layers.

These investigations also show that chlorites, apparently structurally similar, may react differently under the same conditions: the oxidation treatment transforms the IIb brunsvigite into a regularly interstratified chlorite–vermiculite, whereas the same treatment alters the IIb diabantite into a discrete vermiculite with no evidence of a regularly interstratified phase. Detailed structural analyses of the type described by Bailey (1975) are probably necessary to determine whether the alteration process is structurally controlled. Such analyses may also explain the differences in weathering behaviour of chlorites that appear to have the same structure.

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