

EXPERIMENTAL TRANSFORMATION OF A CHLORITE INTO A VERMICULITE*

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Abstract—An orthochlorite (sheridanite) was heated to 610°C to dehydroxylate the hydroxide sheet and to oxidize ferrous iron. The heated sample was shaken for 20 min in a mixed solution of 0.2 N HCl and 0.2 N NaCl to dissolve the dehydroxylated hydroxide sheet. X-ray diffraction, thermal, infrared absorption and chemical analyses showed that the resulting product was similar to Kenya vermiculite. The procedure shows promise for the individual determination of the composition of the hydroxide sheet and of the mica layer in the chlorite structure. The experiments indicate that the hydroxide sheet in orthochlorites must be structurally disturbed before it can be selectively removed. In nature, structural disorganization of the hydroxide sheet of chlorite by dehydroxylation and oxidation of ferrous iron might occur during metamorphic processes, and chlorite to vermiculite transformation could take place during subsequent acid weathering. In pedogenic weathering conditions it is likely that oxidation of ferrous iron plays a major role in initiation of the structural disorder required for the selective removal of the hydroxide sheet in the weathering of chlorite to vermiculite.

INTRODUCTION

Although evidence for the weathering of chlorite to vermiculite in nature has been reported (Bradley and Weaver, 1956; Brown and Jackson, 1956; Gjems, 1960; Ross and Mortland, 1966) such evidence is less conclusive and less well supported by experimental weathering studies than the evidence for the natural weathering of mica to vermiculite. Caillère *et al.* (1952) observed that 'swelling chlorites' could easily be changed to montmorillonites by acid treatment but that the corresponding transformation with true chlorites was very difficult to achieve. Ross (1969) also found no evidence for a preferential dissolution of the hydroxide sheet in true chlorites by acid treatment and showed that the octahedral and tetrahedral sheets in the chlorite structure were attacked at equal rates. More recently, Makumbi and Herbillon (1972) using a variety of treatments on an iron-rich chlorite found that only the treatments with sodium dithionite or sodium sulfite soln resulted in the formation of a chlorite-vermiculite regularly interstratified mineral. They emphasized the importance in the transformation of chlorite of the irreversible oxidation of iron and its subsequent removal.

From the literature cited thus far, it seems that the hydroxide sheet in a true chlorite must be structurally disturbed before it can be preferentially removed and expansion can occur. If this is true, structural disorganization due to dehydroxylation of the hydroxide

sheet and to oxidation of ferrous iron in a true chlorite followed by acid treatment might result in selective removal of the hydroxide sheet with attendant structural expansion. This investigation was designed to examine this supposition by comparing the initial chlorite with the products obtained after a partial dehydroxylation and acid-washing procedure.

EXPERIMENTAL

The 0.2–2 μm fraction of an orthochlorite from Brewster, New York was used. This chlorite was analyzed previously and classified as sheridanite (Ross, 1969). The X-ray powder pattern indicated that this sheridanite has the I1b polytype structure according to the definition of Brown and Bailey (1963).

Previous work (Ross, 1968) showed that the hydroxide sheet of this chlorite dehydroxylates between 550 and 600°C and the remaining octahedral sheet between 810 and 870°C. Hence a 200 mg sample was heated to 610°C, a temperature which marked the maximum wt loss due to dehydroxylation of the hydroxide sheet. The heating was done at 5°C/min with a TGA apparatus which consisted of an analytical balance and a Fisher Balance Assembly mounted over a cylindrical furnace containing a suspended Pt dish with the sample. Thirty mg of the heated material were transferred to a 100 ml polyethylene centrifuge tube which contained 50 ml of a mixed 0.2 N HCl and 0.2 N NaCl solution. The contents were shaken for 20 min and then centrifuged. The sample was centrifuged once

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more with 50 ml 0.2 N NaCl. To be certain of complete Na saturation, the material was then shaken overnight in 50 ml 0.5 N NaCl. The sample was subsequently washed with H₂O until free of chloride and then freeze-dried.

The treated samples were digested with HF and HClO₄ for elemental analysis. Aluminum, Fe, Ca, Mg, Na and K were determined by atomic-absorption spectrophotometry. Silicon was determined by the molybdosilicic acid method after fusion of the sample with Na₂CO₃ (Jackson, 1958). Ferrous iron of the altered chlorite was determined by the method of Reichen and Fahey (1962).

X-ray diffraction analysis on basally and randomly oriented samples was done with a Philips diffractometer using Fe-filtered Co radiation. Basally oriented specimens were obtained by dispersing 20 mg of the sample in 1 ml H₂O and pipetting this suspension on a 3.5 × 2.5 cm glass slide. Randomly oriented specimens were prepared by packing freeze-dried material in a depression on a glass slide.

Differential thermal analysis (DTA) curves were obtained over a temperature range of 25–1000°C at a heating rate of 10°C/min using a R.L. Stone DTA apparatus. The samples were diluted 50:50 with alumina. Thermogravimetric analysis (TGA) was done at a heating rate of 5°C/min with an instrument described above. A differential thermogravimetric analysis (DTGA) curve for one of the samples was plotted manually.

Infrared absorption curves were obtained with a Beckman i.r. 12 grating spectrophotometer with the samples dispersed in KBr disks at a concentration of 1 mg sample per 400 mg KBr.

RESULTS

Figures 1(A) and (B) show the small decrease in basal spacings and the drastic change in intensities of the basal reflections which occur upon dehydroxylation of the hydroxide sheet (see also Brindley, 1961). The heated sample after acid treatment and Na saturation, labelled vermiculitized chlorite (Fig. 1D), has a basal spacing of 14.9 Å at 100 per cent r.h. and shows an integral series of basal reflections (see Table 1). The observed d_{001} spacing is almost identical to those of the Na-forms of vermiculites reported by Walker (1961). The non-basal reflections also agreed with the

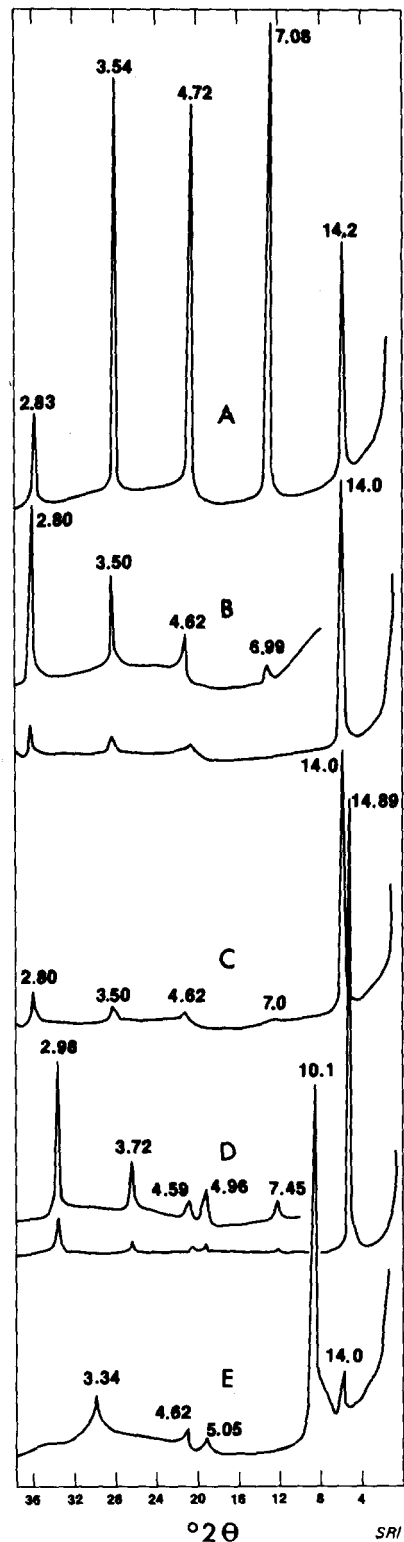


Fig. 1. X-ray diffraction patterns of original chlorite (A); chlorite after heating to 610°C and run at 0% r.h. (B), at 100% r.h. (C); vermiculitized chlorite run at 100% r.h. (D) and at 0% r.h. (E). The upper patterns in (B and D) are the lower patterns 10 times amplified. Indicated spacings in angstrom units.

Table 1. X-ray diffraction data obtained for the Na-saturated, vermiculitized chlorite sample at room temperature and 100 per cent r.h.

<i>n</i>	<i>d</i> (Å)	<i>nd</i> (Å) = <i>d</i> ₍₀₀₁₎	<i>I</i>	<i>F</i> * _{obs}	<i>F</i> _{calc} †
1	14.89	14.89	1000	169	+ 181
2	7.45	14.90	15	31	+ 13
3	4.96	14.88	24	52	- 48
4	3.723	14.89	26	69	+ 99
5	2.980	14.90	86	153	+ 153
6	2.480	14.88	~ 1	19	+ 21
7	2.127	14.89	39	142	- 61
8	1.860	14.88	6	65	- 61
9	1.656	14.90	~ 1	36	+ 26
10	1.490	14.90	12	115	+ 91
mean <i>d</i> ₍₀₀₁₎ = 14.89 ± 0.01 (Å)					

* Intensities corrected for absorption effect.

† *F*-values are based on chemical formula per O₂₀(OH)₄ anionic unit.

data published by Walker (1961). In particular, the intensities of the reflections at 2.66 and 2.09 Å were as strong as those at 2.60 and 2.05 Å, respectively, whereas in the original chlorite the intensities of the former set of reflections were much weaker than the latter. At 0 per cent r.h. (Fig. 1E) the first order basal reflection occurs at 10.1 Å, except for a small peak at 14.0 Å which indicates a small amount of unaltered chlorite. The 10.1 Å reflection is somewhat asymmetrical, and higher orders are broadened which also indicates the presence of hydrated vermiculite and chlorite layers.

Since the material was well dispersed on a glass slide, a nearly perfect orientation was assumed. The observed structure factors ($|F|_{\text{obs}}$) in Table 1 were evaluated from the experimental intensities using the

angular factor for a single crystal after correction for the absorption effect due to the thin specimen. The vermiculitized chlorite was Na-saturated, and therefore the intensity distribution was not quite the same as that of Mg-vermiculite (Mathieson, 1958) as indicated by the rather large value of 0.32 for the *R* factor ($(\sum |F_{\text{obs}} - F_{\text{calc}}| / \sum |F_{\text{obs}}|)$). As shown in Table 2, the chemical formula of the vermiculitized chlorite is almost the same as that of the Mg-vermiculite from Kenya, except for its interlayer components. Therefore, structure factors for the basal reflections were calculated by assuming that the silicate layer of the Na-form was basically the same as that of the Mg-form except that only the interlayer configuration (interspace and cationic species) was modified. This reduced the *R* fac-

Table 2. Chemical analysis and calculated formulas of chlorite, vermiculitized chlorite and Kenya vermiculite

	As % of ignited wt		
	Chlorite	Vermiculitized chlorite	Kenya vermiculite
SiO ₂	31.27	43.36	43.71
TiO ₂	0.11	n.d.	1.01
MnO ₂	0.00	0.00	0.05
Al ₂ O ₃	24.18	19.88	16.74
Fe ₂ O ₃	0.67	6.69	8.48
FeO	5.69	0.05	1.48
MgO	37.84	27.34	30.04
CaO	0.03	n.d.	0.28
Na ₂ O	0.16	4.08	n.d.
K ₂ O	0.03	n.d.	0.00
	99.98	101.40	101.79
C.E.C. m-equiv 100 g ⁻¹ air dry wt	—	110	130
Chlorite (Ross, 1969)	(Al _{1.00} Fe _{0.04} ³⁺ Fe _{0.39} ²⁺ Mg _{4.72}) (Si _{2.62} Al _{1.38}) O ₁₀ (OH) ₈		
Vermiculitized chlorite	(Al _{0.22} Fe _{0.32} ³⁺ Mg _{2.57}) (Si _{2.74} Al _{1.26}) O ₁₀ (OH) ₂ [Na _{0.50}] ^{+0.50}		
Kenya vermiculite (Brydon and Turner, 1972)	(Fe _{0.40} ³⁺ Fe _{0.08} ²⁺ Ti _{0.05} Mg _{2.54}) (Si _{2.76} Al _{1.24}) O ₁₀ (OH) ₂ [Ca _{0.02} Mg _{0.28}] ^{+0.60}		

tor to 0.22. The observed deviations are, therefore, considered to be largely due to the interlayer arrangement. Due to the limited precision of the data, no further structural refinement was attempted.

The DTA curves of sheridanite (Figs. 2A and B) show the disappearance of the first dehydroxylation endotherm at 622°C after previously heating the chlorite to 610°C. However, a small endotherm is still present at 487°C. This suggests that the previous dehydroxylation of the hydroxide sheet may not have been complete. It is also possible that some rehydroxylation may have occurred, despite careful preventative measures. The endotherms at 96 and 127°C in the curve for the vermiculitized chlorite (Fig. 2C) indicate the presence of adsorbed and interlayer H₂O, respectively.

The TGA data in Fig. 3 agree with the DTA data in Fig. 2. The TGA curves show that the main wt loss due to dehydroxylation of the hydroxide sheet in the original chlorite (Fig. 3A) has shifted down to a large weight loss due to loss of interlayer water in the vermiculitized chlorite (Fig. 3B). This curve, obtained from a sample initially at 30 per cent r.h. shows a total H₂O loss at 16.5 per cent. Because X-ray, thermal and chemical evidence indicated that the sample contained about 10 per cent chlorite, 1.3 per cent of the weight loss was allocated to chlorite OH and 3.9 per cent to vermiculite OH. The remaining weight loss of 11.3 per cent was attributed to adsorbed plus interlayer H₂O. The first small peak in the DTGA curve (Fig. 3C) indicates a rapid weight loss of 2.4 per cent between 25 and 60°C which is considered to be adsorbed H₂O. Hence 8.9 per cent remains for interlayer H₂O, which is equal to 2.4 molecules of H₂O for the formula unit of the vermiculitized chlorite shown in Table 2. This amount corresponds to one in-

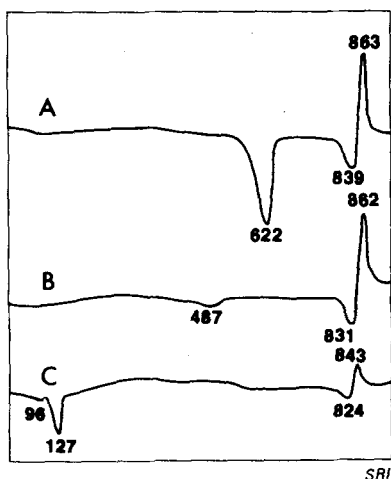


Fig. 2. DTA curves of original chlorite (A); chlorite after heating to 610°C (B); vermiculitized chlorite (C).

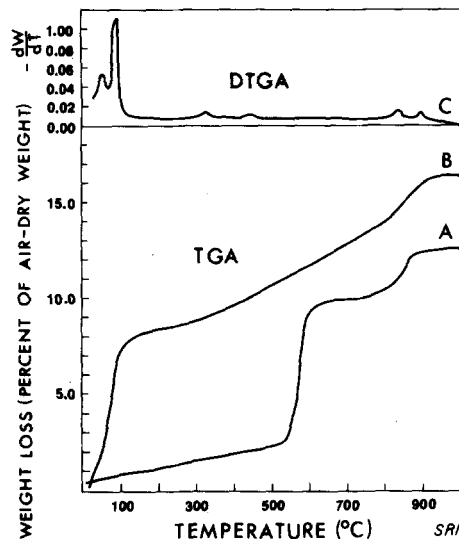
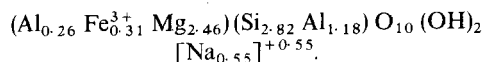


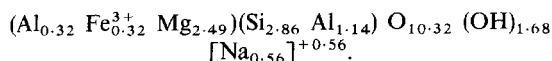
Fig. 3. TGA curves of original chlorite (A); vermiculitized chlorite initially at 30 per cent r.h. (B); DTGA curves of vermiculitized chlorite (C).

terlayer of H₂O (Walker, 1956) and agrees with the d_{001} spacing of 12.5 Å at 30 per cent r.h.

The elemental compositions and structural formulas of the original chlorite, the vermiculitized chlorite and Kenya vermiculite are compared in Table 2. Analysis for Fe²⁺ showed that practically all the ferrous iron was oxidized by the heating procedure. The acid washing removed 41, 32 and 48 per cent of the number of moles (based on ignited wt) of Al, Fe and Mg, respectively, initially present in the chlorite. This represents approx. 2.8 octahedral atoms out of the theoretical number of 3 which should have been removed if the complete hydroxide layer had been selectively dissolved. If it is assumed that 10 per cent chlorite is still present in the vermiculitized chlorite sample and if this is excluded in the calculation of the formula for the vermiculitized chlorite, the formula is



This formula is further modified if the calculation is based on an anion charge of 22 + α per half-unit cell where α is the number of H⁺ ions lost due to oxidation of Fe²⁺ to Fe³⁺ in the mica layer (Rimsaite, 1970). This formula is



Because the estimated amount of chlorite was small, as was the original ferrous iron content, the changes in the above formulas as compared with the formula in

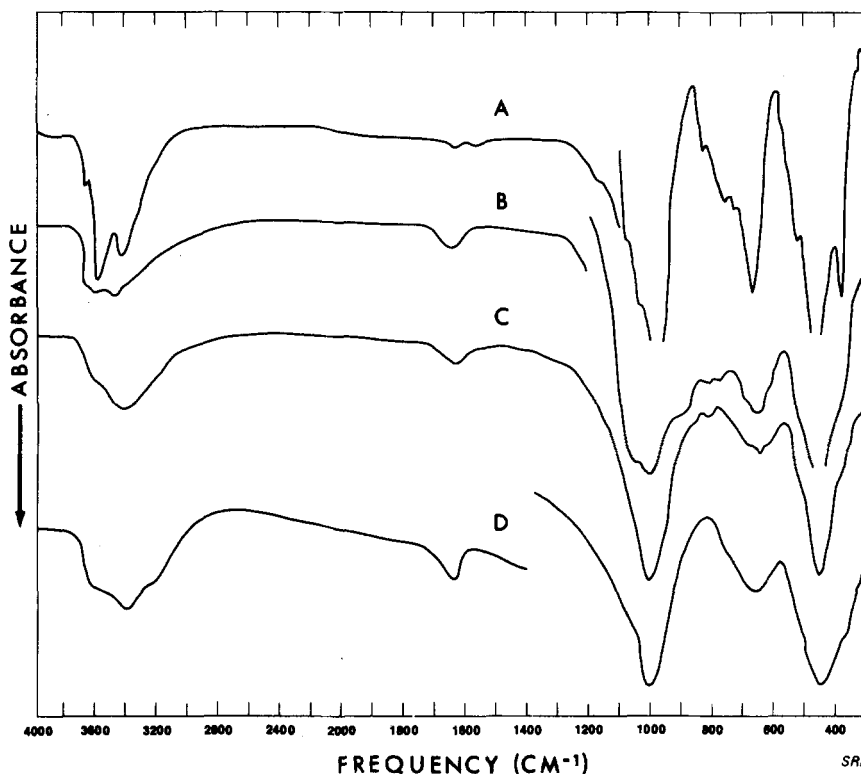


Fig. 4. I.R. curves of original chlorite (A); chlorite after heating to 610°C (B); vermiculitized chlorite (C); Kenya vermiculite (D).

Table 2 are relatively small. The deficiency of hydroxyl according to the last formula suggests that the vermiculitized chlorite may have a strong affinity for K and other monovalent cations of similar size. The formulas for the original chlorite and the vermiculitized chlorite show that the Si to Al ratio of the tetrahedral sheet of the latter is higher. This increase is probably not real, however, and may be the result of an unavoidable acid attack on the mica layer in the chlorite structure during acid treatment. The attacked part would remain as an amorphous silica residue (Ross, 1969) and give rise to an apparent increase in the tetrahedral Si to Al ratio for the vermiculitized chlorite. The formulas for the vermiculitized chlorite are comparable to the formula of Kenya vermiculite.

The i.r. absorption curves in Fig. 4 illustrate the major changes in absorption which occurred after dehydroxylation and vermiculitization of the chlorite. The band at 385 cm^{-1} in the chlorite spectrum has virtually disappeared in the spectra for the heated and for the vermiculitized chlorite (Figs. 4B and C). This disappearance suggests that this band is due to absorption by components of the hydroxide sheet. The absorption at 665 cm^{-1} for Si-O vibration is also markedly

reduced in these spectra. The distinctive OH absorption maxima at 3430 and 3580 cm^{-1} in the chlorite spectrum have lost their distinctness and have broadened to a band at 3500 cm^{-1} due to absorption by OH and adsorbed water in the spectrum for the heated chlorite (Fig. 4B) and to a band at 3400 cm^{-1} due to absorption by OH and interlayer water in the spectrum for the vermiculitized chlorite (Fig. 4C). The spectrum for the vermiculitized chlorite is practically identical to the spectrum of Kenya vermiculite (Fig. 4C and D).

DISCUSSION

The evidence from X-ray diffraction, thermal, and chemical analysis indicates that the hydroxide sheet of the chlorite was largely removed by the procedure used and that the resulting product was similar to Kenya vermiculite. The somewhat higher Si to Al ratio of the tetrahedral sheet of the vermiculitized sample as compared with that of the original chlorite suggests that the acid treatment may have caused some acid attack on the mica layer in the chlorite structure. Further experimental modifications are necessary to obtain complete removal of the hydroxide sheet without signifi-

cant acid attack on the mica layer. Thus it is possible that the composition of the hydroxide sheet and of the mica layer in the chlorite structure may be individually determined.

Previous studies on the dissolution of chlorites by acid in the laboratory failed to give evidence for the preferential removal of the hydroxide sheet from true chlorites (Caillère *et al.*, 1952; Ross, 1969). Apparently, selective removal is successful only after the structure of this sheet has been disturbed. This disturbance may be induced by dehydroxylation and by oxidation of ferrous iron (see also Bain, 1972; Makumbi and Herbillon, 1972).

These experiments suggest the natural conditions in which chlorite may be changed to vermiculite. Temperatures sufficiently high for oxidation of ferrous iron and for dehydroxylation of the hydroxide sheet of chlorites could occur during metamorphic processes, and chlorite to vermiculite transformation could then take place during subsequent acid weathering. In pedogenic weathering, it is likely that irreversible oxidation of ferrous iron in the hydroxide sheet of chlorites plays a major role in the selective dissolution of this sheet. An example of this weathering process may be the formation of vermiculitic soils on chlorite metabasalt in the Middletown Valley of Maryland.* As yet, there is no unequivocal evidence for chlorite to vermiculite transformation in 'true' Podzols (Brydon *et al.*, 1968). It is probable that orthochlorites or their vermiculitized products are not stable in the highly acid weathering conditions prevailing in these soils.

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Résumé—Une orthochlorite (sherdanite) a été chauffée à 610°C pour deshydroxyler la couche hydroxyde et oxyder le fer ferreux. L'échantillon chauffé a été agité pendant 20 mn dans une solution mixte de HCl 0,2 N et NaCl 0,2 N afin de dissoudre la couche hydroxyde deshydroxylée. La diffraction X, les analyses thermiques, spectrométriques infrarouge et chimiques montrent que le produit résultant est semblable à la vermiculite du Kenya. La technique utilisée semble prometteuse pour déterminer spécifiquement la composition de la couche hydroxyde et la structure du feuillet mica dans la chlorite. Les expériences indiquent que la couche hydroxyde des orthochlorites doit acquérir une structure désordonnée avant de pouvoir être extraite sélectivement. Dans la nature, la désorganisation de la structure de la couche hydroxyde de la chlorite, par deshydroxylation et oxydation du fer ferreux, pourrait se passer pendant les phénomènes

métamorphiques, et la transformation de la chlorite en vermiculite pourrait se faire pendant l'altération acide ultérieure. Dans des conditions d'altération pédologiques, il est probable que l'oxydation du fer ferreux joue un rôle prépondérant dans l'initiation du désordre structural requis pour l'extraction sélective de la couche hydroxyde lors de l'altération de la chlorite en vermiculite.

Kurzreferat -- Ein Orthochlorit (Sheridanit) wurde auf 610°C erhitzt, um die Hydroxidschicht zu dehydroxylieren und zweiwertiges Eisen zu oxidieren. Die erhitzte Probe wurde für 20 Minuten in einer Mischung von 0,2 N HCl und 0,2 N NaCl geschüttelt, um die dehydroxylierte Hydroxidschicht aufzulösen. Röntgenbeugungs-, Thermoanalyse, Infrarotsorption und chemische Analysen zeigten, daß das entstehende Produkt dem Kenya-Vermiculit ähnelt. Das Verfahren erweist sich als vielversprechend für die individuelle Bestimmung der Zusammensetzung der Hydroxidschicht und der Glimmerschicht in der Chloritstruktur. Die Versuche zeigen, daß die Hydroxidschicht in Orthochloriten in ihrer Struktur gestört werden muß, bevor sie selektiv entfernt werden kann. In der Natur mag eine strukturelle Auflösung der Hydroxidschicht von Chlorit durch Dehydroxylation und Oxidation zweiwertigen Eisens während metamorpher Prozesse erfolgen, und eine Umwandlung von Chlorit in Vermiculit könnte während einer späteren sauren Verwitterung stattfinden. Unter pedogenen Verwitterungsbedingungen spielt wahrscheinlich die Oxidation von zweiwertigem Eisen bei der Auslösung von Strukturstörungen, die die Voraussetzung einer selektiven Entfernung der Hydroxidschicht bei der Verwitterung von Chlorit zu Vermiculit sind, eine größere Rolle.

Резюме — Ортохлорит (шериданит) нагрели до 610°C для дегидроксилирования гидроокисного покрова и для окисления двухвалентного железа. Для растворения дегидроксилированного покрова нагретый образец встряхивали в течение 20 минут в смешанном растворе 0,2 N HCl и 0,2 N NaCl. Рентгенографическое и термальное исследования, ИК-спектр поглощения и химический анализ показали, что результирующий продукт подобен кенийскому вермикулиту. Эта процедура может оказаться пригодной для индивидуального определения состава гидроокисного покрова и слоя слюды в структуре хлорита. По опытам видно, что структуру гидроокисного покрова в ортохлорите необходимо разрушить до его селективного удаления. В природе, структурная дезорганизация покрова хлорита посредством дегидроксилирования и окисление двухвалентного железа могут происходить во время метаморфических процессов, а переход хлорита в вермикулит может совершиться во время выветривания в результате окисления. При педологическом выветривании, весьма возможно окисление железа играет главную роль в создании структурного беспорядка, требующегося для избирательного удаления гидроокисного покрова в процессе перехода хлорита в вермикулит.