## REFERENCES

Besson, G. and Tchoubar, C., 1972. Determination du groupe de symétrie du feuillet élémentaire de la beidellite. C.R. Acad. Sc. Paris, 275: 633-636.

De Courville, J., Tchoubar, C. and Tchoubar, D., 1978. To be published.

Gaultier, J.P., Besson, G., Plançon, A., Tchoubar, C. and Mamy, J., 1978. To be published.

Kodama, H., Gatineau, L. and Mering, J., 1971. An analysis of X-ray diffraction line profiles of micro-crystalline muscovite. Clays and Clay minerals, 19: 405-413.

Maire, J. and Mering, J., 1960. Chemistry and Physics of Carbon. In P. L. Walker (Editor). Marcel Dekker, Amsterdam, Vol. 6, pp 125-189.

Mamy,J., 1968. Ph. D. Thesis.

Mamy, J. and Gaultier, J.P., 1976. Les phénomènes de diffraction des rayonnements X et électroniques par les réseaux atomiques : application à l'étude de l'ordre cristallin dans les minéraux argileux - II. Annales Agronomiques, 27: 1-16.

Pezerat, H. and Mering, J., 1967. Recherches sur la position des cations échangeables et de l'eau dans les montmorillonites. C.R. Acad. Sc. Paris, 265: 529-532.

Plançon, A. and Tchoubar, C., 1976. Etude des fautes d'empilement dans les kaolinites partiellement désordonnées. II. J. Appl. Crystallogr., 9: 279-285.

Plançon, A. and Tchoubar, C., 1977.a. Determination of structural defects in phyllosilicates by X-ray powder diffraction - I, Clays and Clay Minerals, 25: 430-435.

Plançon, A. and Tchoubar, C., 1977 b. Determination of structural defects in phyllosilicates by X-ray powder diffraction - II, Clays and Clay Minerals, 25: 436-450

Pons, C.H., Ben Brahim, J. and Tchoubar, C., 1978. To be published.

Radoslovitch, E.W., 1960. The structure of Muscovite. Acta Cryst., 13: 919-932.

Ravina, I and Low, P.F., 1977. Change of b-dimension with swelling of montmorillonite. Clays and Clay Minerals, 25: 201-204.

Rousseaux, F. and Tchoubar, D., 1977. Structural evolution of a glassy carbon as a result of thermal treatment between 1000 and 2700°C - II. Carbon, 15: 63-68.

Tettenhorst, R. and Roberson, H.E., 1973. X-ray diffraction aspects of montmorillonites. Amer. Miner., 58: 73-80.

Trunz, V., 1976. The influence of crystallite size on the apparent basal spacings of kaolinite. Clays and Clay Minerals, 24: 84-87.

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# THE FERRIC ANALOGUE OF PYROPHYLLITE AND RELATED PHASES

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## ABSTRACT

**The ferric analogue of pyrophyllite (ideal formula $Fe_2Si_4O_{10}(OH)_2$) and related phases that form evenly expanded or mixed-layer structures with water have been found and identified by means of electron and X-ray diffraction.**

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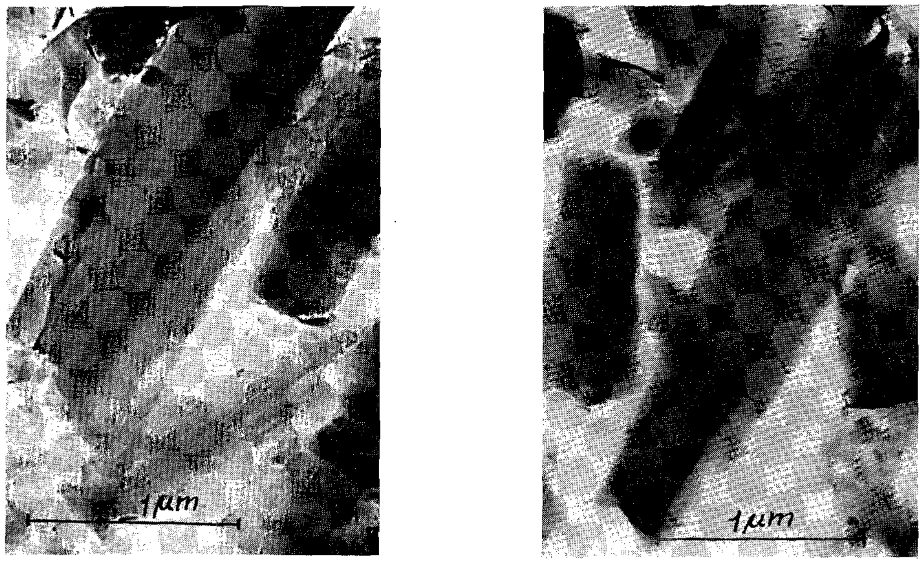
## INTRODUCTION

The phases studied have been found in deposits from Strassenschacht near Eibenstock (GDR) and on Mount Tologay (central Kazakhstan).The samples are cryptocrystalline, yellowish or greenish , and consist of disoriented flakes up to 0.03 mm in dimension. The substance is biaxial, negative, 2V small, $\alpha$ 1.686-1.688, $\beta$ 1.676-1.678, $\gamma$ 1.65-1.66; pleochroism noticeable; specific gravity between 3.01 and 2.97. The microcrystals are generally elongated.

The main components are $SiO_2$, $Fe_2O_3$ and $H_2O$ with minor $Al_2O_3$ and CaO. It is remarkable that the molecular ratio $SiO_2$:$Fe_2O_3$ is nearly 2:1. The DTA- and TG-characteristics display two endotherms at 130° and 500°showing the existence of two kinds of water, and a small exotherm at 835°.

## OBLIQUE-TEXTURE ELECTRON DIFFRACTION PATTERNS (OTEDP)

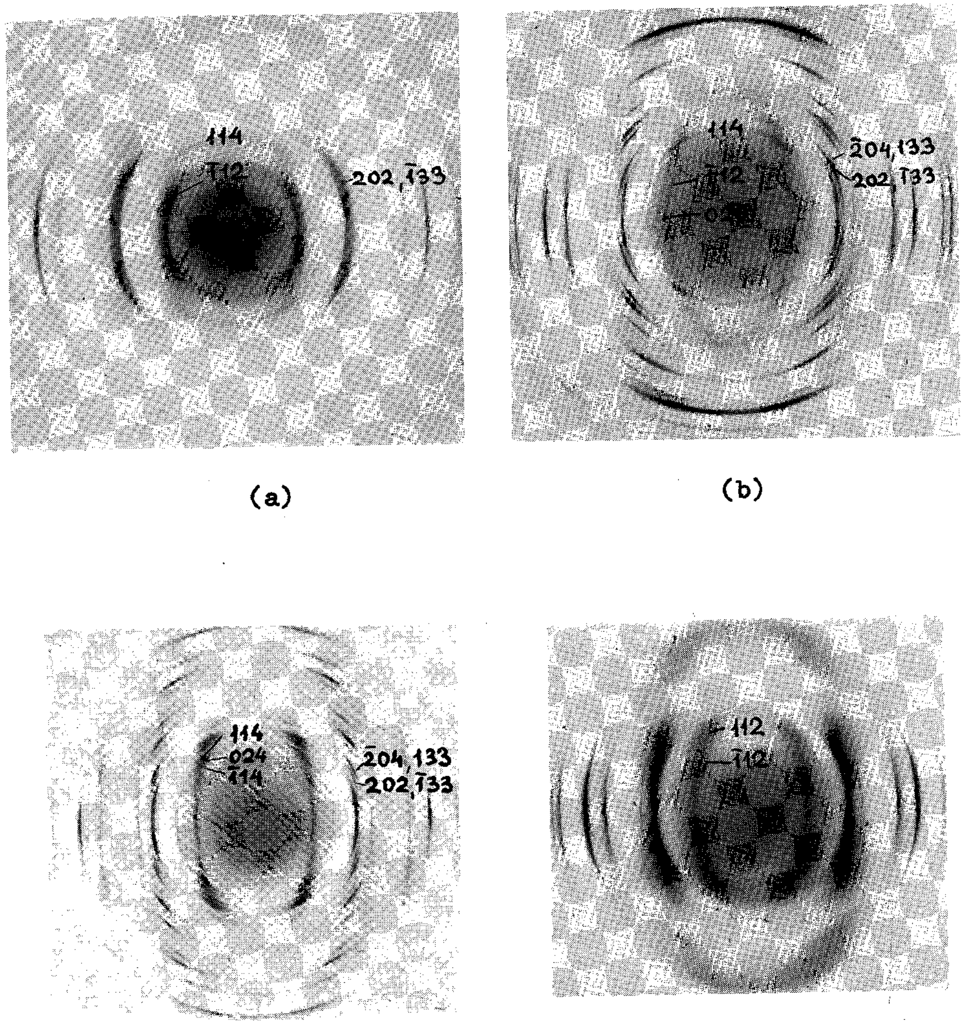
The structural peculiarity of the samples was first established by OTEDP's which revealed the presence of only one crystalline phase with a monoclinic unit cell: a 5.26, b 9.10, c 19.1Å, $\beta$95.5°. The intensities of reflexions in the second ellipse indicate that 2:1 layers are superimposed as in pyrophyllite and talc so that Si-hexagons of adjacent layers do not overlap in the normal projec-



(a) (b)

Fig. 1. Electron micrographs: a) Strassenschacht sample; b) Tologay sample.

tion on the ab plane as in micas, but are displaced to give minimal Si-Si-repulsion. In particular, the pair of coinciding reflexions 202, $\bar{1}33$ (2.46Å) is much stronger than $\bar{2}04$, 133 (2.38Å), while for micas this relation is reversed (cf. Fig's 2a, 2b and 2c). The reflexions in the first ellipse are very distinctive: three reflexions, 020 (4.55Å), $\bar{1}12$ (4.22Å), 114 (3.16Å) are clearly stronger than the others (cf. Figs 2a and 2b). This is a unique feature of a two layer monoclinic polytype 2M - $\sigma_3 \sigma_3 \tau_1 \sigma_3 \sigma_3 \tau_5$.... (Zvyagin et al., 1968) with ideal symmetry C2/c. The sequence of layers expressed by this notation was observed for pyrophyllites while talcs usually have a semirandom structure (ordered only in the projection on the ac plane) or sometimes a one-layer triclinic structure 1TC- $\sigma_2 \sigma_2 \tau_4$ ... (Smolin et al., 1975). The reflexions 261, 401 in the sixth ellipse and 171, 351, 421 in the seventh have comparable intensities, this being an indication that the phyllosilicate is dioctahedral (for trioctahedral phyllosilicates the



(a) (b)

(c) (d)

Fig. 2. Oblique-texture electron diffraction patterns of the studied samples (a), pyrophyllite, (b), muscovite (c), nontronite (d).

former are in general stronger than the latter).

All these structural data together with the evidence of the chemical composition point directly to a ferric analogue of pyrophyllite having $Fe^{3+}$ instead of Al in octahedra and consequently an ideal formula $Fe_2Si_4O_{10}(OH)_2$.

Starting with the value b 9.13Å of talc and using regression coefficients for Mg and $Fe^{3+}$ (Drits, 1969) one may evaluate what b-dimension is to be expected for the ideal composition according to the relation $b = 9.13-0.062(Mg)+0.077(Fe^{3+})$, where $(Fe^{3+})$ is the actual content of $Fe^{3+}$ and (Mg) is the deficit in Mg in comparison with the formula of talc. For the new phase (Mg) = 3 and $(Fe^{3+}) = 2$, so b = 9.098Å. The calculated sp. gr. according to the indicated unit cell containing Z = 4 ideal formula units is 3.05. Such a close agreement between the calculated and experimental values supports the structure proposed for the substance as it exists under the vacuum conditions of electron diffraction.

## X-RAY DATA

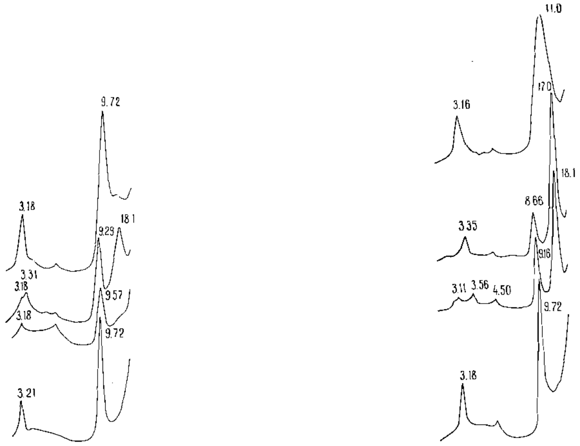
The X-ray study has however revealed some differences and some additional features for both samples. The powder diagram of the Strassenschacht sample has a few lines which may be interpreted with the help of the OTEDP's. One may recognize there the main reflexions mentioned above (202, $\bar{1}33$; 020 (060); $\bar{1}12$) which are related to the three-dimensional pyrophyllite-like structure. There are also basal reflexions 001 (9.6Å), 003 (3.17Å), the last probably coinciding with 114. Without the evidence given by OTEDP's it is easy to interpret such a powder diagram as resulting from a semirandom talc structure (there are slight differences in the basal spacings). The absence of OTEDP's is perhaps a reason why pyrophyllite-like structures with $Fe^{3+}$ in octahedra have not been recognized earlier in the course of current X-ray work.

TABLE 1
The X-ray powder diagram of the Strassenschacht sample

| hkl | d (Å) | I | hkl | d (Å) | I |
|---|---|---|---|---|---|
| 002 | 9.6 | 8 | 202, $\bar{1}33$ | 2.47 | 4 |
| 020 | 4.54 | 10 | 0.0.10 | 1.89 | 1 |
| $\bar{1}12$ | 4.25 | 2 | 150, 241, $31\bar{1}$ | 1.725 | 3 |
| 114,006 | 3.17 | 7 | 208, 139 | 1.665 | 3 |
| $\bar{2}02$,131 | 2.62 | 4 | 060 | 1.518 | 8 |

The X-ray pattern of the oriented specimen has two strong basal reflexions at spacings 9.72 and 3.18Å and a weak peak at 12Å. After heating at 600° the small peak disappeared, the two other

peaks remaining practically unchanged. Saturation with glycerol results in a small displacement of the first reflexion towards greater $\vartheta$ (9.57Å) and in broadening of the reflexion at 3.2-3.3Å. After saturation with ethylene glycol a nonintegral series of basal reflexions appears at 18.1, 9.29, 3.31-3.18Å.



(a) (b)

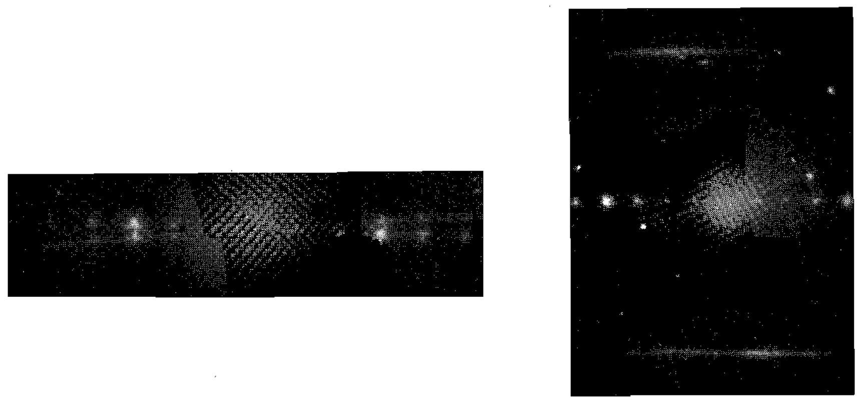
Fig. 3. X-ray diffraction patterns of oriented specimens: a) Strassenschacht sample, b) Tologay sample. Order from top to bottom: natural state; saturated with ethylene glycol; saturated with glycerol; heated at 600°.

On the basis of these data one may conclude that the main part of the Strassenschacht sample does not expand with water. Its structure is essentially the same as indicated by electron diffraction. The small quantity of interlayer water is present in a phase which is a one-layer complex ($d_{001}$ 12Å) not exceeding 5% of the substance. The interaction of the interlayers with polar liquids is greater. With glycerol and ethylene glycol about 15-20% and 40-50% respectively of interlayers expand giving a random interstratification of interlayers with and without polar liquids. However, powder hkl reflexions related to the monoclinic 2M structure are not affected by such treatments, showing that some part of the substance is a non-expanding phase.

According to the X-ray data the main part of the Tologay sample is hydrated. The first basal reflexion is at 12Å for the coarser fraction and at 11Å for the finer fraction. With ethylene glycol 80–90% of interlayers expand giving maxima at 17.0, 8.66, 5.56, 3.35Å. Under glycerol, fewer interlayers expand and the basal spacings are 18.1, 9.16, 4.50, 3.56Å. In this case also reflexions at 4.20, 3.18, 2.46Å are seen after all treatments, indicating the presence of a non swelling phase which however, does not exceed 10–20%, otherwise an additional basal reflexion at 9.6Å would be noticed in the X-ray patterns of the sample saturated with ethylene glycol.

## SELECTED AREA ELECTRON DIFFRACTION DATA

All particles lying normal to the electron beam gave hexagonal spot diagrams with strong $0\overset{\pm}{2}0$ reflexions in accordance with the monoclinic lattice. Comparison with micrographs show that elongation is in the a-direction. Bent edges (Gorshkov, 1970) gave basal reflexions which are characteristic for single particles. It was established that all particles of the Strassenschacht sample give a rational 001 series of a nonexpanded lattice while the majority of particles of the Tologay sample give an irrational 001 series due to a mixed-layer structure. After saturation with ethylene glycol three kinds of basal series have been obtained: a) an integral series from the nonexpanded structure (the first reflexion at 9.6Å) – mainly for the Strassenschacht sample; b) an integral series from a one-layer complex with the first reflexion near 13 Å – mainly for the Tologay sample; c) a nonintegral series of mixed-layer structures with different ratios of expanded and non-expanded interlayers. It is interesting to note that basal series of different kinds have been met both for different particles and for one and the same particle.



(a) (b)

Fig. 4. SAD-patterns: a) rational 001-series with 001 at 9.6Å; b) rational 001-series with 001 at 13Å. Continuous streaks 201 in b) show that the particles are elongated in the a-direction.

## DISCUSSION OF PHASES

The behaviour of the samples following the treatments described indicate the existence of inhomogeneities with different deviations from the ideal structure associated with vacancies and some substitutions of Al for Si accompanied by location of Ca in the interlayers. These inhomogeneities can be localized in different microcrystals or coexist in one and the same particle.

Considering the interaction of the samples with any of the liquids, three phases may be distinguished, one remaining unchanged, the two others forming, respectively, evenly expanded or mixed-layer structures. As the activity of the liquids is different increasing in the order: water – glycerol – ethylene glycol, phases defined according to their interaction with different liquids do not coincide. If combinations of interaction properties with different liquids are considered, the number of phases increases with the number of reagents applied and the distinction between the phases becomes more slight. In the case of two liquids there may be six phases, for three liquids, ten phases. We consider, however, that only the three phases that exist in nature, and that differ in their interaction with water should be accepted as original phases. Any changes of these phases under the action of glycerol and ethylene glycol may be regarded as effects of artificial transformations and the resulting mixed-layer or completely expanded structures as derivative products, like those which arise in the interaction of kaolinite with potassium acetate.

Phase 1 does not expand in water and has the above-mentioned pyrophyllite-like 2M structure. It is a close $Fe^{3+}$ -analogue of pyrophyllite. A name "ferripyrophyllite" is reserved for it until the final decision of the CNM IMA.

Phase 2 has an evenly expanded structure which exhibits a regular alternation of 2:1 – layers with single layers of water molecules and attains the 2M structure of phase 1 after dehydration: this is the principal difference between phase 2 and nontronite, which has two layers of water molecules between the 2:1-layers and usually attains on dehydration a semirandom structure sometimes displaying features of a mica-like 1M polytype (cf. Figs 2a and 2d). The stackings of layers of the mica and pyrophyllite types are crystallochemically and geometrically nonequivalent and the corresponding polytypes belong to independent families. The formation of the different layer stackings of micas and pyrophyllites requires some special although not always detectable features of structure and composition. If $Fe^{3+}$-smectites that have in the dehydrated state mica- and pyrophyllite-like structures really exist one may be sure that they are essentially different. Therefore a name "hydroferripyrophyllite" is reserved for phase 2. Such a special name is necessary to underline its peculiar properties in view of which it should not be confused with nontronite.

Phase 3 is a random interstratification of phases 1 and 2 with the ratio of water interlayers varying between 0 abd 1. It also attains the pyrophyllite-like 2M structure after removal of the interlayer water. According to the existing rules, its name should be a derivative of the names of phases 1 and 2, i.e. "ferripyrophyllite-hydroferripyrophyllite".

## COMPOSITION AND OTHER PROPERTIES OF THE PHASES

The sample from Strassenschacht consists mainly of phase 1, but also contains phase 3 with a low ratio of water interlayers and a small admixture of phase 2. The sample from Tologay consists mainly of phase 2, but also contains phase 3 with a high ratio of water interlayers and a small admixture of phase 1. It may be accepted therefore that the properties of phase 1 (ferripyrophyllite) and phase 2 (hydroferripyrophyllite) are approximated respectively by the properties of the two samples. The properties of the mixed-layer phase are intermediate depending on the ratio of interlayers.

These conclusions, deduced from all the diffraction data allowed a better understanding of the results given by other methods.

Recalculating the bulk chemical analyses the following averaged structural formulas have been obtained.

Strassenschacht sample:

$Ca_{0.05}\,Fe^{3+}_{1.96}Mg_{0.11}(Si_{3.80}Al_{0.13}Fe^{3+}_{0.07}O_{10})(OH)_2.H_2O$

Tologay sample:

$Ca_{0.18}(Na,K)_{0.03}Fe^{3+}_{1.97}Mg_{0.02}(Si_{3.74}Al_{0.23}O_{10})(OH)_2.1.5H_2O$

The deviation of these formulas from the ideal are not great and may be attributed to inhomogeneities and to the presence of different phases. The differences of the formulas in the quantities of Al, Ca, $H_2O$ are in agreement with the distribution of phases in the samples. Accordingly, the ideal formula $Fe_2Si_4O_{10}(OH)_2$ may be accepted for phase 1 (ferripyrophyllite) in analogy with $Al_2Si_4O_{10}(OH)_2$ for the usual pyrophyllite. Phase 2 (hydroferripyrophyllite) may be described by an approximate formula $Ca_{0.2}Fe_{1.95}Si_{3.75}Al_{0.25}O_{10}(OH)_2.(1.5\text{-}2.0)H_2O$. The degree of replacement of Si by Al in this phase is less than in nontronites; although not great this difference is evidently essential for the swelling properties and structural ordering after removal of interlayer water.

In view of the structural data the thermal behaviour of the samples becomes clear. The endothermic effects are due to the loss of interlayer $H_2O$ and structural (OH). The shapes of the DTA- and TG-curves indicate there is no a sharp energetic boundary between the two kinds of water, presumably as a result of structural imperfections. The lower temperature of the dehydroxylation, compared with those of pyrophyllite and talc (i.e. 500° instead of 800° and 1000° resp. Mackenzie, 1957) is a consequence of the composition and lesser stability of the structure.

The IR spectra of both specimens are consistent with the proposed structures, and clearly distinguish these phases from nontronite.

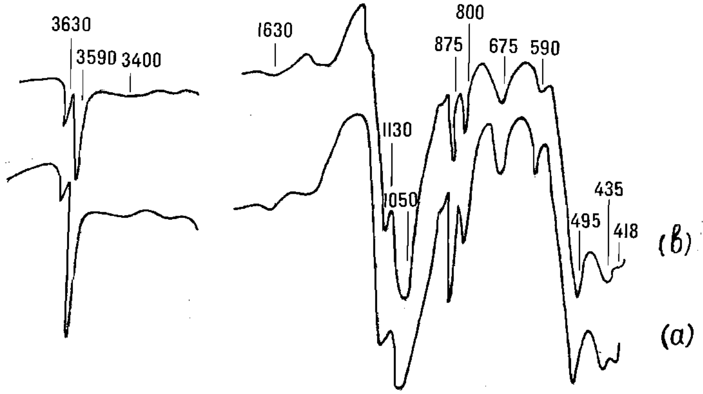


Fig. 5. IR-spectra: a) Strassenschacht sample; b) Tologay sample.

Most obviously, their OH stretching (3590 $cm^{-1}$) and bending (842 $cm^{-1}$) vibrations lie at higher frequencies than those of nontronite (3570 and 818 $cm^{-1}$). The same relationship exists between these vibrations in pyrophyllite (3675 and 950 $cm^{-1}$) and those in beidellite (3661 and 940 $cm^{-1}$) or montmorillonite (3630 and 915 $cm^{-1}$).

The formation of phase 1 (ferripyrophyllite) is possible in media with a high content of $Fe^{3+}$. If nontronite is a mineral of the hypergenesis zone, the $Fe^{3+}$-analogue of pyrophyllite is a precipitate from low-temperature hydrothermal solutions. The swelling phases are likely to be formed as a result of later transformations.

## ACKNOWLEDGEMENTS

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## REFERENCES

Drits V.A. 1969. Proceedings of the Intern. Clay Conf., Tokyo, September 5-10. Israel Universities Press, Jerusalem, pp.51-59.

Farmer V.C. 1974. Infrared Spectra of Minerals, London.

Gorshkov A.I. 1970. Izvestiya AN SSSR, ser. geol., N 3.(in Russian).

Mackenzie R. (Edit.). 1957. The Differential Thermal Investigations of Clays, London.

Smolin P.P., Zvyagin B.B., Drits V.A., Sidorenko O.V., Alexandrova V.A. 1975. Crystallochimiya mineralov i geologitcheskie problemy, Nauka, Moscow, pp. 91-99. (in Russian).

Zvyagin B.B., Mishtshenko C.S. and Soboleva S.V. 1968. Crystallographiya, 13, N 4. (in Russian).

## ADDENDUM

The mineral name ferripyrophyllite has been approved by the IMA Commission on New Minerals and Mineral Names in September 1978.

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# MÖSSBAUER SPECTRA OF CHLORITES AND THEIR DECOMPOSITION PRODUCTS

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## ABSTRACT

Nine trioctahedral chlorite specimens, having a wide range of compositions, have been investigated by $^{57}Fe$ Mössbauer spectroscopy. In all samples the major oxidation state is ferrous with a principal component that has parameters similar to those from $Fe^{2+}$ at the site with cis OH groups in biotite. With all spectra an additional ferrous component was required for a statistically-acceptable fit to the data, but this does not necessarily correspond to a different crystallographic site. Ferric iron was also present in all samples and some spectra contained a component with isomer shift characteristic of 4-coordination in addition to the 6-coordinate component more generally observed.

Five specimens were heated to various temperatures and also subjected to the chemical treatment of Ross and Kodama (1974) with the object of forming vermiculite. Spectra were recorded at all stages and the samples exhibited a behaviour that apparently depended on the iron content of the original sample. The low-iron chlorites could be completely oxidized and partially vermiculitized but there was no evidence for the production of vermiculite with the iron-rich species.

## INTRODUCTION

Chlorites have a 2:1 layer structure with an interlayer hydroxide sheet and general formula $(M^{2+}_{6-x} M^{3+}_{x}) (Si_{4-x} M^{3+}_{x})O_{10} (OH)_{8}$. Because of isomorphous substitution within the hydroxide sheet and in the tetrahedral and octahedral positions in the 2:1 layer, a large number of species exists and a wide variation in chemical composition is encountered. Various attempts have been made by X-ray diffraction (XRD) techniques to estimate the chemical composition of chlorites and to determine tetrahedral and octahedral cation populations and, although detailed information can be obtained from a comprehensive single crystal study (e.g. Bailey and Riley, 1977), methods applicable to powder specimens (Bailey, 1972) give only an indication of the difference between the cation distributions in the two octahedral sheets and cannot provide precise information on the positions of the octahedral cations.