

## NICKEL CONTAINING REGULARLY INTERSTRATIFIED CHLORITE–SAPONITE FROM SZKLARY, LOWER SILESIA, POLAND

ANDRZEJ WIEWIÓRA

Research Centre of Geological Sciences, Polish Academy of Sciences

and

KAZIMIERZ SZPILA

Institute of Geochemistry, Mineralogy and Petrology, Warsaw University, Poland

(Received 20 September 1974)

**Abstract**—The present paper describes a new mineral species, namely a regularly interstratified chlorite—trioctahedral smectite bearing as much as 24% NiO. The high Ni content proves it to be nickel mineral.

On the diffractogram of the raw sample, an integral series of reflections with  $ld(001) = 30.1 \text{ \AA}$  was obtained. To study the nature of the component layers, X-ray examinations of glycerol saturated samples and also dehydrated by heating were accomplished. Thermal and chemical analyses were performed in the usual way.

The crystallochemical formula can be presented as follows: saponite layer— $(\text{Mg,Ni})_{3.00}(\text{Si}_{3.75}\text{Al}_{0.25})\text{O}_{10}(\text{OH})_2$ , charge  $-0.25$ ;  $\text{Ca}_{0.06}(\text{Mg,Ni})_{0.06}\text{K}_{0.01} \cdot 4.07 \text{ H}_2\text{O}$ , charge  $+0.25$ ; chlorite layer— $(\text{Mg,Ni})_{2.02}(\text{Al,Fe}^{3+})_{0.65}(\text{Si}_{3.76}\text{Al}_{0.24})\text{O}_{10}(\text{OH})_2$ , charge  $-0.25$ ;  $(\text{Mg,Ni})_{2.75}(\text{Al,Fe}^{3+})_{0.25}(\text{OH})_6$ , charge  $+0.25$ .

The full mineral and chemical characteristics lead to precise conclusions concerning the composition and structure not only of the nonexpanding chlorite layers, but especially of the expanding layers. The latter show the chemical composition of saponite but the interlayer material is composed partly of exchange cations and molecular water and partly of "brucite-like pillows".

### INTRODUCTION

The nickel deposit in Szklary near Zabkowice, Lower Silesia, was formed by serpentinization of ultramafic rocks followed by chemical weathering of the resulting serpentinites. The ore minerals are so-called *sensu lato* garnierites—hydrated nickel-containing silicates of varied chemical composition and structure, very fine grained, and frequently poorly crystallized. Their exact mineralogical identification is often difficult, especially when they form mixtures on the unit cell level.

Complex geochemical processes caused the mineralogical complexity of the Ni-ores in Szklary. The resulting minerals have fascinated many investigators from the 19th century onwards (see, e.g. Traube, 1888). Among more recent studies may be mentioned those of Spangenberg and Müller (1949) and Ostrowicki (1965). The latter gave much detailed information on nickel-bearing minerals, including chemical composition, thermal properties and X-ray data. According to Ostrowicki, the major Ni-bearing minerals in Szklary are: pimelite (17.34–31.81% NiO), a talc-like mineral, and schuchardtite (5.16–19.31% NiO), believed to be a Ni-form of vermiculite. A similar conclusion regarding schuchardtite has been reached by Brindley and de Souza (private communication). A mixed-layer mineral, which is the subject of the present paper, was not mentioned by Ostrowicki. However, traces of the mineral might be detected

in the diffractogram of schuchardtite presented by him in his paper (Fig. 23, p. 68).

The mixed-layer mineral now studied occurs in veinlets less than 1 mm to some centimeters thick and is probably common throughout the regolith in Szklary. It is matt in appearance, light green in color, soft and forms massive aggregates composed of fine flakes, which may be distinguished under the binocular microscope. Sometimes, black spots or black flakes probably of manganese oxides may be noticed. It resembles pimelite in Ostrowicki's description. Under the microscope, the fine-grained masses show anisotropy and directional orientation of the flakes with crossed nicols. In a thin section distinctly larger flakes of lower birefringence form irregular aggregates or irregular veinlets. They might represent a regular chlorite-like mineral.

### X-RAY ANALYSIS

X-ray analysis was performed with the aid of a Cristalobloc 31 diffractometer made by CGR, France. The curved quartz monochromator was adjusted for the reflection method (reflection plane  $10\bar{1}1$ , radius of curvature 250 mm). Oriented aggregates sedimented onto glass slides were used, and only 00l reflections appeared in the diffractograms. Samples equilibrated over saturated NaCl solution (r.h. = 75 per cent) and saturated with glycerol were studied

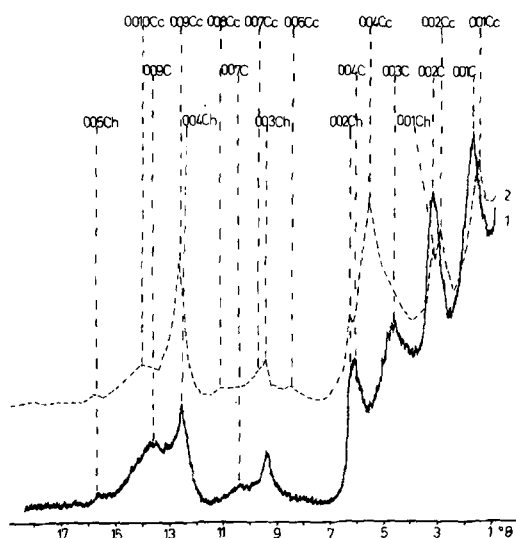


Fig. 1. X-ray diffractograms of oriented aggregates. (1) Raw sample, (2) saturated with glycerol. C, Ni-chlorite-saponite; Cc, Ni-chlorite-saponite-glycerol complex; Ch, Chlorite.

at first. On the diffractogram of the raw sample, an integral series of reflections with  $l.d(00l) = 30.1 \text{ \AA}$  ( $l = 1 \dots 10$ ) was obtained. A similar integral series of reflections from the glycerol saturated sample gave  $l.d(00l) = 32.3 \text{ \AA}$ . Negligible deviations from integrality prove that both the water and the glycerol complexes are quite regular.

The data presented in Figs. 1 and 2 illustrate the regular interstratification of nonexpanding and expanding layers. High  $d(001)$  value and sensitivity to glycerol treatment prove the presence of expanding 2:1 layers, besides nonexpanding layers. To study the nature of the component layers, X-ray examinations of samples dehydrated over saturated solutions giving r.h. 75 and 32 per cent and also dehydrated by heating at 100, 200, 300 and 500°C were accomplished (Fig. 2). In this series of experiments, we observed a systematic decrease of intensity of the 001 reflection accompanied by an increase of the background in the low angle region due to disordering of the structure of the interlayer water. Ordering of the water molecules is restored by rehydration over NaCl saturated solution (r.h. 75 per cent). During heating, further collapse of the structure, and transformation of the clay-water complex to anhydrous clay takes place. At the same time, the disordering of the structure increases as shown by  $l.d(00l)$  values ranging from 24 to 25.6 Å. Examination of the X-ray data presented in Table 1 showing the changes of the  $d(00l)$  values for the samples saturated with glycerol or heated leads us to the conclusion that the mineral is composed of regularly interstratified nonexpanding chlorite-like layers and expanding smectite layers. This explains  $d(001)$  values for the raw sample equal to  $30.1 = 14.4 + 15.7 \text{ \AA}$ , and for the glycerolated sample equal to  $32.3 = 14.4 + 17.9 \text{ \AA}$ . The X-ray pattern obtained from a nonoriented aggregate (Fig. 3) shows reflections corresponding to

the most important reflections of chlorites besides the basal reflections of the long spacing series. However  $hkl$  reflections appeared to be very broad and weak, which is rather common for two-dimensionally developed phases. The 020 and 060 reflections are rather strong. Close to 060, the 062, 331 reflection is visible. With  $d(060) = 1.530 \text{ \AA}$ , the  $b$  parameter is  $9.18 \text{ \AA}$ , which agrees well with  $b = 9.18\text{--}9.30 \text{ \AA}$  characteristic for chlorites (Brindley, 1961) and is close to  $b = 9.20 \text{ \AA}$  characteristic for saponite (MacEwan, 1961).

In the diffractograms of oriented aggregates, especially those heated or glycerolated, the weak basal reflections of the regular chlorite are well visible. They prove that the formation of the regularly interstratified mineral was followed by the segregation phenomenon of the chlorite layers. The not-quite-integral series of basal reflections in the diffractograms of oriented aggregates heated to 300 or 500°C indicates a not-very-regular distribution of collapsed layers within the structure of the mineral.

The lowest  $l.d(00l)$  value equal to  $24 \text{ \AA}$  for  $l = 7$  may be looked upon as evidence that besides the chlorite layers with  $d(001) \approx 14 \text{ \AA}$ , there must occur collapsed saponite layers with  $d(001) \approx 10 \text{ \AA}$ . At the same time higher  $l.d(00l)$  values reaching  $25 \text{ \AA}$  show that some of the smectite layers did not collapse to  $d(001) = 10 \text{ \AA}$ . An average  $d(001)$  value for the collapsed smectite layers is close to  $11 \text{ \AA}$ . Such a value

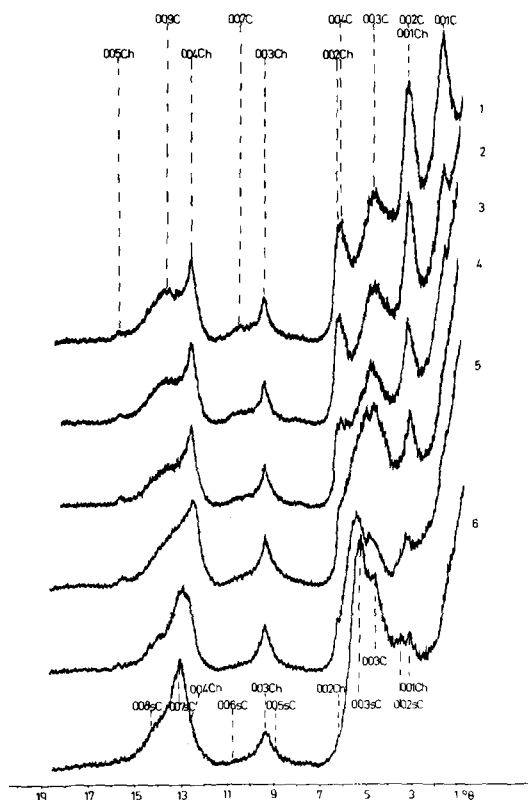


Fig. 2. X-ray diffractograms of oriented aggregates of the samples: (1) equilibrated in 75% r.h., (2) equilibrated in 32% r.h., (3) heated at 100°C, (4) heated at 200°C, (5) heated at 300°C and (6) heated at 500°C. C, Ni-chlorite-saponite; Ch, chlorite; sC, collapsed Ni-chlorite-saponite.

Table 1.  $d(001)$  values for Ni-chlorite-saponite from Szklary

	r.h. 75%		300°C		500°C		Glycerol saturated		Ethylene glycol sat:		Na-sat. r.h. 50%	
	$d(001)$	I	$d(001)$	I	$d(001)$	I	$d(001)$	I	$d(001)$	I	$d(001)$	I
001												
001	30.1	10					32.5	4	31.5	4	27.6	4
002	15.03	9	28.1	2	25.6	2	15.9	5	15.9	5	27.6	6
			14.03	2							14.30	
001ch			14.4	1	14.4	1	14.2	3	14.2	3	14.30	10
003	10.04	7	9.47	5	9.72	6						
			8.40	8	8.51	10						
004	7.49	5					8.10	10	7.97	10		4
002ch	7.20	4	7.20	3	14.4	2	7.15	3	7.18	4	7.16	4
005					5.04	1/2					5.40	1
006					4.17	1/2					4.56	3
003ch	4.79	3	4.78	3	4.79	3	5.34	1	5.22	1/2	4.77	2
007	4.30	1	3.43	7	25.0	8	4.73	2	4.77	3	4.77	3
008			3.11	1/2	3.43	1/2	4.61	1	4.55	1	4.31	1
004ch	3.59	4	3.58	4	25.1	1/2	4.05	1			3.37	8
009	3.33	7	3.18	1/2			3.56	8	3.56	4	3.56	3
010							3.23	3	3.50	7	14.24	
005ch	2.88	1	2.85	1/2					2.86	1/2		

I = visual estimate; ch = chlorite.

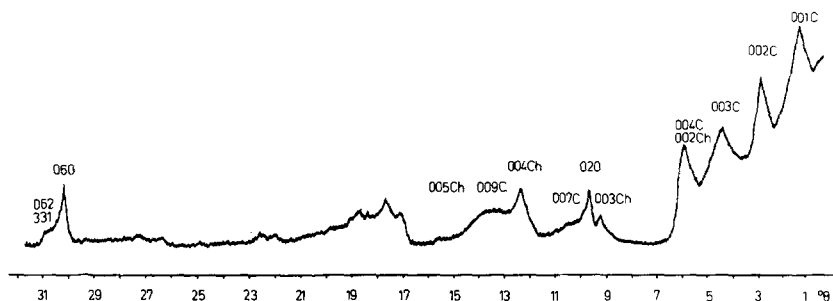


Fig. 3. X-ray diffractogram of a fully disoriented aggregate under r.h. 75%.

may be explained by supposing that an interlayer space is filled not only by the exchange cations but also by "brucite pillows" which prevent a full collapse of the layers. We may not exclude the possibility of some exchange cations existing in the octahedral brucite sheet.

#### THERMAL ANALYSIS

The thermal analyses were performed with the aid of a derivatograph of the system Paulik–Paulik–Erdey (MOM Budapest) with simultaneous registration of T, DTA, TG and DTG curves in the range of 20–1000°C; 300 mg of substance was used and the rate of heating was 10°C per min.

In the DTA curves, five endothermic and one exothermic effects appeared. All the endothermic effects are due to mass loss, which is evident from the TG and DTG curves. A total mass loss of the run presented in Fig. 4 was 14 per cent, but this value is not quite constant. Depending on the r.h. of the atmosphere, it changes from about 13.7 to 17.5 per cent of the air-dry mass. This is no doubt due to the presence of expanding layers.

The shape of the DTA curve is similar to that of corrensites given by Ivanowa (1961). They differ only in the relative intensity ratio of the endothermic

effects and in the shape of the first peak, which is single, whereas in corrensite it is double.

The endothermic effect at 155°C is due to loss of the interlayer water, and at 730°C is due to dehydroxylation of the octahedral sheet of the smectite structure (MacEwan, 1961). The high temperature endothermic effect at 920°C is characteristic for smectites generally. It is caused by the decay of the anhydrous structure (Stoch, 1967); however, an easily visible mass loss can hardly be neglected. Rozinova and Kasatov (1970) ascribe this mass loss to removal of the remaining OH<sup>-</sup> from the octahedral layers. This is followed by the decomposition of the anhydrous structure.

The endothermic effects at 625 and 830°C are no doubt due to dehydroxylation of the brucite and octahedral sheets in the 2:1 layer of the chlorite structure (Orcel and Caillère, 1938; Orcel and Renaud 1941), respectively. The very low intensity of the dehydroxylation of the "brucite" layer may seem somewhat puzzling. However, in the light of the X-ray analysis this may be understood if one agrees that the brucite layers contain a number of exchange cations, which coordinate H<sub>2</sub>O (not OH<sup>-</sup>), and that this H<sub>2</sub>O left the structure at 155°C. The exothermic peak at 850°C is characteristic for the chlorite-like component.

#### CHEMICAL COMPOSITION

Chemical analysis was performed by classical methods, but the NiO and MgO contents were revised by the X-ray fluorescence method. This method has been applied successfully for CEC measurement by the strontium method (Wiewióra, 1973). The water content was taken from the TG curve obtained on the same day when a sample for chemical analysis was weighed. The chemical data and the calculation of the chemical formula are presented in Table 2.

The derivation of the crystallochemical formula was based on the model of Sudo and Kodama (1957) in their study of a regularly interstratified aluminous chlorite-montmorillonite. The X-ray data proved the mineral to be composed of chlorite and trioctahedral smectite (saponite) layers interstratified in a regular way. Thus a total negative charge supplied by oxygens and hydroxyls is taken as 28 (chlorite) + 22 (saponite) = 50. The total positive charge supplied

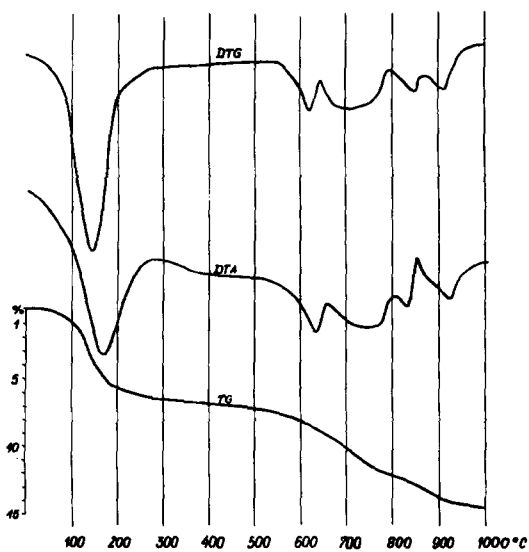


Fig. 4. DTA, TG and DTG curves.

Table 2. Chemical composition of a regularly interstratified Ni-Chlorite-saponite

Component	Weight (%)	Mol. ratio	Atomic ratio	Cation charges	Cation charges recalculated to 50	Number of cations per formula unit
SiO <sub>2</sub>	39.46	6.570	6.570	26.280	30.006	7.502
TiO <sub>2</sub>	0.05	0.006	0.006	0.024	0.027	0.007
Al <sub>2</sub> O <sub>3</sub>	4.90	0.486	0.972	2.916	3.330	1.110
Fe <sub>2</sub> O <sub>3</sub>	2.05	0.122	0.244	0.732	0.836	0.279
FeO	—	—	—	—	—	—
NiO	24.12	3.229	3.229	6.458	7.374	3.687
MgO	14.52	3.626	3.626	7.252	8.280	4.140
MnO	0.02	0.003	0.003	0.006	0.007	0.003
CaO	0.23	0.057	0.057	0.114	0.130	0.065
K <sub>2</sub> O	0.05	0.005	0.011	0.011	0.012	0.013
Na <sub>2</sub> O	—	—	—	—	—	—
Total	85.40	sum of the cation charges		43.793	50.002	
H <sub>2</sub> O	14.30	7.944	15.888	15.888	18.141	18.141
Total	99.70					
SrO <sub>exch.</sub>	1.22	0.118	0.118	0.236	0.270	

by cations should then be 50. To achieve this result, cation charges are multiplied by 1.1418 obtained from the ratio 50:43.793 (see Table 2). For practical formula derivation, a 2:1 trioctahedral smectite-like layer, a layer of hydrated cations with 4 H<sub>2</sub>O per unit layer, a 2:1 chlorite-like layer and a "brucite"-like octahedral sheet are distinguished. The Si has been distributed between the two types of 2:1 layers. Tetrahedral cations was made up with Al. The octahedral sites in saponite are filled by Mg and Ni. In this way the saponite 2:1 layer has a charge of -0.25 which is balanced by interlayer cations Ca, Mg (Ni), K. If the 2:1 layer in chlorite is charged -0.25, then the "brucite"-like octahedral sheet requires +0.25 which then accounts for all the cations of the chemical data in Table 2.

The crystallochemical formula derived in this way can be presented as follows: saponite layer—(Mg,Ni)<sub>3.00</sub> (Si<sub>3.75</sub>Al<sub>0.25</sub>) O<sub>10</sub> (OH)<sub>2</sub>, charge -0.25; Ca<sub>0.06</sub> (Mg,Ni)<sub>0.06</sub> K<sub>0.01</sub>· 4.07 H<sub>2</sub>O, charge +0.25; chlorite layer—(Mg,Ni)<sub>2.02</sub> (Al,Fe<sup>3+</sup>)<sub>0.65</sub> (Si<sub>3.76</sub>Al<sub>0.24</sub>) O<sub>10</sub> (OH)<sub>2</sub>, charge -0.25; (Mg,Ni)<sub>2.75</sub> (Al,Fe<sup>3+</sup>)<sub>0.25</sub> (OH)<sub>6</sub>, charge +0.25.

Excellent agreement between the charge formula unit and the value of exchangeable Sr introduced into the interlayer space of the mineral supports this formula.

If 'brucite pillows' are assumed to exist in both the chlorite and the saponite layers, then they probably differ from each other less than was visualized in the derived formula. A new formula may be calculated with the same charge formula unit and with the same substitutions in the octahedral sheet of both layers: (Mg,Ni)<sub>2.51</sub> (Al,Fe<sup>3+</sup>)<sub>0.327</sub> (Si<sub>3.75</sub>Al<sub>0.25</sub>) O<sub>10</sub> (OH)<sub>2</sub>, charge -0.25; Ca<sub>0.06</sub> (Mg,Ni)<sub>0.06</sub> K<sub>0.01</sub>· 4.07 H<sub>2</sub>O, charge +0.25; (Mg,Ni)<sub>2.51</sub> (Al,Fe<sup>3+</sup>)<sub>0.323</sub> (Si<sub>3.76</sub>Al<sub>0.24</sub>) O<sub>10</sub> (OH)<sub>2</sub>, charge -0.25; (Mg,Ni)<sub>2.75</sub> (Al,Fe<sup>3+</sup>)<sub>0.25</sub> (OH)<sub>6</sub>, charge +0.25.

Obviously, other compositional variations are possible within the limits of the present analytical data.

#### DISCUSSION AND CONCLUSIONS

Chlorites themselves can be considered as regularly interstratified minerals, composed of alternating 2:1 layers and 'brucite layers'. Chlorite layers frequently participate in the structures of both regularly interstratified and irregularly interstratified minerals, e.g. chlorite-vermiculite (Bradley and Weaver 1956; Johnson 1964; Gallitelli 1956), chlorite-smectite (Early *et al.*, 1956; Earley and Milne 1956; Kossovskaja *et al.*, 1971; Sudo and Kodama 1957; Blatter *et al.* 1973). The interstratification of expanding chlorite and nonexpanding chlorite layers has been described by Lippmann (1954) and independently by Martin-Vivaldi and MacEwan (1960) under the name of corrensite. Heckrodt and Roering (1965) described interstratification of high aluminous expanding and nonexpanding chlorite layers.

The present paper describes a new mineral species, namely a regularly interstratified chlorite-trioctahedral smectite bearing as much as 24% NiO. This mineral should appear in a list of the regularly interstratified layer silicates. The high Ni content proves it to be nickel mineral. Field observations in Szklary and laboratory examination of several samples have shown that the mineral is distributed in abundance in the weathering zone and that it plays an important role among the hydrated nickel silicates. It should be included in the classification of Ni-silicates such as these proposed by Brindley and Maksimovic (1974).

The full mineral and chemical characteristics lead to precise conclusions concerning the composition and structure not only of the nonexpanding chlorite layers, but especially of the expanding layers. The latter show the chemical composition of saponite but the interlayer material is composed partly of exchange cations and molecular water and partly of 'brucite-like pillows'.

The authors propose the name Ni-corrensite, or Ni-chlorite-saponite for the mineral studied.

The investigations did not clear up the particular structural role of nickel, which is treated together with Mg in the derivation of the crystallochemical formula.

*Acknowledgement*—Finally we thank Professor G. W. Brindley for discussion and correction of the English text.

#### REFERENCES

- Blatter, C. J., Roberson, H. E. and Thompson, G. R. (1973) Regularly interstratified chlorite-dioctahedral smectite in dike-intruded shales, Montana: *Clays and Clay Minerals* **21**, 207–212.
- Bradley, W. F. and Weaver, C. E. (1956) A regularly interstratified chlorite-vermiculite clay mineral: *Am. Miner.* **41**, 497–504.
- Brindley, G. W. (1961) Chlorite Minerals. In *The X-ray identification and crystal structure of clay minerals* (Edited by Brown, G.) Mineralogical Society, London.
- Brindley, G. W. and Maksimovic, Z. (1974) The nature and nomenclature of hydrous nickel-containing silicates: *2nd meeting European Clay Groups*, Strasbourg.
- Earley, J. W., Brindley, G. W., McVeagh, W. J. and Vanden Heuval, R. C. (1956) A regular interstratified montmorillonite-chlorite: *Am. Miner.* **41**, 258–267.
- Earley, J. W. and Milne, I. R. (1956) Regularly interstratified montmorillonite-chlorite in basalt: *4th Nat. Clay Conf.* 381–384.
- Gallitelli, F. (1956) Chlorite-vermiculite: *Rend. Accad. Naz. Lincei* **21**, 146–154.
- Heckroodt, R. O. and Roering, C. (1965) A high-aluminous chlorite-swelling chlorite regular mixed-layer clay mineral: *Clay Minerals* **6**, 83–90.
- Iwanowa, W. P. (1961) Termogramy mineralov: *Zap. Vses. Min. Obshch. ser. (2)* **90**, 50–90.
- Johnson, L. J. (1964) Occurrence of regularly interstratified chlorite-vermiculite as a weathering product of chlorite in a soil: *Am. Miner.* **49**, 556–573.
- Kossovskaja, A. G., Dritz, V. A. and Sokolova, T. H. (1971) O specificke formirovaniya glinistykh mineralov v raznykh facyalno-klimaticheskikh obstanovkakh. *Epigenez i jego mineralnye indikatory. Trans.* **221**, 35–53.
- Lippman, F. (1954) Keuper clay from Zaisersweiher: *Heidelberg Beitr. Min.* **4**, 130–134.
- MacEwan, D. M. C. (1961) Montmorillonite Minerals. In *The X-ray identification and crystal structures of clay minerals* (Edited by Brown, G.) Mineralogical Society, London.
- Martin-Vivaldi, J. L. and MacEwan, D. M. C. (1960) Corrensite and swelling chlorite: *Clay Minerals Bull.* **4**, 173–181.
- Orcel, J. and Caillère, S. (1938) Thermal transformations in magnesian prochlorites: *C. r. Acad. Sci., Paris* **207**, 788–790.
- Orcel, J. and Renaud, P. (1941) Dehydration of ferro-magnesian chlorites: *C. r. Acad. Sci., Paris* **212**, 918–921.
- Ostrowicki, B. (1965) Minerale niklu strefy wietrzenia serpentynitów w Szklarach (Dolny Śląsk): *Oddz. PAN w Krakowie, Prace Mineralogiczne* **1**, 7–92.
- Spangenberg, K. and Müller, M. (1949) Die lateritische Zersetzung des Peridotits bei der Bildung der Nickelerz-lagerstätte von Frankenstein im Schiesien: *Heidelberg Beitr. Min. Petr.* **1**, 560–572.
- Stoch, L. (1967) Fizyczno-chemiczne podstawy interpretacji wyników termicznej analizy różnicowej: *Oddz. PAN w Krakowie, Prace Mineralogiczne* **7**, 7–77.
- Sudo, T. and Kodama, H. (1957) Aluminian mixed-layer montmorillonite-chlorite. *Z. Krist.* **109**, 379–387.
- Traube, (1888) *Die Minerale Schlesiens* Breslau.
- Wiewióra, A. (1973) Krystallochemiczne studium mieszanopakietowych minerałów kaolinit-smektyt: *Arch. Mineral.* **31**, 5–112.