

Maria CZAJA*

THE OCCURRENCE OF MIXED-LAYER CHLORITE/VERMICULITE AT LUBIECHOWA (THE KACZAWSKIE MTS)

UKD 549.623.7:549.623.59:552.323.5:548.736.64(438—14 Lubiechowa)

Abstract. One of clay minerals filling up vesicles in melaphyres at Lubiechowa was subjected to various treatments involving saturation with Mg and K ions and treatment with ethylene glycol and glycerol. It has been found that the mineral in question consists of chlorite and mixed-layer chlorite/vermiculite. Using Mering's method it has been shown that two types of structure are present: the content of chlorite layers is 80% in one type and about 30% in the other. The effect of acetic acid treatment on the layers making up the structure of the mineral was also studied.

INTRODUCTION

Minerals filling up vesicles in melaphyres have been the object of mineralogical studies over the past decades. Clay minerals in vesicles of the Lubiechowa melaphyres are represented by seladonite and dioctahedral smectite, but a dark-green mineral forming fine-grained, compact aggregates has also been noted there. In some vesicles this mineral has been found to change to a flaky substance of golden-brown colour. Some other vesicles are filled up completely with such golden-brown flaky substance. The results of the present studies suggest that these minerals represent the successive stages of transformation of chlorite to mixed-layer chlorite/vermiculite.

Mixed-layer chlorite/vermiculites were discussed by Weaver (1956), Tamara (1957), Ross (1975), Rossband Kodama (1976), Wiewióra and Iwasinska (1978), April (1980). The stability of transitional vermiculite-chlorite complexes was also studied (Harward et al. 1969, Carstea et al. 1970).

EXPERIMENTAL

Investigations were carried out on the golden-brown flaky substance occurring in vesicles in melaphyres. To identify its constituent layers, the mineral was subjected to the following treatments:

— saturation with magnesium and potassium ions;

* Department of Earth Sciences, Silesian University, Sosnowiec, ul. Mielczarskiego 60.

- saturation of the natural ("n") sample and its Mg- and K-modifications with glycol and glycerol;
- treatment with 10% acetic acid to remove calcite, and the saturation of the "a.a" (after acid) sample with Mg and K ions and then with glycol;
- heating of the natural sample and its Mg- and K-modifications at 110, 300, 450 and 500°C.

X-ray analysis was made with a Rigaku diffractometer, using Ni-filtered CuK_α radiation. The instrument settings were: U=30 kV I=20 mA, scanning speed 1°/min., chart speed 10 mm/min. All the analyses were made on oriented samples. Glycol and glycerol vapours were used for saturation. Ion exchange was carried out in 0.25 M MgCl₂ and KCl solutions at 70°C, changing the electrolyte several times. The experimental conditions were the same for all samples.

RESULTS

The above investigations suggest that the mineral studied consists of chlorite and mixed-layer chlorite/vermiculite. This can be inferred from the effects of saturation with Mg and K cations and organic liquids, which are shown in figures.

In the X-ray diffraction pattern of the untreated sample (Fig. 1), the reflections are not single but multiple. Moreover, the distribution of their relative intensities is typical of neither chlorite nor vermiculite. Glycol saturation separated several reflections into lines arising from a non-swelling phase and ones produced by a swelling mineral. The lines of the non-swelling mineral are sharp, single and form an integral series. They correspond to chlorite. The swelling mineral displays broad, usually multiple reflections forming a non-integral series.

Glycol saturation has also revealed the presence of mixed-layer structures. A broad, not very intense line $d = 29-30 \text{ \AA}$ appeared, these values being closed to

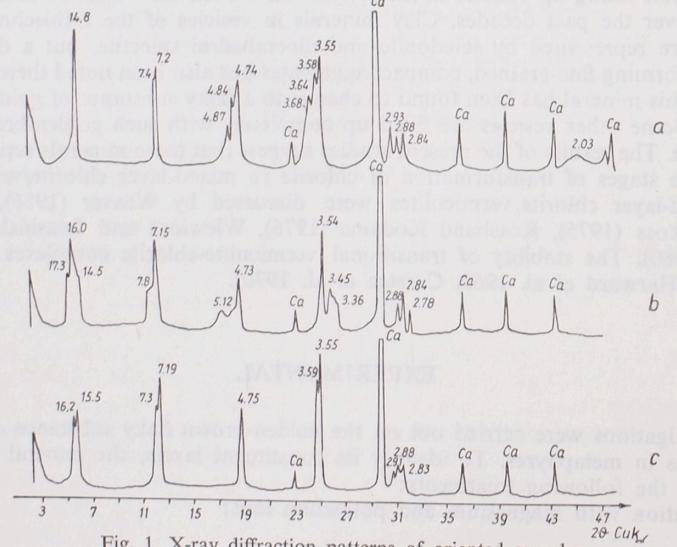


Fig. 1. X-ray diffraction patterns of oriented samples

a — natural sample ("n"), b — "n" sample saturated with ethylene glycol, c — "n" sample saturated with glycerol

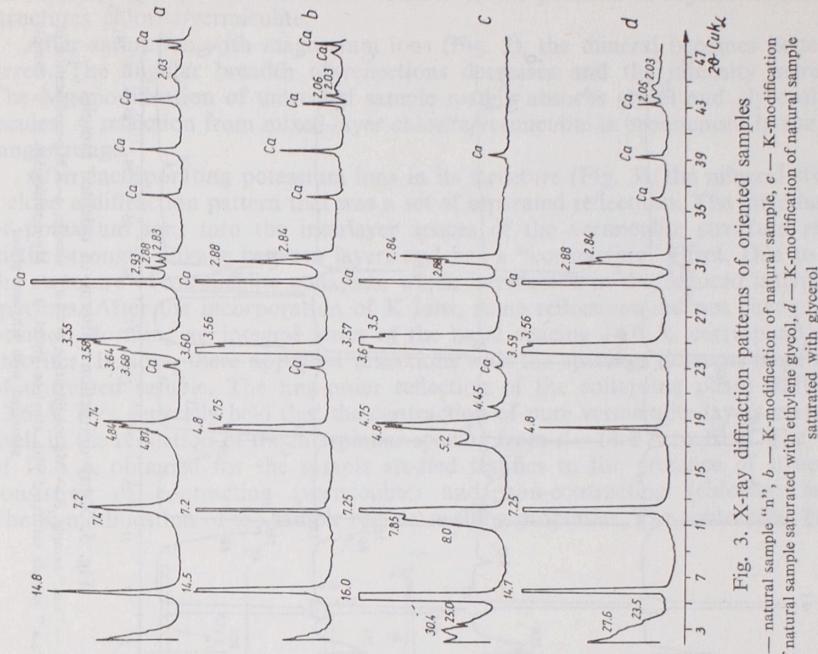


Fig. 3. X-ray diffraction patterns of oriented samples

a — natural sample "n", b — Mg-modification of natural sample, c — K-modification of natural sample saturated with ethylene glycol, d — K-modification of natural sample saturated with glycerol

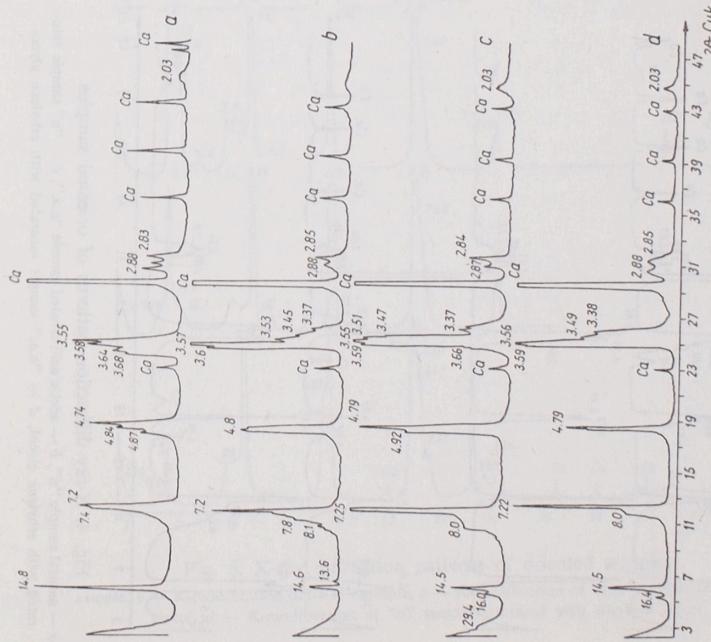


Fig. 2. X-ray diffraction patterns of oriented samples

a — natural sample "n", b — Mg-modification of natural sample, c — K-modification of natural sample saturated with ethylene glycol, d — K-modification of natural sample saturated with glycerol

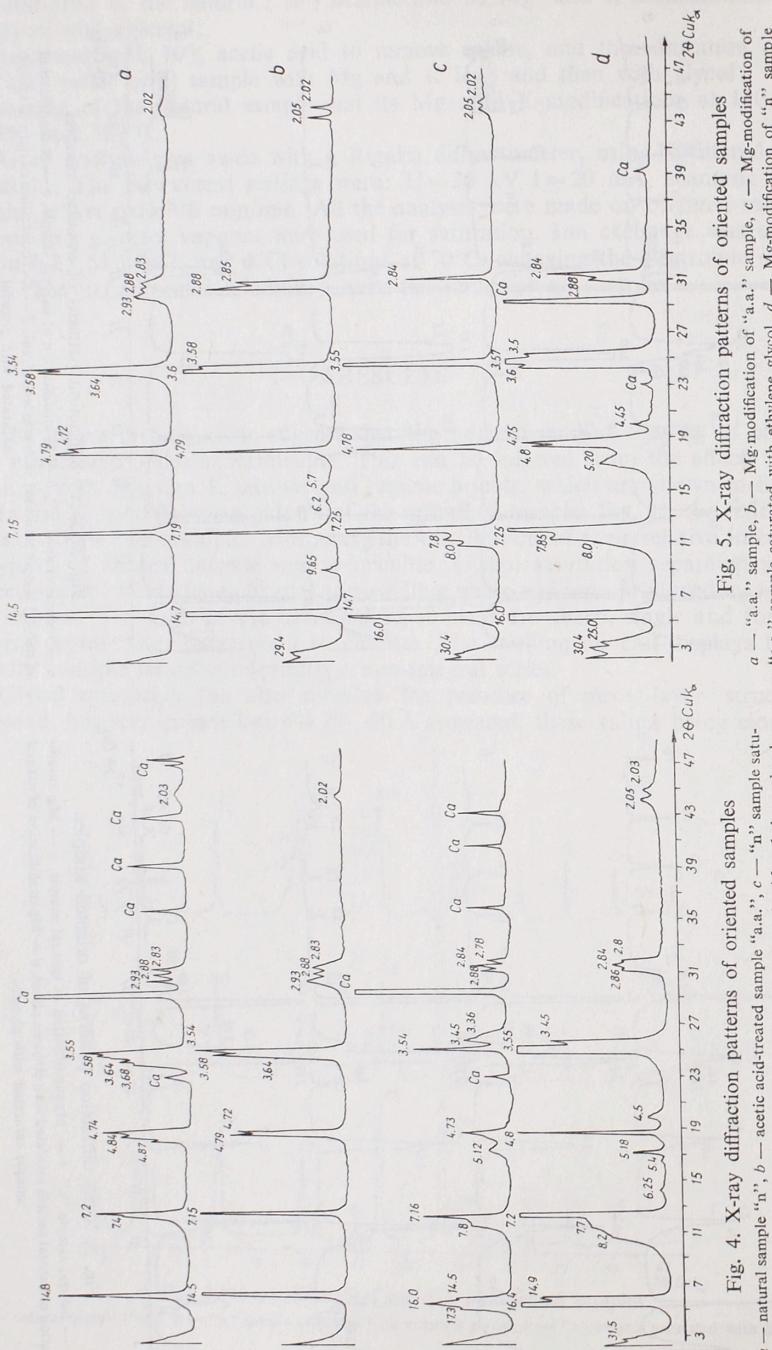


Fig. 4. X-ray diffraction patterns of *Colletotrichum* spp.
a — natural sample "n", *b* — acetic acid-treated sample "a.a.", *c* — "n" sample saturated with ethylene glycol
d — "a.a." sample saturated with ethylene glycol

Fig. 5. X-ray diffraction patterns of oriented samples
a — "a.a." sample, *b* — Mg-modification of "a.a." sample, *c* — Mg-modification of "a.a." sample saturated with ethylene glycol, *d* — Mg-modification of "n" sample saturated with ethylene glycol

the sum of $d_{ch} + d_v$. This reflection testifies to the presence of regular mixed-layer structures chlorite/vermiculite.

After saturation with magnesium ions (Fig. 2), the mineral becomes better ordered. The angular breadth of reflections decreases and the intensity increases. The Mg-modification of untreated sample readily absorbs glycol and glycerol molecules. A reflection from mixed-layer chlorite/vermiculite is pronounced in the low-angle range.

After incorporating potassium ions in its structure (Fig. 3), the mineral studied yielded a diffraction pattern that was a set of separated reflections. The introduction of potassium ions into the interlayer spaces of the vermiculite structure results in the stronger linkage between layers and has a "contracting" effect. Due to this, the structure of vermiculite collapses, which is reflected in the reduced interplanar spacings. After the incorporation of K ions, some reflections did not change their position, forming an integral series of the basal spacing 14.6 Å, corresponding to chlorites. Besides, there appeared reflections with the spacings different from those of untreated sample. The first-order reflection of the collapsing phase shifted to 13.6 Å. It is generally held that the contraction of pure vermiculite layers manifests itself in the reduction of the interplanar spacing from $d = 14.4$ Å to 10 Å. The value of 13.6 Å obtained for the sample studied testifies to the presence of structures consisting of contracting (vermiculite) and non-contracting (chlorite) layers. The K-modification of the sample retains swelling properties. The contracting phase,

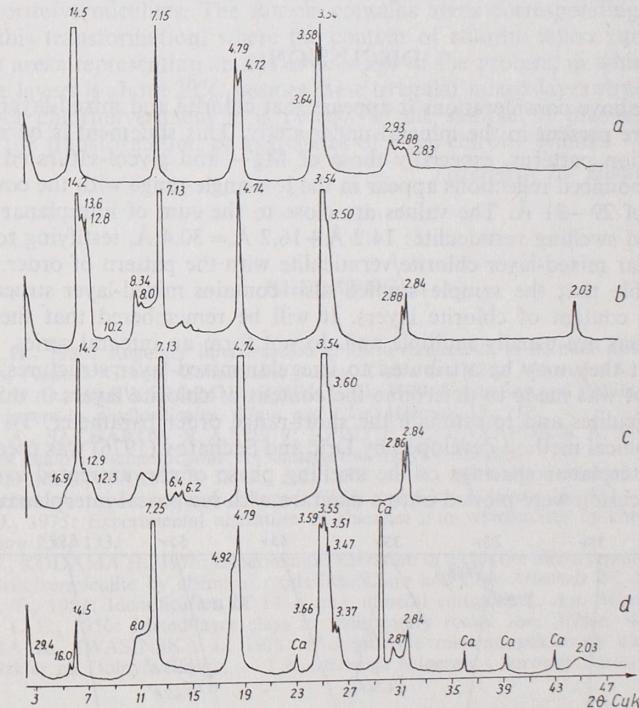


Fig. 6. X-ray diffraction patterns of oriented samples

a — "a.a." sample, *b* — K-modification of "a.a." sample, *c* — K-modification of "a.a." sample saturated with ethylene glycol, *d* — K-modification of "n" sample saturated with ethylene glycol

vermiculite, admits organic molecules into the interlayer spaces, causing the 13.6 Å reflection to shift to 16.0 and 16.4 Å.

The swelling properties and ion-exchange capacity of a sample treated with acetic acid were studied. From X-ray diffraction patterns (Fig. 4) it appears that the acid-treated ("a.a.") sample shows worse swelling properties than the untreated sample. The results of saturation of the "a.a." sample with Mg ions and glycol are presented in Fig. 5. It is evident that either its swelling properties have deteriorated, or that it contains fewer layers capable of admitting organic molecules. After saturation with K ions and glycol (Fig. 6), the "a.a." sample showed a stronger lattice contraction than the untreated sample "n". The interplanar spacings were 13.6, 12.8 or even 10 Å, remaining virtually unchanged after saturation with glycol. It seems that vermiculite layers have almost completely lost their swelling properties and the bonding of potassium in the interlayer spaces has become stronger than in the untreated sample.

The dehydration of vermiculite entering into the composition of mixed-layer chlorite.vermiculites was also studied. The untreated sample and its magnesium modification show the collapse of the swelling phase at 500°C. A peak appears at 12.3 Å besides the chlorite reflection at 14.2 Å. The potassium modification of chlorite.vermiculite loses water molecules already at 300°C, which is in accordance with anticipations as the magnesium cation has a stronger polarizing power and forms stronger bonds with water dipoles than the potassium cation.

DISCUSSION

From the above considerations it appears that chlorite and mixed-layer chlorite.vermiculite are present in the mineral under study. This statement is borne out by X-ray diffraction patterns, especially those of Mg— and glycol-saturated samples, on which pronounced reflections appear in the low-angle range with the corresponding *d* values of 29—31 Å. The values are close to the sum of interplanar spacings of chlorite and swelling vermiculite: 14.2 Å + 16.2 Å = 30.4 Å, testifying to the presence of regular mixed-layer chlorite.vermiculite with the pattern of order ABAB...

It is feasible that the sample studied also contains mixed-layer structures differing in the content of chlorite layers. It will be remembered that the swelling phase reflections are usually multiple and do not form an integral series. It seems, therefore, that they may be attributed to irregular mixed-layer structures.

An attempt was made to determine the content of chlorite layers in mixed-layer chlorite.vermiculites and to estimate the short-range order parameter. To this end, Mering's graphical method developed by Dric and Sacharov (1976) was used (Fig. 7). Reciprocal interplanar spacings of the swelling phase of the untreated sample and its Mg-modification were plotted onto a diagram with reciprocal interplanar spacings

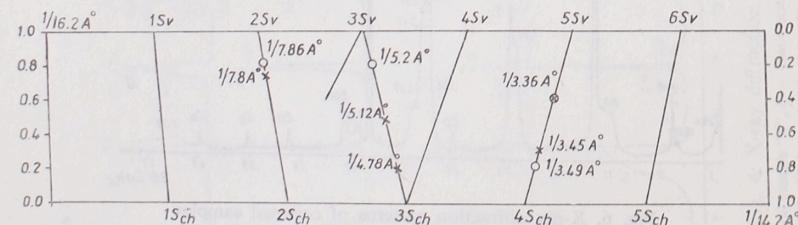


Fig. 7. Diffraction peaks of glycol-saturated natural sample (x) and of glycol-saturated Mg-modification of natural sample (o), presented in reciprocal space (Mering's method)

of chlorite and swelling vermiculite. For mixed-layer chlorite.vermiculite the ranges $2_{s-ch}/2_{s-v}$ and $2_{s-ch}/3_{s-v}$ are sensitive to the type of order. If the short-range order parameter $S=0$, then a reflection appears only on the $2_{s-ch}/2_{s-v}$ line. However, if $S=1$, two peaks appear, one on the $2_{s-ch}/2_{s-v}$ line and the other on the $2_{s-ch}/3_{s-v}$ line. In the case considered $S=0$, yet the approximation of all the points on the diagram corresponding to reflections from the swelling phase by a single line is not possible, as the points form two seemingly independent groups in the upper and lower parts of the diagram. It will be noticed that double reflections appear on the $003_{ch}/003_v$ and $004_{ch}/005_v$ lines, and this fact may only testify to the presence of two types of mixed-layer structures, one of which contains 80% and the other about 30% chlorite layers.

It has been found that treatment with acetic acid caused a deterioration of the swelling properties of the mineral. It is feasible that under the influence of acetic acid, the brucite sheet in a large number of layers has been destroyed, and groupings of magnesium cations coordinated by water molecules have formed in its place. These new-formed, "fresh" layers show the features of typical vermiculite: they have only insignificant, if any, swelling properties. They also undergo contraction after accommodating potassium ions at the interlayer cation sites. The stronger lattice contraction in the "a.a." sample than in the "n" sample is evidently due to the increased amount of vermiculite layers.

The mineral studied represents a stage of transformation of chlorite to mixed-layer chlorite.vermiculites. The sample contains areas corresponding to the initial stage of this transformation, where the content of chlorite layers runs up to 80%, as well as areas representing an advanced stage of the process, in which the content of chlorite layers is about 30%. Besides these irregular mixed-layer structures, regular mixed-layer chlorite.vermiculite is present in the sample. It presumably owes its origin to the transformation of aggregates of large chlorite grains.

Translated by Hanna Kisielewska

REFERENCES

- APRIL R. H., 1980: Regularly interstratified chlorite.vermiculite in contact metamorphosed red beds, Newark Group, Connecticut Valley. *Clays and Clay Minerals* 18, 1.
- CARSTEA D. D., HARWARD M. E., KNOX E. G., 1970: Formation and stability of hydroxy-Mg interlayers in phyllosilicates. *Clays and Clay Minerals* 18, 213.
- DRIC W. A., SACHAROW B. A., 1976: ДРИЦ Р. А., САХАРОВ Б. А. Рентгеноструктурный анализ смешанослоистых минералов. Наука. Москва.
- HARWARD M. E., CARSTEA D. D., SAYEGH A. H., 1969: Properties of vermiculites and smectites — expansion and collapse. *Clays and Clay Minerals* 16, 437.
- ROSS G. J., 1975: Experimental alteration of chlorites into vermiculites by chemical oxidation. *Nature* 255, 133.
- ROSS G. J., KODAMA H., 1976: Experimental alteration of a chlorite into a regularly interstratified chlorite.vermiculite by chemical oxidation. *Clays and Clay Minerals* 24, 183.
- TAMARA T., 1957: Identification of 14 Å clay mineral component. *Am. Miner.* 42, 107.
- WEAVER C. E., 1956: Mixed-layer clays in sedimentary rocks. *Am. Miner.* 41, 214.
- WIEWIÓRA A., IWASINSKA I., 1978: Nieregularne mieszanopakietowy chloryt-wermikulite ze Szklar na Dolnym Śląsku. — I Konferencja Mineraly i Surowce Ilaste, Bolesławiec, 95.

WYSTĘPOWANIE CHLORYTU-WERMIKULITU W LUBIECHOWEJ (GÓRY KACZAWSKIE)

Streszczenie

Badaniom poddano złotobrunatny, łuskowaty minerał występujący w pęcherzach melafirów w Lubiechowej. Obserwacje makroskopowe i mikroskopowe sugerowały, że jest on efektem procesu przemiany ciemnozielonego, zwartej minerału — chlorytu. Dyfraktogram próbki naturalnej nie był typowy ani dla chlorytu, ani dla wermikulitu.

W celu przeprowadzenia identyfikacji pakietów zawartych w tym minerale zastosowano następujące zabiegi: nasycanie próbki naturalnej glikolem i gliceryną, nasycanie jonami Mg^{2+} i K^+ , a następnie glikolem i gliceryną. Czynności te przeprowadzono także dla próbki wcześniej odmytej w 10% kwasie octowym. Analizy dyfrakcyjne wykonano dla preparatów orientowanych.

Przeprowadzone badania wykazały, że minerał składa się z chlorytu i struktur mieszanopakietowych chloryt/wermikulit. Po nasyceniu cieczami organicznymi, a także jonami Mg^{2+} i K^+ część refleksów pozostała nie zmieniona. Odpowiadały one chlorytowi. Natomiast pozostałe refleksy, często szerokie i wielokrotne, były bardzo czułe na rodzaj kationu wymiennego i przesuwały swoje położenie po nasyceniu jonami potasu, a także cieczami organicznymi. Stwierdzono, że refleksy te pochodzą od struktur mieszanopakietowych chloryt/wermikulit.

Stosując metodę Meringa oszacowano, że parametr bliskiego uporządkowania dla tych struktur wynosi zero ($S = 0$). Położenie punktów odpowiadających ugięciom od fazy pęczniającej, zwłaszcza na liniach $003_{ch}/003_v$ oraz $004_{ch}/005_v$, wskazuje, że istnieją dwa typy struktur. W jednym z nich udział pakietów chlorytowych wynosi 80%, a w drugim około 30%.

OBJAŚNIENIA FIGUR

Fig. 1. Dyfraktogramy preparatów orientowanych

a — próbka naturalna "n", *b* — próbka naturalna nasyciona glikolem etylenowym, *c* — próbka naturalna nasyciona gliceryną

Fig. 2. Dyfraktogramy preparatów orientowanych

a — próbka naturalna "n", *b* — Mg — odmiana próbki naturalnej, *c* — Mg — odmiana próbki naturalnej nasyciona glikolem etylenowym, *d* — Mg — odmiana próbki naturalnej nasyciona gliceryną

Fig. 3. Dyfraktogramy preparatów orientowanych

a — próbka naturalna "n", *b* — K — odmiana próbki naturalnej, *c* — K — odmiana próbki naturalnej nasyciona glikolem etylenowym, *d* — K — odmiana próbki naturalnej nasyciona gliceryną

Fig. 4. Dyfraktogramy preparatów orientowanych

a — próbka naturalna "n", *b* — próbka po kwasie octowym "a.a.", *c* — próbka "n" nasyciona glikolem etylenowym, *d* — próbka "a.a." nasyciona glikolem etylenowym

Fig. 5. Dyfraktogramy preparatów orientowanych

a — próbka "a.a.", *b* — Mg — odmiana próbki "a.a.", *c* — Mg — odmiana próbki "a.a." nasyciona glikolem etylenowym, *d* — Mg — odmiana próbki "n" nasyciona glikolem etylenowym

Fig. 6. Dyfraktogramy preparatów orientowanych

a — próbka "a.a.", *b* — K — odmiana próbki "a.a.", *c* — K — odmiana próbki "a.a.", nasyciona glikolem etylenowym, *d* — K — odmiana próbki "n" nasyciona glikolem etylenowym

Fig. 7. Dyfrakcyjne maksima próbki naturalnej nasycionej glikolem (x) oraz Mg — odmiany próbki naturalnej nasycionej glikolem (o) przedstawione w przestrzeni odwrotnej (metoda Meringa)

НАХОЖДЕНИЕ ХЛОРИТА-ВЕРМИКУЛITA В ЛЮБЕХОВОЙ (КАЧАВСКИЕ ГОРЫ)

Резюме

Исследовался золото-бурого цвета чешуйчатый минерал, присутствующий в пузырьках мелафиров в Любеховой. Макроскопические и микроскопические наблюдения наводили на мысль, что он является результатом процесса изменения темнозеленого плотного минерала — хлорита. Дифрактограмма естественного образца не была типична ни для хлорита, ни для вермикулита.

С целью проведения идентификации пакетов, содержащихся в этом минерале, применялись следующие операции: насыщение естественного образца гликолем и глицерином, насыщение ионами Mg^{2+} и K^+ , а потом гликолем и глицерином. Эти действия проводились также для образца ранее промытого 10% уксусной кислотой. Дифракционные анализы проведены на ориентированных препаратах.

Проведенные исследования обнаружили, что минерал состоит из хлорита и смешанно-пакетных структур хлорит/вермикулит. После насыщения органическими жидкостями, а также ионами Mg^{2+} и K^+ , часть отражений осталась неизмененной. Они соответствовали хлориту. Остальные же линии, часто широкие и многократные, были чувствительны на вид обменного катиона, и сдвигали свое положение после насыщения ионами калия, а также органическими жидкостями. Констатировано, что эти отражения происходят от смешанно-пакетных структур хлорит/вермикулит.

Применяя метод Меринга, оценивается, что параметр ближнего упорядочения этих структур составляет нуль ($S=0$). Положение точек, соответствующих дифракции от вспучивающейся фазы, с частности на линиях $003_{ch}/003_v$, а также $004_{ch}/005_v$, указывает на существование двух типов структур. В одном из них доля хлоритовых пакетов составляет 80%, а во втором около 30%.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Дифрактограммы ориентированных препаратов

a — естественный образец "n", *b* — естественный образец, насыщенный этиленовым гликолем, *c* — естественный образец, насыщенный глицерином

Фиг. 2. Дифрактограммы ориентированных препаратов

a — естественный образец "n", *b* — модификация естественного образца, насыщенного этиленовым гликолем, *c* — Mg-модификация естественного образца, насыщенного глицерином

Фиг. 3. Дифрактограммы ориентированных препаратов

a — естественный образец "n", *b* — K-модификация естественного образца, насыщенного этиленовым гликолем, *c* — K-модификация естественного образца, насыщенного глицерином

Фиг. 4. Дифрактограммы ориентированных препаратов

a — естественный образец "n", *b* — образец после трактования уксусной кислотой "a. a.", *c* — образец "n" насыщенный этиленовым гликолем, *d* — образец "a.a.", насыщенный этиленовым гликолем

Фиг. 5. Дифрактограммы ориентированных препаратов

a — образец "a. b.", *b* — Mg-модификация образца "a. a.", *c* — Mg-модификация образца "a. a.", насыщенный этиленовым гликолем, *d* — Mg-модификация образца "n", насыщенного этиленовым гликолем

Фиг. 6. Дифрактограммы ориентированных препаратов
 а — образец “а. а.”, б — К-модификация образца, “а. а.”, в — К-модификация образца “а. а.”, насыщенного этиленовым гликолем, г — К-модификация образца “п”, насыщенного этиленовым гликолем
 Фиг. 7. Дифракционные максимумы естественного образца, насыщенного гликолем (х) а также Mg-модификации естественного образца, насыщенного гликолем (о), представленные в обратном пространстве (метод Меринга)