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*Marek MUSZYŃSKI, Piotr WYSZOMIRSKI**

MINERALS OF CRANDALLITE GROUP IN SOME TONSTEINS OF THE LUBLIN COAL BASIN

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Abstract. So called „Graupen" — tonsteins occur among clay rocks of the Lublin Coal Basin. Their major component is Tc — kaolinite accompanied by subordinate amounts of quartz, potassium feldspar (sanidine), strongly altered biotite and, in minute concentrations, carbonates and pyrite. Phosphate minerals appear locally in rather small amounts. They are represented by minerals of apatite and crandallite groups. These phases either coexist or occur separately. Minerals of the crandallite group form microaggregates. Their chemical composition is diversified, corresponding either to gorceixite (sample K-17/9) or to mixed phases of intermadiate chemical composition between crandallite *sensu stricto*, gorceixite and goyazite (sample K-11/4).

When accepting volcanogenic origin of tonsteins, we may assume that glass and minerals of primary pyroclastic material were the source of elements contained in minerals of the crandallite group. It is supposed that these minerals were formed by decomposition of primary material during early diagenesis of tonstein sediments.

INTRODUCTION

Minerals of crandallite group were reported from very few occurrences in Poland. Kubisz (1963) found these minerals in Ordovician sandstones near Sandomierz in association with clay minerals and jarosite. Recently, their presence was reported in fine-grained fractions of some Lower Silesian kaolins (Szpila, Dzierżanowski 1978) and in weathering products of basalts in Turoszów, Lower Silesia (Szpila, Stępisiewicz 1979). Besides, minerals of crandallite group occur in some allitic rocks of the Lublin region (Cebulak et al. 1982). Till now, there were no data on their occurrence in Polish tonsteins, though they were found in similar Carboniferous rocks in Great Britain (Price, Duff 1969) and in analogous kaolinite rocks of Ruhrgebiet, FRG (Stadler, Werner 1962).

Inspection of chemical analyses of rocks accompanying coal beds in the Lublin Coal Basin has shown that some of them display increased P_2O_5 content — up to ca. 2 wt. percent. This suggests the possibility of occurrence of phosphates of crandallite group in them.

* Institute of Geology and Mineral Deposits, Aćademy of Mining and Metallurgy, Cracow (Kraków, al. Mickiewicza 30).

EXPERIMENTAL

The samples were collected from bore-hole material. They were examined using microscope, X-ray and electron microprobe analyses. X-ray study has been carried out by means of DRON-1,5 diffractometer with scintillation counter recording, using filtered CuK_α radiation. Electron microprobe analysis has been carried out by means of ARL SEMQ microprobe analyzer. Accelerating voltage applied was 20 kV, the current of electron beam 125 μA, probe current ca. 15 nA and counting time 20 per sec. As analytical spectral lines PK_α, CaK_α, BaK_α, SrK_α, AlK_α were used, whereby InP, $CaCO_3$, BaF_2, SrF_2 and metallic Al were applied as standards respectively. Because of very small sizes of the analyzed grains of minerals of crandallite group and the resulting difficulties in obtaining precise microprobe analytical data, we had not to take into account the corrections on the effects of absorption, fluorescence and difference of atomis numbers.

MINERALOGICAL AND PETROGRAPHICAL CHARACTERISTICS OF SOME TONSTEINS FROM THE LUBLIN COAL BASIN

The rocks which were supposed to contain minerals of the crandallite group belong to so called "Graupen" — tonsteins according to Schüller's (1951) classification. They consist predominantly of lenticular, oval or diffused microcrystalline kaolinite aggregates (Phot. 1), generally 0.1 to 0.5 mm and, but sporadically up to 2 mm in size. These aggregates are densely packed or embedded in basal clayey or clay-organic matrix. Clay substance of the latter is represented by microcrystalline, weakly birefringent kaolinite. Among secondary components, there occur vermicular, columnar kaolinite aggregates, quartz grains, potassium feldspars displaying optical properties of sanidine, usually strongly altered mica flakes (probably of biotite) and, locally, carbonate minerals as well as spherical aggregates of bacterial pyrite. Accessory apatite is observed. Minerals of crandallite group cannot be recognised in thin section by means of optical microscope.

X-ray examinations have confirmed that Tc-kaolinite, showing high-grade structural ordering (Fig. 1), is the main component of tonsteins, containing phosphate minerals of apatite and crandallite groups. This ordering is evidenced by the value of X-ray index $\frac{I_{020}}{I_{\bar{1}\bar{1}1}}$ (Stoch, Sikora 1966), which amounts to 0.65—0.75.

The occurrence of minerals of apatite group is manifested by the presence of diffraction lines $d_{21\bar{3}1} \approx 2.80—2.76$ Å and $d_{30\bar{3}0} \approx 2.71—2.70$ Å. Sometimes we also observed weaker reflexions of these minerals as eg. 3.45, 3.17, 3.07, 2,63, 2.25, 1.936, 1.885, 1.838, 1.795, 1.768, 1.720 Å. The presence of minerals of crandallite group is indicated by the following diffraction lines: $d_{10\bar{1}1} = 5.72$ Å, $d_{10\bar{1}2} = 4.90$ Å, $d_{11\bar{2}3} = 2.96$ Å, $d_{20\bar{2}4} = 2.43$ Å and $d_{12\bar{3}2} = 2.16$ Å. They do not coincide with the reflexions of other mineral components of these rocks.

In the examined samples, the phosphate minerals in question either coexist (sample K-17/9) or occur independently. In some of them there appears only apatite (samples L-74/24 and L-129/14), whereas in others there occur exclusively minerals of crandallite group (sample K-11/4, Fig. 1).

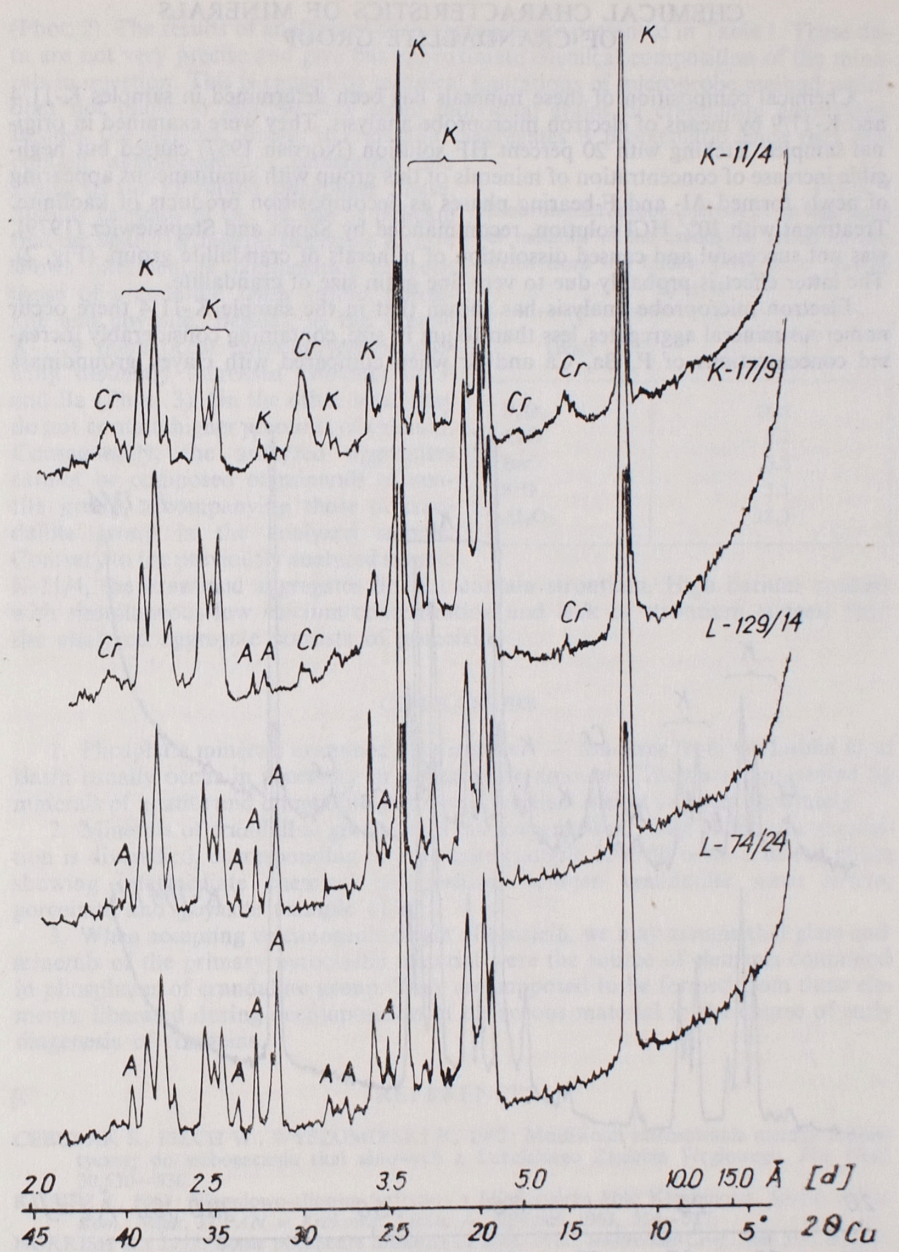

Fig. 1. X-ray diffractometer patterns of some tonsteins from the Lublin Coal Basin (original samples K-11/4, K-17/9, L-74/24 and L-129/14)

K — kaolinite, *Cr* — minerals of crandallite group, *A* — minerals of apatite group

Chemical composition of these minerals has been determined in samples K-11/4 and K-17/9 by means of electron microprobe analysis. They were examined in original samples. Etching with 20 percent HF solution (Norrish 1957) caused but negligible increase of concentration of minerals of this group with simultaneous appearing of newly formed Al- and F-bearing phases as decomposition products of kaolinite. Treatment with 10% HCl solution, recommanded by Szpila and Stępisiewicz (1979), was not successful and caused dissolution of minerals of crandallite group. (Fig. 2). The latter effect is probably due to very fine grain size of crandallite.

Electron microprobe analysis has shown that in the sample K-11/4 there occur numerous mineral aggregates, less than 10 μm in size, containing considerably increased concentrations of P, Ba, Ca and Sr when compared with clayey groundmass

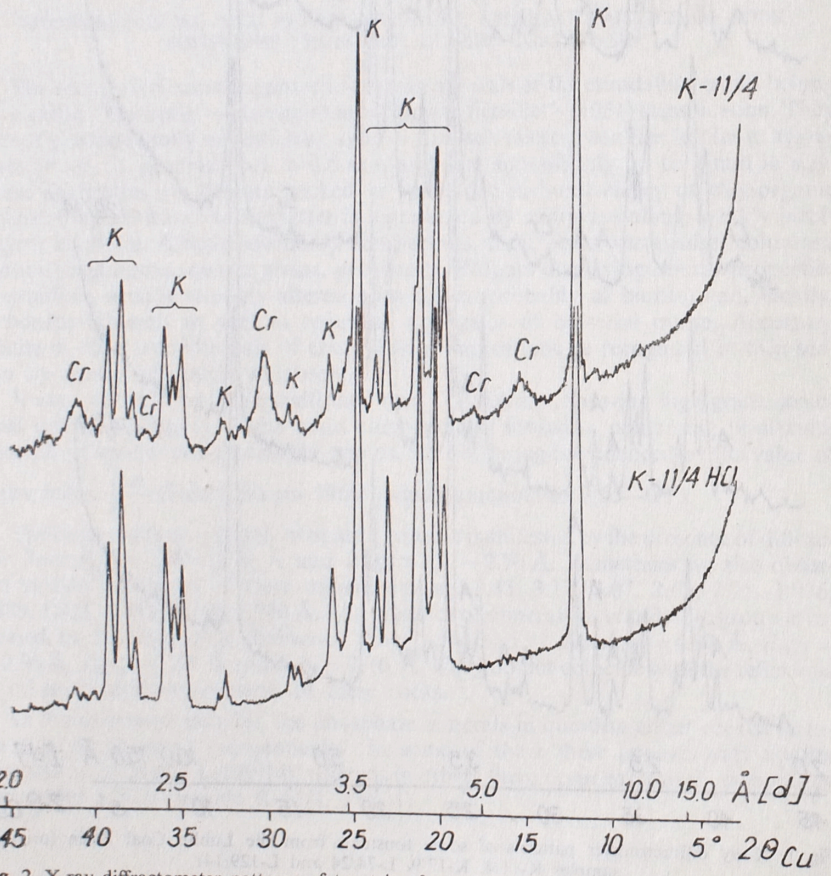

Fig. 2. X-ray diffractometer patterns of tonsteins from the Lublin Coal Basin — sample K-11/4 before (a) and after (b) treatment with 10% HCl solution
K — kaolinite, *Cr* — minerals of crandallite group

(Phot. 2). The results of analysis of such aggregate are presented in Table 1. These data are not very precise and give but approximate chemical composition of the minerals in question. This is caused by technical limitations of microprobe method which does not allow to analyse very small individual grains of crandallite aggregates. Besides, the alumina content in crandallite aggregates is problematic since they also contain aluminosilicates cementing fine grains of the examined phosphate phase. Similar contents of Ca, Ba and Sr indicate that the analyzed mineral in sample K-11/4 shows intermediate composition between those of crandallite *sensu stricto*, gorceixite and goyasite. Besides, in the sample K-17/9 there occur microaggregates showing distinctly increased contents of P and Ba (Phot. 3). On the other side, they do not contain higher amounts of calcium. Consequently, the analyzed aggregates cannot be composed of minerals of apatite group, accompanying those of crandallite group in the analyzed sample. Contrary to the previously analyzed sample K-11/4, the examined aggregates do not contain strontium. High barium content with simultaneous low calcium concentration and lack of strontium suggest that the analyzed aggregate consists of gorceixite.

Table 1
Electron-microprobe analysis of an aggregate of minerals of the crandallite group in tonsteins from the Lublin Coal Basin (sample K-11/4)

Oxide	Content (wt. per cent)
P_2O_5	16.5
CaO	5.2
BaO	5.8
SrO	3.5
Al_2O_3	23.3

CONCLUSIONS

1. Phosphate minerals examined in "Graupen" — tonsteins from the Lublin Coal Basin usually occur in accessory or subordinate amounts. They are represented by minerals of apatite and crandallite group which either coexist or occur separately.
2. Minerals of crandallite group form microaggregates. Their chemical composition is diversified, corresponding to gorceixite (sample K-17/9) or to a mixed phase showing intermediate chemical composition between crandallite *sensu stricto*, gorceixite and goyasite (sample 11/4).
3. When accepting volcanogenic origin of tonstein, we may assume that glass and minerals of the primary pyroclastic material were the source of elements contained in phosphates of crandallite group. They are supposed to be formed from these elements, liberated during decomposition of tuffaceous material in the course of early diagenesis of tonsteins.

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Marek MUSZYŃSKI, Piotr WYSZOMIRSKI

MINERAŁY GRUPY CRANDALLITU W NIEKTÓRYCH TONSTEINACH Z LUBELSKIEGO ZAGŁĘBIA WĘGLOWEGO

Streszczenie

Wśród minerałów ilastych Lubelskiego Zagłębia Węglowego występują m. in. „Graupen"-tonsteiny. Podstawowym ich składnikiem jest Tc-kaolinit. Podrzędnie występują w nich: kwarc, skalenie potasowe typu sanidynu, silnie zmieniony biotyt, rzadziej — minerały węglanowe i piryt. Niekiedy w ilościach akcesorycznych lub sporadycznie podrzędnych pojawiają się minerały fosforanowe. Są one reprezentowane przez przedstawicieli grupy apatytu i crandallitu. Fazy te współwystępują lub pojawiają się oddzielnie. Minerały grupy crandallitu tworzą mikroagregaty. Skład chemiczny tych minerałów jest zróżnicowany; odpowiada on gorceixytowi (próbka K-17/9) lub fazom o mieszanym składzie chemicznym między crandallitem *sensu stricto*, gorceixytem i goyazytem (próbka K-11/4).

Skłaniając się ku wulkanogenicznej teorii powstania tonsteinów można przyjąć, że źródłem pierwiastków wchodzących w skład minerałów grupy crandallitu było szkliwo i minerały pierwotnego materiału piroklastycznego. Tworzenie się omawianych minerałów fosforanowych z pierwiastków uwalniających się w trakcie rozkładu tego materiału przypuszczalnie odbywało się na etapie wczesnej diagenezy tonsteinów.

OBJAŚNIENIA FIGUR

Fig. 1. Dyfraktogramy niektórych tonsteinów z LZW w stanie naturalnym (próbki K-11/4, K-17/9, L-74/24, L-129/14)
K — kaolinit, *Cr* — minerały grupy crandallitu, *A* — minerały grupy apatytu

Fig. 2. Dyfraktogramy tonsteinu z LZW (próbka K-11/4) przed (*a*) i po (*b*) traktowaniu 10-procentowym roztworem HCl
K — kaolinit, *Cr* — minerały grupy crandallitu

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Agregaty mikrokrystalicznego kaolinitu w „Graupen" — tonsteinie z LZW (próbka L-129/14). Nikole ×. Powiększenie około 35×

Fot. 2. Agregat minerałów grupy crandallitu (współrzędne x, y) w tonsteinie z LZW (próbka K-11/4)
a — elektronowy obraz topograficzny, *b* — obraz scanningowy PK_{α}, *c* — obraz scanningowy CaK_{α}. Wielkość obrazu 95×73 μm

Fot. 3. Agregaty minerałów grupy crandallitu (współrzędne x_1, y_1 oraz x_2, y_2) w tonsteinie z LZW (próbka K-17/9)
a — elektronowy obraz topograficzny, *b* — obraz scanningowy PK_{α}, *c* — obraz scanningowy BaK_{α}, *d* — obraz scanningowy CaK_{α}. Wielkość obrazu 19×15 μm

Марек МУШИНЬСКИ, Пётр ВЫШОМИРСКИ

МИНЕРАЛЫ ГРУППЫ КРАНДАЛЛИТА В НЕКОТОРЫХ ТОНШТЕЙНАХ ИЗ ЛЮБЛИНСКОГО УГЛЕНОСНОГО БАССЕЙНА

Резюме

Среди глинистых минералов Люблинского угленосного бассейна развиты между прочим «граупен»-тонштейны. Основным их компонентом является Тс-каолинит. Подчиненное значение имеют: кварц, калиевые полевые шпаты типа санидина, интенсивно измененный биотит, реже карбонатные минералы и пирит. Иногда в акцессорных, или же в спорадически подчиненных, количествах появляются фосфатные минералы. Они представлены минералами группы апатита и крандаллита. Эти минеральные фазы встречаются вместе, или появляются отдельно. Минералы группы крандаллита образуют микроагрегаты. Химический состав этих минералов дифференцирован, он соответствует горсейкситу (образец К-17/9), или фазам смешанного химического состава между собственно крандаллитом, горсейкситом и гойязитом (образец К-11/4).

Склоняясь к вулканогенной теории образования тонштейнов, надо полагать, что источником химических элементов, входящих в состав минералов группы крандаллита, было вулканическое стекло и минералы первичного пирокластического материала. Образование обсуждаемых фосфатных минералов из химических элементов, освобождающихся в ходе разложения этого материала, по-видимому, происходило на этапе раннего диагенеза тонштейнов.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Дифрактограммы некоторых тонштейнов из Люблинского угольного бассейна в естественной состоянии (образцы К-11/4, К-17/9, L-74/24, L-129/14).
K — каолинит, *Cr* — минералы группы крандаллита, *A* — минералы группы апатита

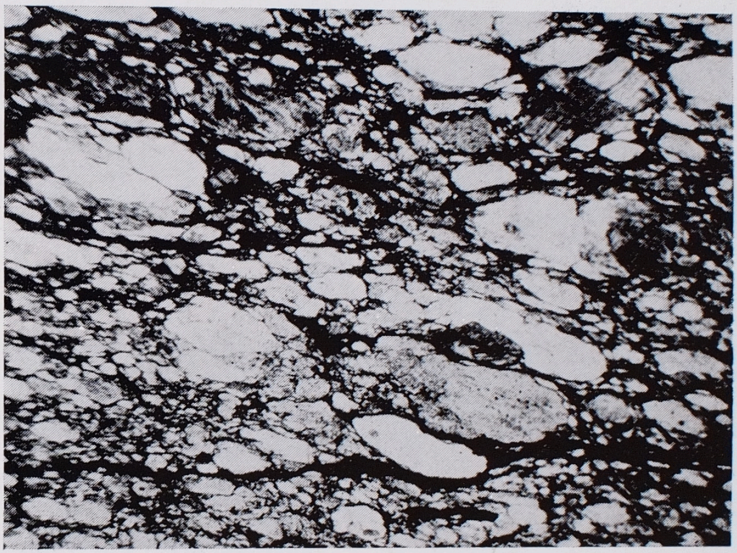
Фиг. 2. Дифрактограммы тонштейна из Люблинского угольного бассейна (образец К-11/4) до (*a*) и после (*b*) обработки 10% раствором
K — каолинит, *Cr* — минералы группы крандаллита

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

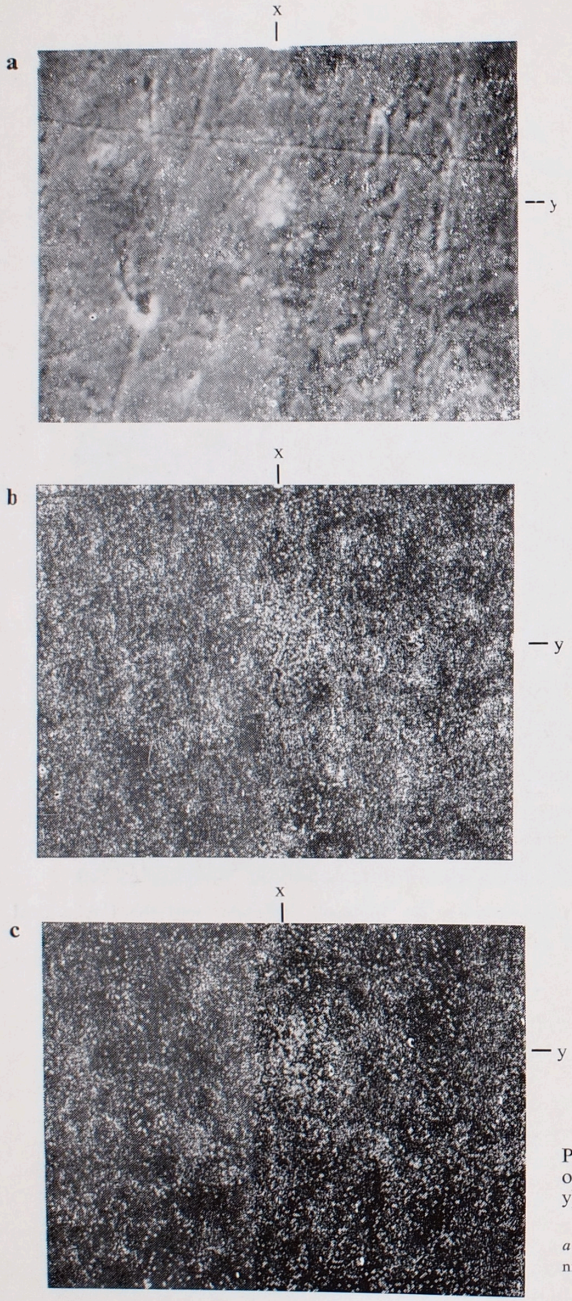
Фото 1. Агрегаты микрокристаллического каолинита в «граупен»-тонштейне из Люблинского угольного бассейна (образец L-129/14). Скрещенные николи. Увел. около × 35

Фото 2. Агрегат минералов группы крандаллита (координаты x_1, y_1) в тонштейне из Люблинского угольного бассейна (образец К-11/4)
a — электронное топографическое изображение, *b* — сканированное изображение PK_{α}, *c* — сканированное изображение CaK_{α}
Размеры микроучастка 95×73 мм

Фото 3. Агрегаты минералов группы крандаллита (координаты x_1, y_1, а также x_2, y_2) в тонштейне из Люблинского угольного бассейна (образец К-17/9)
a — электронное топографическое изображение, *b* — сканированное изображение PK_{α}, *c* — сканированное изображение BaK_{α}, *d* — сканированное изображение CaK_{α}
Размеры микроучастка 19×15 мм



Phot. 1. Aggregates of microcrystalline kaolinite in "Graupen" - tonstein from the Lublin Coal Basin (sample L-129/14). Crossed nicols. Magn. 35×



Phot. 2. An aggregate of minerals of crandallite group (coordinates x, y) in tonstein from the Lublin Coal Basin (sample K-11/4).

a — topographic electron image, *b* — scanning image PK_{α}, *c* — scanning image CaK_{α}. Size of the image 93 × 75 μm

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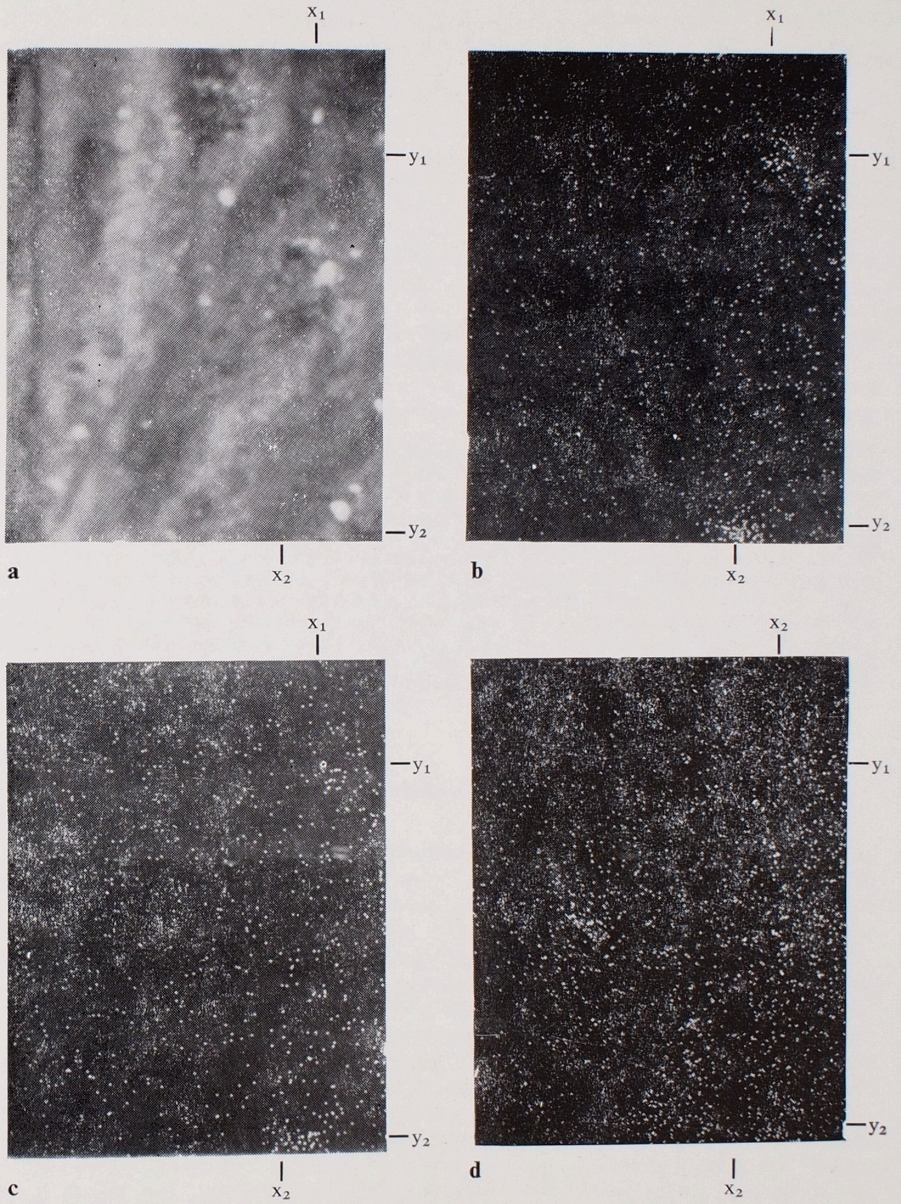

Phot. 3. Aggregates of minerals of crandallite group (coordinates x_1, y_1 and x_2, y_2) in tonstein from the Lublin Coal Basin (sample K-17/9)

a — topographic electron image, *b* — scanning image PK_{α}, *c* — scanning image BaK_{α}, *d* — scanning image CaK_{α}. Size of the image 19 × 15 μm

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