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VERSITA

Phosphorus minerals in tonstein; coal seam 405 at Sośnica-Makoszowy coal mine, Upper Silesia, southern Poland

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ABSTRACT:

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The paper presents results of research on tonstein, which constitutes an interburden in coal seam 405 at the Sośnica-Makoszowy coal mine, Makoszowy field (mining level 600 m), Upper Silesia, southern Poland. The mineral and chemical compositions of the tonstein differ from the typical compositions described earlier for tonsteins from Upper Silesia Coal Basin area. Additionally, minerals present in the tonsteins include kaolinite, quartz, kaolinitised biotite and feldspars. The presence of the phosphatic minerals apatite and goyazite has been recognized. The presence of gorceixite and crandallite is also possible. The contents of CaO (5.66 wt%) and P_2O_5 (6.2 wt%) are remarkably high. Analysis of selected trace elements demonstrated high contents of Sr (4937 ppm) and Ba (4300 ppm), related to the phosphatic minerals. On the basis of mineral composition the tonstein has been identified as a crystalline tonstein, transitional to a multiplied one.

Key words: Tonstein; Załęże beds; Goyazite; Gorceixite; Apatite; Phosphorus; Barium; Strontium.

INTRODUCTION

During the research on samples of rocks which accompany coal seams within the Załęże beds, of the Upper Carboniferous (Westphalian A) coal-bearing succession of the Upper Silesia (southern Poland), it has been found out that one from 134 collected samples demonstrates different petrographic character than the others. Results of the tests allowed to determine that this sample contains tonstein, not mentioned previously in literature, which has been found in the interburden in coal seam 405 (level 600 m) at Sośnica-Makoszowy coal mine – field Makoszowy.

Tonsteins are rocks of tuffogenic origin, comprising separate genetic types of clay rock rich in kaolinite. They are formed in peat bogs from pyroclastic material, volcanic ash (Dopita and Kralik 1977; Gabzdyl 1984, 1990; Ryszka and Gabzdyl 1986; Łapot 1992). In Poland they are present mainly in coal seams of the Upper Silesia Coal Basin (USCB), where they form interburdens of thickness from a few to dozens of centimetres.

The rocks in Poland have been the subject of numerous earlier reports, due to their interesting genesis, position in the systematics of rocks, properties, and also due to the possibility of using them as marker horizons in correlation and identification of coal seams (Kuhl and Kapuściński 1968; Kuhl 1972; Środoń 1972; Gabzdyl 1984, 1990; Gabzdyl and Duźniak 1986; Ryszka and Gabzdyl 1986; Łapot 1992; Adamczyk 1993, 1997, 1998; Święch and Kwiecińska 2003). They can be also considered as a valuable raw material (fire-resistant shale) for the industry of fire-resisting materials (Kuhl 1957, 1974). Therefore any information on the presence of fire-resistant shales in the USCB is interesting, because it improves the possibilities for correlation of the seams and more detailed research on conditions of their genesis etc.

As in Poland, tonsteins have been investigated in other parts of the world. The dynamic growth of hard coal production, which takes place mainly in Asiatic countries (China, India, Indonesia, Russia), countries of South and North America (Columbia, USA, Canada) as well as in Australia and RSA has resulted in increasing interest in coal seams, including tonsteins present in them. Modern research methods, especially geochemical, has made possible the determination of lithogenetic indicators in tonsteins. On the basis of this research, new divisions and classifications are being proposed.

According to chemical and mineral compositions, silicic, alkaline, and mafic tonsteins can be distinguished (Zhou *et al.* 2000, Dai *et al.* 2007). Some authors classify tonsteins on the basis of their main mineral component; thus they distinguish kaolinitic and smectic tonsteins (Bohor and Triplehorn 1993). Additionally to the primary mineral components of tonsteins represented by clay minerals, quartz, and feldspars, the rocks may contain also biotite, zircon, apatite and phosphatic minerals – crandallite, xenotime, and monazite (Ward 2002; Admakin 2001).

In genetic terms orthotonsteins and paratonsteins are presently distinguished. Orthotonsteins are products of the transformation of aeolian volcanic ash; paratonsteins are the sedimentary products of dispersed kaolinic material (Admakin 1995). Some authors see the genesis of some tonsteins as related to the accumulation of weathering products of basaltic rocks (Dai *et al.* 2007).

On the basis of geochemical testing of tonsteins indicators are being formulated which give a background for determining the nature of the magma and types of volcanism involved in the origin of tonstein (Kramer *et al.* 2001).

METHODOLOGY

A sample of tonstein was studied in transmitted light and identification of mineral phases was by X-ray diffraction. The chemical composition and presence of trace elements were also determined. Observations under a scanning microscope completed the range of the investigation.

Microscopic description in the transmitted light has been conducted with use of polarizing microscope AXIOSKOP manufactured by ZEISS company, equipped with an image analyser.

Mineral identification by X-ray diffraction was conducted on a HZG-4 diffractometer with a copper lamp and nickel filter; conditions of the analysis were voltage 35 kV, current 18 mA.

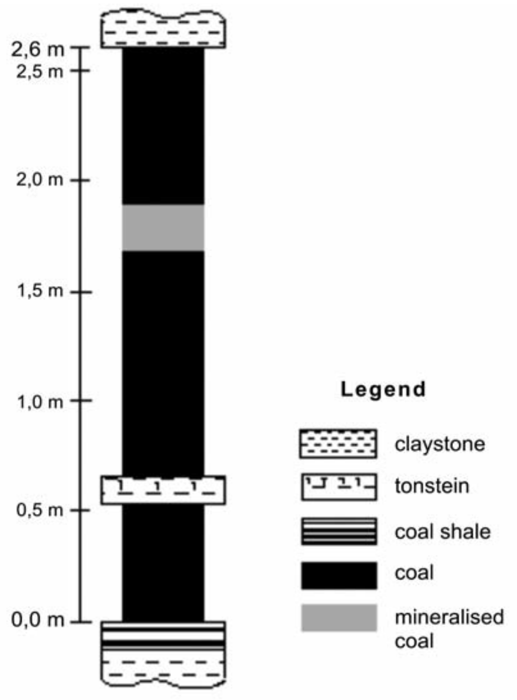
Chemical analysis included measurements of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, MnO, S and loss on ignition. Concentrations of the following trace elements were measured: Au, Ag, As, Ba, Be, Bi, Br, Cd, Co, Cr, Cs, Cu, Hf, Hg, Ir, Mo, Ni, Pb, Rb, Sb, Sc, Se, Sr, Ta, Th, U, V, W, Y, Zn, Zr, La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu.

The measurements were made by mass spectrometry with inductively coupled plasma (ICP-MS) in the Canadian laboratory Activation Laboratories Ltd. – ACTLABS.

Scanning microscopy was done on a scanning electron microscope with a cold cathode (FEG) Hitachi S-4200, equipped with X-ray detector with energy dispersion (EDS) manufactured by THERMO company. Observations of samples were conducted in the technique of secondary electrons (SE) by acceleration voltage of 15.0 kV. The results obtained were analysed with the use of NSS (Noran System Seven) software. Before testing the samples were sputtered with graphite.

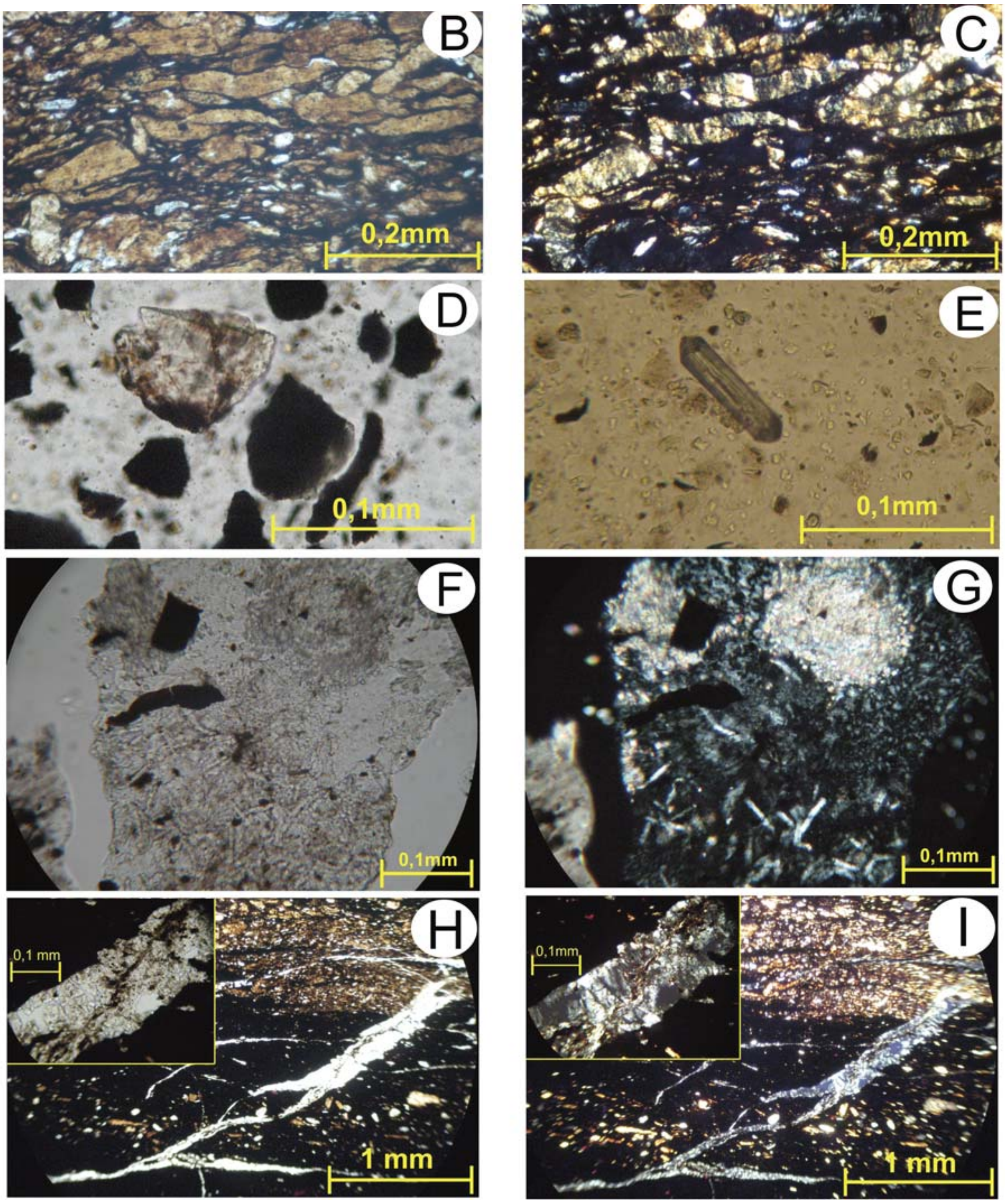
In order to identify the heavy minerals present in the tonstein, the sample was split in bromoform. The heavy mineral concentrate was investigated microscopically and phases identified by X-ray diffraction.

White minerals present in cleavage fractures in coal adjoining the tonstein were also separated. These min-



Text-fig.1. Lithological profile of coal seam 405 with the tonstein layer

Text-fig. 2. **A** – Tonstein from coal seam 405. In the upper part white minerals, filling cleavage fractures in the glance coal (vitrain) are visible; **B** – Vermicular forms of kaolinite, locally fine quartz grains. Transmitted light, magnification 100x, one nicol; **C** – As B, crossed nicols; **D** – Glaze of sharp edges. Powdered specimen. Transmitted light, magnification 250x, one nicol; **E** – Idiomorphic zircon crystal. Powdered specimen. Transmitted light, magnification 250x, one nicol; **F** – Accretion of phosphatic minerals (pole-shaped crystals at the bottom) with opal (in the middle and on the right) and carbonates (at the top). Minerals separated from the cleavage fracture, powdered specimen, transmitted light, magnification 100x, one nicol; **G** – As on F, crossed nicols; **H** – A vein filled with goyazite, crandallite, and chalcedony. Transmitted light, magnification 40x, closed-up part 250x, one nicol; **I** – As on H, crossed nicols.



erals were investigated microscopically and phase identification was by X-ray diffraction.

RESULTS

Tonstein has been found in the Załęże beds, in one of the interburdens of coal seam No. 405 in “Sośnica-Makoszowy” coal mine, Makoszowy field, at a level of 600 m. It forms a layer up to 0.08 m thick (Text-fig. 1).

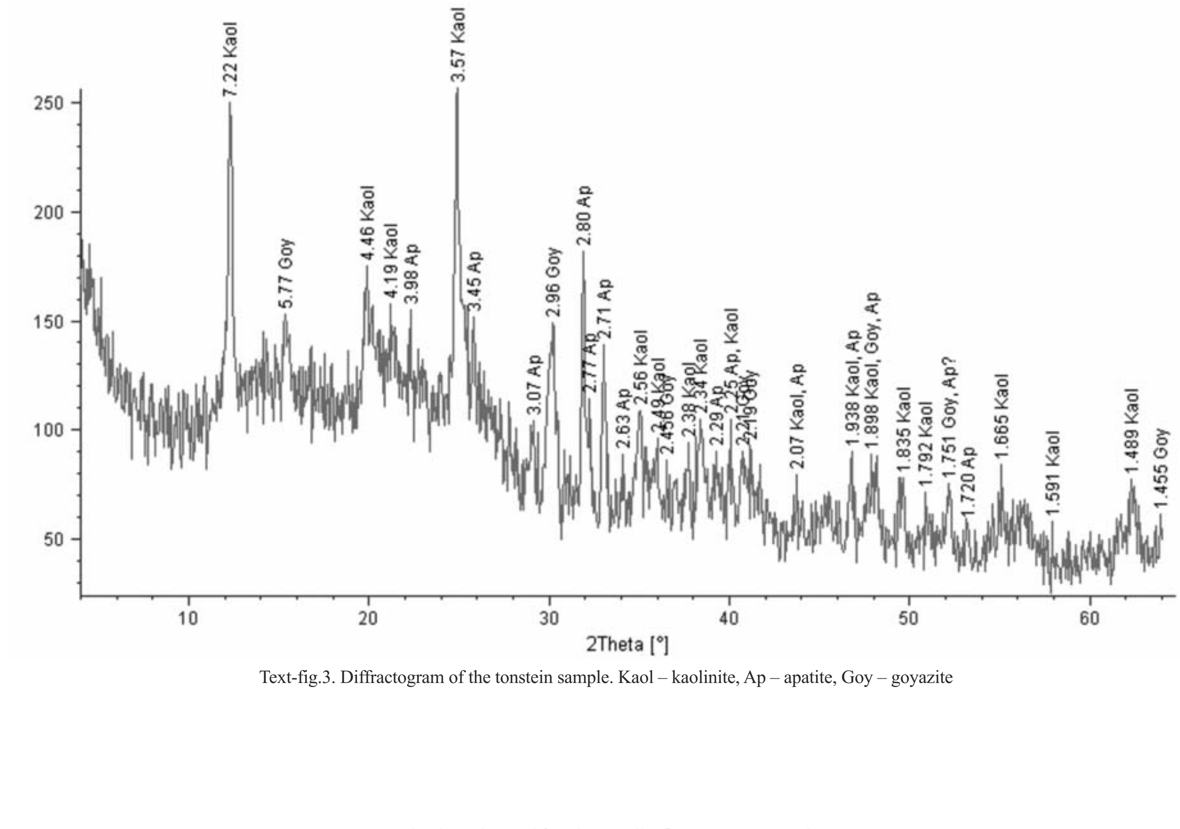
The tonstein is russet-gray; after scratching the surface it is clear russet. The rock demonstrates an aleuritic structure, locally psammitic, with visible larger, clearer clusters of kaolinite. The texture of the rock is compact, locally directional, emphasized by parallel laminae of coal of maximum thickness 1.50 mm. At the contact of the tonstein with the coal seam, fine pyrite crystals are present, and the appearance of rind-formed white minerals, which fill cleavage fractures in the glance coal (vitrain) adjoining the rock, have been also noted (Text-fig. 2A).

Microscopically, kaolinite, quartz, biotite, feldspars, and also glass and organic matter (coal), have been identified. In the powdered specimens made from the heavy minerals concentrate zircon crystals and the phosphatic minerals apatite, goyazite or gorceixite have been identified, whilst siderite, dolomite and goyazite or gorceixite have been separated from cleavage fractures.

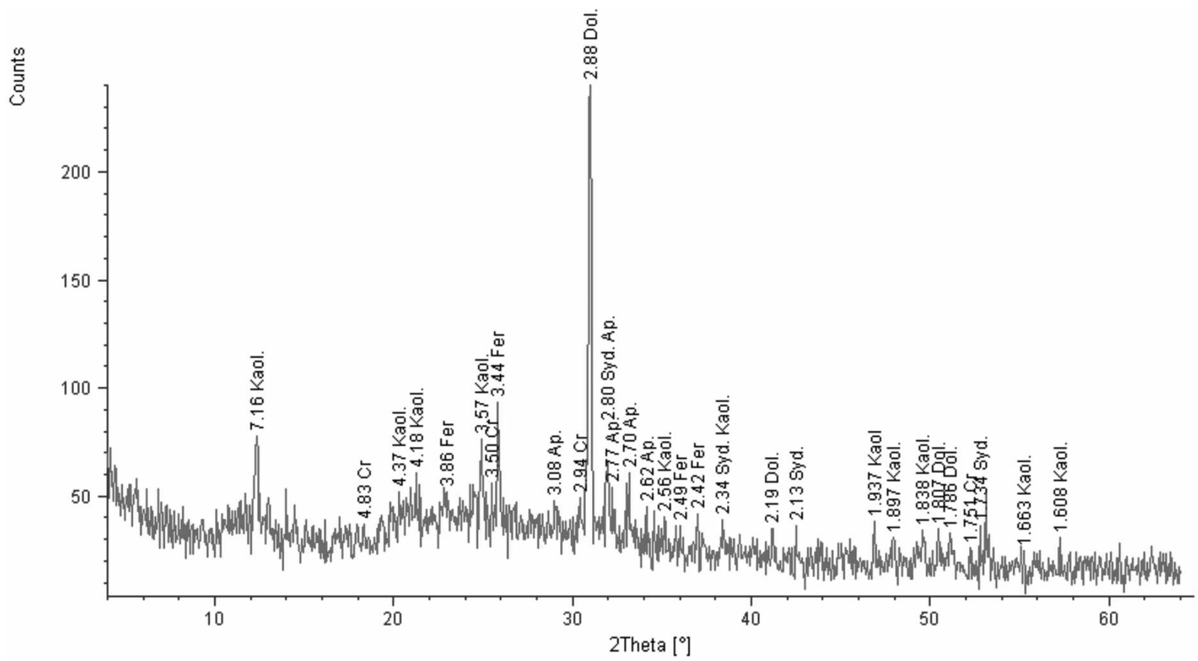
Kaolinite is present mainly in tabular forms, pseudomorphs after feldspars or vermicular aggregates (Text-figs 2B, C). Quartz is present in small amounts, forming poniard-shaped, elongated grains of pyroclastic origin. Sharp-edged or poorly grinded grains of terrigenous character have been observed. Quartz grains do not exceed 0.1 mm. Biotite occurs as plates from 0.03 to 0.07 mm with strong yellow-russet pleochroism. Biotite is often partly kaolinitised. It forms sheaf-shaped biotite-kaolinite aggregates. Feldspar plates (0.02–0.1 mm) are mainly kaolinitised or sericitised, thus the disappearance of twin fringes has been observed. The surface of the grains is strongly turbid, so that cleavage could not be observed. Locally russet pieces of volcanic glass with characteristic sharp edges (Text-fig. 2D) or oval are visible. Usually the glass is isotropic, but locally a weak anisotropy has been observed, pointing to incipient devitrification of the glass. Zircon, found in the heavy minerals concentrate, forms idiomorphic crystals up to 0.12 mm size (Text-fig. 2E).

Carbonates, dolomite and siderite, found in the cleavage fractures of the coal (vitrain) layer adjoining the tonstein, formed microcrystalline aggregates and accretions with goyazite, gorceixite, and crandallite (Text-figs 2F, G). Accretions of goyazite, gorceixite, and silica (probably chalcedony) formed aggregations in the form of veins in the tonstein of up to 0,1 mm thick (Text-figs 2H, I).

The mineralogical characteristics of the tonstein suggest that it is crystalline tonstein, transitional to multi-component, in the classification of Łapot (1992). The classification as a crystalline tonstein results from the presence of vermicular, tabular crystals and aggre-



Text-fig.3. Diffractogram of the tonstein sample. Kaol – kaolinite, Ap – apatite, Goy – goyazite

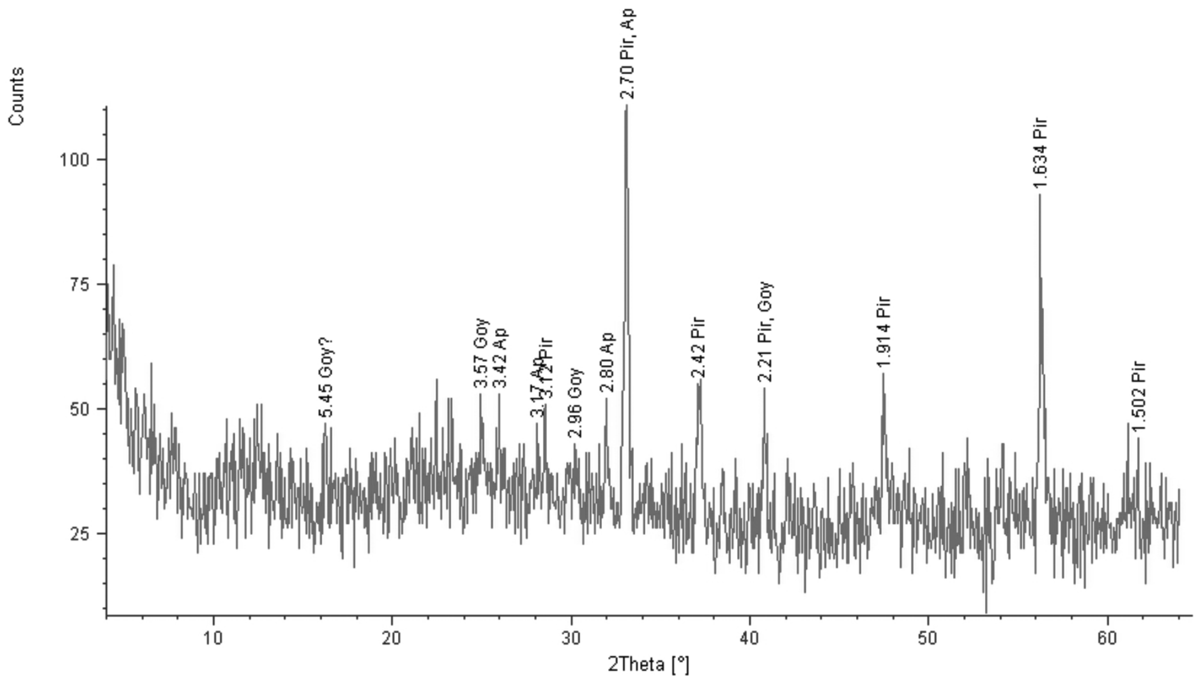


Text-fig. 4. Diffractogram of the white minerals from the cleavage fractures in coal adjoining the tonstein. Dol – dolomite, Syd – siderite, Kaol – kaolinite, Ap – apatite, Cr – crandallite, Fer – ferringtonite

gates of kaolinite and small amount of resistates. Its multi-component character is suggested by the presence of pyroclastic quartz, volcanic glass, and also zircon and phosphatic minerals.

The identification of phases by X-ray diffraction method allowed us to identify kaolinite, apatite and goyazite. In the case of apatite, the best fit of the reflectogram occurred for fluorapatite (Bayliss *et al.* 1986). It can be proven, amongst others, by the presence of the most significant reflex at 2.80 Å (Text-fig. 3) on the diffractogram.

Goyazite, an acidic phosphate with chemical formula $SrAl_3H[(OH)_6|(PO_4)_2]$, occurs rarely in nature. It has been identified in tonsteins from the Lublin Coal



Text-fig. 5. Diffractogram of heavy mineral concentrate from tonstein. Pir – pyrite, Ap – apatite, Goy – goyazite

Basin (Muszyński and Wyszomirski 1998, Lipiarski *et al.* 1993). It has not yet been recorded in USCB tonsteins. Probably also present in the sample are other phosphates: gorceixite of chemical formula $BaAl_3H[(OH)_6|(PO_4)_2]$, and crandallite of formula $CaAl_3H[(OH)_6|(PO_4)_2]$. However, due to the fact that d_{hkl} values of the most intensive reflexes from these minerals are similar to the d_{hkl} values of reflexes from goyazite, their identification is equivocal.

The rise of the reflectogram's background by a small range of 2Θ angle indicates the presence in the sample of an amorphous substance, resulting from the large amounts of organic matter and glass.

The identification of phases within the white rind forms, which fill cleavage fractures in the vitrain layer adjoining the tonstein (Text-figs 2A, 4), allowed us to determine the presence of kaolinite, carbonates: dolomite and siderite, and apatite. Weak reflexes in the diffractogram probably came from crandallite and ferringtonite.

In the heavy mineral concentrate, in additional to apatite and probable goyazite, clear reflexes from pyrite have also been identified (Text-fig. 5).

Chemical composition of tonstein

The main components of the tonstein are Al_2O_3 (15.91 %) and SiO_2 (14.79 %), mainly reflecting the high amount of kaolinite, which was determined both microscopically and by use of X-ray diffraction. There are also high abundances P_2O_5 (6.20%), CaO (5.66%), Fe_2O_3 (2.50%) and S (1.93%). The content of TiO_2, Na_2O, K_2O, MgO and MnO does not exceed 1% (Table 1).

Attention can be drawn to the high amounts of loss of ignition (LOI), which reach 50.81%. This mainly results from the large content of organic matter, which undergoes oxidation (combustion), and kaolinite, which undergoes dehydroxylation. Other important mineral components, which can influence the loss of ignition, are the phosphates (apatite and goyazite) and carbonates (dolomite and siderite).

The chemical composition is significantly different from the tonsteins already described from the USCB (Gabzdyl 1990, Łapot 1992). The very high P_2O_5 content (6.20 wt%) makes the analysed tonstein similar to the tonsteins from coal seams 377 and 382 in the Lublin Coal Basin, whose P_2O_5 contents range from 2.21 to 2.72 wt% (Muszyński and Wyszomirski 1998). Compared to other tonsteins in the USCB, CaO is relatively high (5.66 wt%). Similar values have been determined earlier only in tonstein from coal seams 349 and 326.

The low value of the molecular ratio SiO_2/Al_2O_3 (1.58) (Table 1) is evidence of intensive kaolinitisation of the primary material. An advanced stage of kaolinitisation can be confirmed by the ratio of $(SiO_2/Al_2O_3)/(K_2O/Al_2O_3)$ (53) (Table 1), which indicates the level of kaolinitisation of the primary material for formation of the tonstein (Adamczyk 1998).

Another important indicator of change taking place in the pyroclastic material in the environment of coal

Component	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	S	LOI
Value	14.79	15.91	2.50	0.01	0.46	5.66	0.51	0.48	0.75	6.20	1.93	50.81
Molecular ratio	SiO_2/Al_2O_3 1.58			K_2O/Al_2O_3 0.03			TiO_2/Al_2O_3 0.06			$\frac{SiO_2/Al_2O_3}{K_2O/Al_2O_3}$ 53		

Table 1. Chemical composition of tonstein from 405 coal seam at "Sośnica – Makoszowy" coal mine [% mass]

Element	Value	Element	Value	Element	Value
Au*	< 5	Eu	5.3	Se	< 3
Ag	< 0.5	Hf	6	Sm	15
As	9	Hg	< 1	Sr	4937
Ba	4300	Ir	< 5	Ta	< 1
Be	7	La	88	Tb	2.9
Bi	< 2	Lu	1.07	Th	33.8
Br	10	Mo	2	U	14.8
Cd	0.6	Nd	92	V	127
Ce	182	Ni	55	W	< 3
Co	7	Pb	100	Y	148
Cr	46	Rb	< 20	Yb	8.3
Cs	4.2	Sb	7.5	Zn	38
Cu	70	Sc	16.4	Zr	89

*- in ppb

Table 2. Concentration of trace elements in tonstein from coal seam at "Sośnica Makoszowy" coal mine [ppm]

formation, is the K_2O/Al_2O_3 ratio, what relates to the kaolinitisation of components containing K. Simultaneously this indicator is also related to the level of illinitisation of aluminosilicates; the higher the level, the higher is its value.

Among the trace elements, the highest values are for Sr (4937 ppm) and Ba (4300 ppm) (Table 2). These elements are probably related to the minerals of the phosphate group. Barium could also be present in biotite as a replacement of K; Sr and Ca can be present in carbonates. However, the confirmed presence of goyazite and the probable occurrence of gorceixite allow us to conclude that these minerals are the main carriers of Ba and Sr in the tonstein. The relationship between the high concentrations of Ba and Sr and the presence of goyazite and gorceixite has been found in tonsteins from coal seams 377 and 382 in the Lublin Coal Basin (Muszyński and Wyszomirski 1998).

Attention should be given also to the high levels of rare earth elements: Ce 182 ppm, Y 148 ppm, Nd 92 ppm, La 88 ppm, Th 34 ppm, Sc 16.4 ppm, Sm 15 ppm, Yb 8.3 ppm, Eu 53 ppm, and Lu 1.07 ppm. The presence of these elements should be correlated with the phosphatic minerals.

For the other elements, the highest concentrations have been determined for V 127 ppm, Pb 100 ppm, Zr 89 ppm, Cu 70 ppm, Ni 55 ppm, Cr 46 ppm, Zn 38 ppm, and U 14.8 ppm. The content of other elements determined did not exceed 10 ppm.

The occurrence of trace elements in tonstein depends, *inter alia*, on the level of kaolinitisation and on the degree of crystallisation of kaolinite (Łapot 1992).

Chemical component	Measuring point		
	6/5	7/5	10/5
CaO	56.36	54.89	56.60
Na_2O	0.46	0.00	0.00
FeO	0.68	0.00	0.00
P_2O_5	42.02	39.41	39.29
SiO_2	0.00	3.84	2.27
F	0.48	1.86	1.84
Total	100	100	100
In recalculation for 26 Oxygen atoms			
Ca	10.39	10.01	10.42
Na	0.15	0.00	0.00
Fe	0.10	0.00	0.00
P	6.12	5.68	5.72
Si	0.00	0.65	0.39
(F, O, OH)	1.00	1.00	1.00

Table 3. Chemical composition of apatite on the basis of measurements in the micro-area

The presence of biotite-kaolinite aggregates favours higher concentrations of trace elements (Hanak and Kokowska-Pawłowska 2005a,b). During kaolinitisation of biotite some elements are released, which then are absorbed by clay minerals. Organic matter, here in large amounts, also carries many elements.

A characteristic feature of tonstein from coal seam 405 at "Sośnica-Makoszowy" coal mine is the high concentration of P_2O_5. Thus, detailed research aimed at an explanation of the form of occurrence of this component has been conducted.

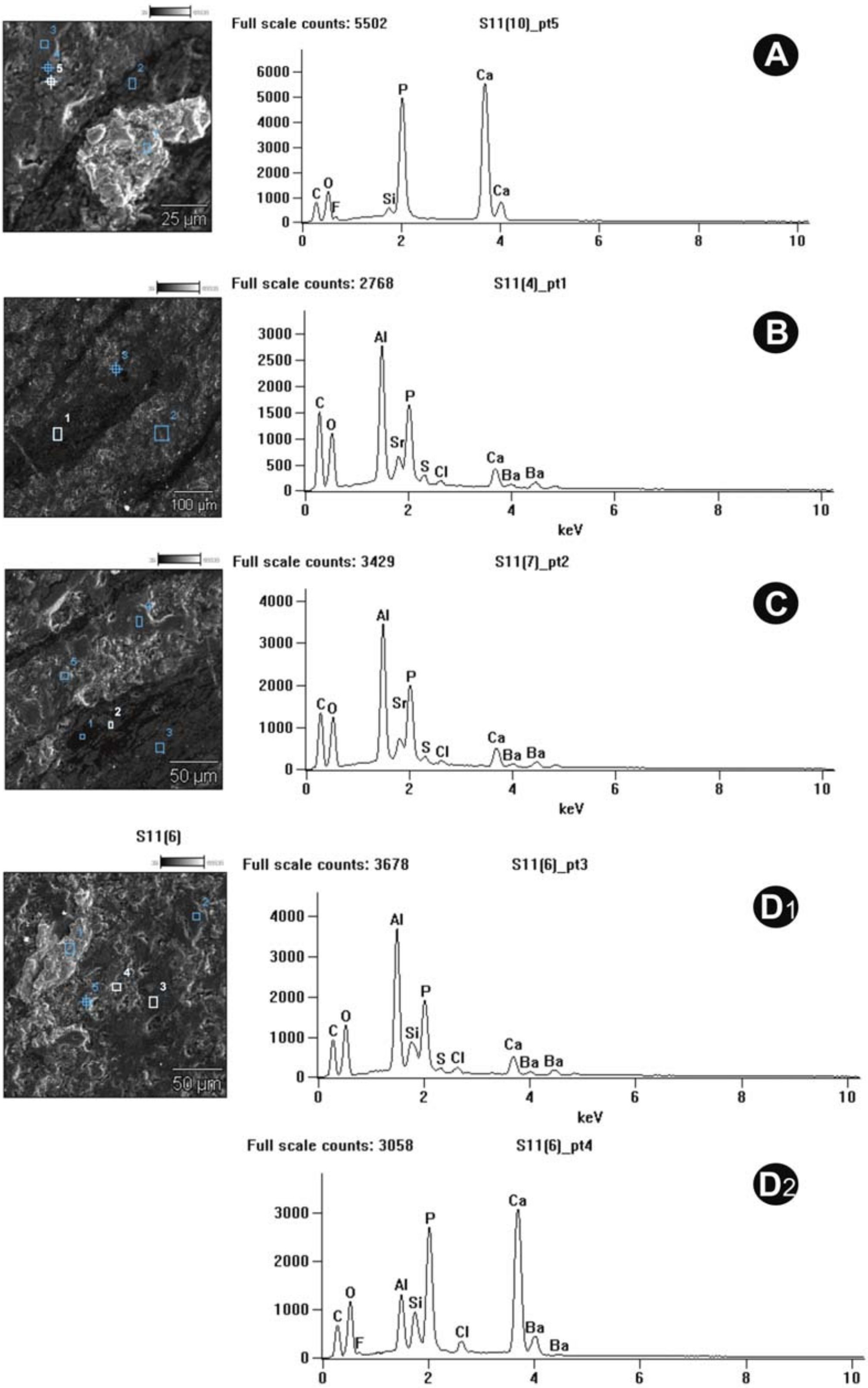
Composition measurements in the micro-areas revealed three chemically different types of mineral grains in the phosphates.

The first group consists of apatite grains (Table 3, Text-fig. 6A), whose composition suggests fluorapatite. Additional elements included in the composition are Na, Fe and Si. It could be seen that Na and Fe are present in the grains, whereas Si is absent (Text-fig. 6A, Table 3). Silicon, probably in the form of the $[SiO_4]^{4-}$ ion, replaces the ion $[PO_4]^{3-}$. This is possible due to their similar radii. The existence of phosphate ions containing up to 11% SiO_2 is known (Bolewski and Manecki 1993). Sodium, probably due to similar ionic radii, replaces heterovalent Ca.

The second group is phosphates of Al, Ca, Sr and Ba, which contain Cl (Table 4, Text-fig. 6B, C). Identification of phases by X-ray diffraction revealed in the tonstein the presence of goyazite (phosphate of Sr and Al) and the probable presence of gorceixite (phosphate of Ba and Al) and crandallite (phosphate of Ca and Al). Because Ca, Sr, and Ba are coexist in the micro-areas, it should be assumed that the analysed grains form accretions of these minerals. The coexistence of these three minerals has been described in tonstein

Chemical component	Measuring point				
	4/1	7/2	7/3	9/1	10/2
P_2O_5	36.27	36.92	36.46	35.94	36.29
Al_2O_3	34.16	34.54	34.32	35.02	34.83
SiO_2	-	-	-	-	-
CaO	7.93	8.13	7.95	7.71	7.59
SrO	8.30	7.92	9.05	8.95	8.60
BaO	7.58	7.01	7.92	8.03	7.86
Fe_2O_3	-	-	-	-	0.78
SO_3	4.63	4.27	3.54	3.50	3.30
Cl	1.13	1.21	0.76	0.85	0.75
Total	100	100	100	100	100
CaO+BaO+SrO	23.81	23.06	24.92	24.69	24.05

Table 4. Chemical composition of goyazite, gorceixite and crandallite [% mass]



Text-fig. 6. A – Picture (BSE, SEM image) of measurement micro-area and one of the obtained apatite spectra (measuring point 5). In the bottom-right corner iron sulphide (pyrite) is visible. B, C – Pictures of measurement micro-areas and example of spectra obtained from accretions of goyazite, gorceixite, and crandallite; D1, D2 – Picture of measurement micro-area and examples of spectra given by accretions of crandallite, gorceixite, and chalcedony.

Chemical component	Measuring point				
	3/3	6/3	7/4	2/1	6/4
P_2O_5	17.88	32.56	26.68	26.66	26.34
Al_2O_3	32.06	39.32	37.03	37.00	36.57
SiO_2	32.61	8.48	19.34	19.33	19.10
CaO	11.68	8.43	7.60	7.59	7.51
SrO	-	-	-	-	-
BaO	3.88	8.37	6.20	6.20	6.12
K_2O	0.71	-	0.33	0.33	0.33
SO_3	0.84	2.30	2.49	2.49	2.46
Cl	0.34	0.55	0.32	0.41	0.66
F	-	-	-	-	0.92
Total	100	100	100	100	100
CaO+BaO+SrO	15.56	16.79	13.80	13.79	13.63

Table 5. Chemical composition of crandallite, gorceixite, and chalcedony accretions [wt%]

from Lublin Coal Basin (Muszyński and Wyszomirski 1982, 1998). Measurement points 4/1, 7/2, 7/3, 9/1, and 10/2 demonstrated very similar compositions, whilst P_2O_5 concentration were around 36%, Al_2O_3 changed between 34 and 35%, and the sum of CaO, BaO, and SrO ranged from 23 to almost 25%. The presence of SO_3 has been also noted in amounts of 3.3–4.6% and around 1% Cl has been observed.

The third group of phosphatic minerals comprises grains, whose main component, apart from P_2O_5, Al_2O_3 and CaO, is SiO_2 (Table 5, Text-fig. 6D1, D2). In these grains there is a complete lack of Sr and the amount of Ba is significantly lower than in the second group. The total amount of CaO and BaO ranges from 13.63 up to 16.79 wt%. The high level of SiO_2 (19.77 wt% on average) demonstrates that these grains are probably accretions of silica, most probably chalcedony, with gorceixite and crandallite. The occurrence of K should also be noted. However this component is present in small amounts (0.42 wt% on average) and in point 6/3 its presence has not been confirmed. K can point to the ways of transformations that took place in the primary material. Accretions of silica and phosphatic minerals, as has been proven by microscopic observations, occur as elongated lenses or veins (Text-figs 2H, I). Thus, it can be assumed that their crystallisation took place as a result of kaolinitisation of K feldspar and/or biotite, with simultaneous crystallisation of crandallite and gorceixite. As a result of the kaolinitisation of minerals containing K, kaolinite was formed, part of the silica crystallized as chalcedony, and K replaced Ba in gorceixite.

SUMMARY

Tonstein in the interburden in coal seam 405 (level 600 m) at "Sośnica-Makoszowy" coal mine, Makoszowy field, is characterized by the presence of kaolinite, mainly in tabular forms, pseudomorphs after feldspars or vermicular crystal aggregates, and by smaller amounts of quartz, most frequently in poniard-shaped forms of pyroclastic orgin. Biotite in the sample is kaolinitised in to different levels and often forms sheaf-shaped biotite-kaolinite aggregates. Sporadically feldspars have been found in the tonstein, mainly kaolinitised or sericitised. Locally russet pieces of partly devitrified volcanic glass with sharp edges or oval form have been found. The presence of siderite as microcrystal aggregates and of dolomite has been demonstrated and results probably from carbonisation. The accessory minerals apatite and zircon form single idiomorphic crystals. In addition to apatite, the presence of goyazite and probably gorceixite and crandallite has been demonstrated. The mineralogical characteristics of the tonstein show that it is a crystal tonstein, transforming into multi-component.

The main components of the tonstein are typical of the rock type; however, a distinctive feature is the occurrence of phosphatic minerals (goyazite, gorceixite, and crandallite), which have rarely been identified in tonsteins. Their presence has been demonstrated in a coal seam in the southern Sydney Basin of New South Wales (Loughnan and Ward 1970) and in the Grootegeluk Formation in the Waterberg Coalfield (South Africa) (Faure *et al.* 1996). The occurrence of minerals from the goyzite group has been mentioned also in some tonsteins from coal beds in Europe, South Africa, USA and Canada (Wilson *et al.* 1966; Triplehorn and Bohor 1986; Spears *et al.* 1988; Hill 1988).

The chemical composition of the sample differs significantly from tonsteins described earlier from the USCB. The high level of P_2O_5 (6.2 wt%) makes this tonstein similar to samples from coal seams 377 and 382 from Lublin Coal Basin (LCB). Also high is the amount of CaO (5.66 wt%). Such high concentrations of P_2O_5 and CaO also have not been noted in the literature. The reported concentrations of P_2O_5 most frequently range from a hundredth to a few tenth parts of a percent (Dai *et al.* 2011; Kramer *et al.* 2001; Faure *et al.* 1996; Grevenitz *et al.* 2003). In turn, the concentration of CaO most often amounts to a few tenths of a percent, sometimes slightly exceeding one percent. The study tonstein exhibits very high LOI, reaching 50.81 wt%. In the literature this value ranges mainly from a few to a dozen percent, sometimes reaching over 20%. Only in tonsteins from the Songzao coalfield in Chongqing, Southwest China, have similarly high LOI values been measured (Dai *et al.* 2011).

However, the amounts of Al_2O_3 and SiO_2 are lower than in typical USCB area tonsteins and in tonsteins worldwide. Also the low value of the molecular ratio SiO_2/Al_2O_3 may point to an advanced stage of kaolinitisation of the primary material (biotite, feldspars).

An indicator of changes occurring in the pyroclastic material at the site of coal formation is the ratio K_2O/Al_2O_3, which is related to the kaolinitisation of components containing K. The molecular ratios suggest a crystalline structure of the tonstein.

Among the trace elements, the highest concentrations are exhibited by Sr and Ba. Probably the main carriers of these elements in the tonstein are goyazite and gorceixite. Similarly high amounts of these elements have been found in two occurrences of tonsteins in (LCB). Increased concentrations of these elements have been also reported in tonsteins outside Poland; however they do not reach such high levels (Dai *et al.* 2011; Kramer *et al.* 2001; Faure *et al.* 1996; Grevenitz *et al.* 2003). High concentrations of Ce, Y, Nd, La, Th, Sc, Sm, Yb, Eu and Lu are related to phosphatic and also clay minerals.

The atypical chemical composition and abundances of trace elements imply that an unambiguous interpretation of the genesis of the tonstein is currently impossible. Although the mineral composition, including the presence of glass, may suggest that this could be an orthotonstein, small dispersion of the analysed tonstein points to a likely paratonstein origin. The TiO_2/Al_2O_3 ratio shows that the tonstein could be considered as alkaline (Spears and Kanaris-Sotriou 1979); however the high LOI value makes it more similar to coals rather than to tonsteins (Dai *et al.* 2011). Also the relatively low amount of alkalies (K_2O and Na_2O) distinguishes the tonstein from typical alkaline tonsteins.

In advantageous conditions additional samples should be collected from the interburden in the coal seam 405 at "Sośnica-Makoszowy" coal mine, Makoszowy field and from other locations in that seam. Research on a larger number of tonstein samples will allow us to determine whether the mineralogical and chemical compositions of the tonstein, unusual for the USCB, appear only locally or are relatively constant over the whole area of its occurrence.

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