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PIXE analysis of Kupferschiefer samples*

PIXE multielement analyses of Kupferschiefer samples have been performed. Thick target PIXE (TTPIXE) detection limits (MDLs) for different matrices are reported. The best MDLs were found in light matrices, i.e. in organic carbon (kerogen-thucholite) and black shale. The poorest results were obtained in sulphides. The adventage of using PIXE versus other methods relies on: (1) fast and non destructive determination of all elements starting from $Z = 18$ in the studied case; (2) relatively low detection limits, in the order of ppm.

INTRODUCTION

A growing need for precious metals has directed the attention of economic geology and geochemistry students towards black shales in general, and the Kupferschiefer in particular. Their enrichment in precious metals is well known, but it is not completely and precisely documented.

The average concentration of pay metals in black copper-bearing shale in Poland is (ppm): Hg 1–20, Ag 50–1000, Au 0.01–0.1 and Pt 0.01–0.2. However, locally, in places where black shale rests directly on the red sandstone the enrichment in noble metals due to autooxidation and desulphurization of organic matter is observed (H. Kucha, 1981, 1982, 1983). In such places the precious metal content may reach (W. Salamon, 1979): Hg 200–1500 ppm, Ag 2–1100 ppm, sometimes up to 5780 ppm, Au 5–200 ppm, exceptionally 3000 ppm, Bi 100–2000 ppm, Pt 10–370 ppm, Pd 10–120 ppm, sometimes up to 1000 ppm, 0.006–1.75 wt. % of Co, 0.060–0.400 wt. % of Ni and 0.026–0.480 wt. % of Mo. The above listed metals form either own minerals or are present as refractory admixtures in common minerals (H. Kucha, 1975, 1981, 1982, 1983). Routine microprobe analyses provide good results concerning the chemical composition of minerals and main trace elements. However, the detection limits of this method for sulphides are not better than a few hundred ppm, which is much higher than the concentration ranges of refractory precious metal admixtures in the studied sulphides and arsenides. Therefore, a successful study of refractory noble metals requires analytical techniques with a better detection limit than that of electron microprobe. There are several new analytical methods good detection limits in the order of single ppm: the proton microprobe (micro-PIXE), the synchrotron miniprobe (SXRF), the ion microprobe (SIMS) and accelerator mass spectrometry (AMS). It has been demonstrated that a combination of two methods, the electron microprobe and micro-PIXE, provides very good results concerning contents of main and trace elements in sulphide minerals (H. Blank, K. Traxel, 1984; L. J. Cabri *et al.*, 1984*a*, *b*; J. L. Campbell *et al.*, 1987; G. Remond *et al.*, 1987; L. J. Cabri, 1988). The use of micro-PIXE instead of microprobe improves the MDL of EPMA by a factor of about 3 in the case of Ga, Ge, Hg and by factor of about 10 to 30 for Se, Ag, Cd and In (G. Remond *et al.*, 1987). It seems that using synchrotron X-ray fluorescence (SXRF) it is possible to lower the MDL down to 0.8–3 ppm in the case of gold (J. R. Chen *et al.*, 1987). This method, however, does not eliminate some important inconveniences common to all methods based on X-ray fluorescence detection by semiconductor detectors, such as peak overlaps of different elements. This is not the case when the ion microprobe SIMS is used. The use of ion implantation to produce standards closely matching the composition of analysed samples allows us to achieve detection limits not available with other methods, e.g. it allows us to analyse the concentration of gold in sulphides starting from 0.5 ppm of Au (S. L. Chryssoulis *et al.*, 1987). Even more promising results have been obtained with accelerator mass spectroscopy (AMS). This method eliminates molecular interferences that strongly affect SIMS analyses, but the method is still at the experimental stage (J. C. Rucklidge *et al.*, 1982; J. C. Rucklidge, L. R. Kilius, 1986).

Based on our experience of analysis of multielement geological samples by PIXE (W. Przybyłowicz *et al.*, 1986) we decided to analyse the Kupferschiefer samples on the PIXE assembly in Cracow without having access to the proton microbeam. Hence we regard the obtained results as complementary to those obtained with the use of ICP and atomic absorption and also with EPMA. Another aim of the study was to establish the detection limits it is possible to obtain for the samples and to test the experimental conditions (like the thickness of the absorbing Al filters needed to minimize pile-up of the matrix K X-ray signals) that should be applied in future analyses with the proton microprobe.

EXPERIMENTAL

The PIXE analyses were carried out in the Laboratory of Applied Nuclear Spectroscopy, Institute of Nuclear Physics in Cracow. Polished sections of samples previously measured with EPMA were used. For a more detailed description of the target chamber see S. Szymczyk *et al.* (1981). Small cyclotron C-48 was used as the source of protons. The proton energy was ca. 2.6 MeV and the beam intensity was up to 5 μA. The beam diameter on the target was about 3 mm. The X-rays emitted by the target were detected by an ORTEC Si (Li) semiconductor detector, 5.4 mm thick, of 30 mm^2 effective area and with a resolution of ca. 200 eV (at 5.9 keV $Mn_{K\alpha}$). The target-detector distance was aprox. 25 mm. CAMAC electronics and a CIA-70 multichannel analyzer (with an IBM personal computer for on-line processing of the results) were used. The beam intensity was monitored by counting the protons scattered from the aluminium foil placed across the beam path, with a ring-shaped silicon surface-barrier detector. The measurements were normalized to an equal number of scattered protons. Final processing of the spectra involving the least-squares fitting of individual peak areas to Gaussian functions was carried out on an IBM-XT/AT personal computer. To determine the peak areas in the spectrum and to calculate the concentration of the elements a package of specially developed programs was used (J. Kajfosz, 1987). The background of PIXE spectra was estimated by nonpolynomial approximation (J. Kajfosz, W. M. Kwiatek, 1987).

To prevent backscattered protons from entering the detector and to minimize pile-up from low energy X-rays, aluminum absorbers were placed between the target and the detector. 11 mg/cm^2 and sometimes 22 mg/cm^2 thick aluminum foils (ca. 80 and 160 µm respectively) were needed to attenuate matrix K X-ray signals (mainly Fe and Cu in the higher energy region). With these absorbers the elements with atomic numbers higher than 26 can be determined in one run. The detector was shielded with 2.75 mg/cm^2 (ca. 10 µm) thick Al-foil when searching for elements in the K to Fe range ($19 < Z < 26$).

The concentration of the elements was calculated using two multielement standards made by the International Atomic Energy Agency SOIL-5 (R. Dybczyński *et al.*, 1978) and SOIL-7 (L. Pszonicki *et al.*, 1984). To check the validity of quantitative results two other multielement standards were analyzed: limestone KH and greisen GnA, made by Zentrales Geologisches Institut, Berlin, formerly GDR. It has been shown before (e.g. R. D. Willis *et al.*, 1977; S. A. E. Johansson, T. B. Johansson, 1976) that thick targets can be successfully used in quantitative trace element analysis. A high homogeneity of the target is required, otherwise the analyses of small parts of the target may be unrepresentative for the whole sample. In quantitative analysis of powdered targets the comparative method is commonly used. It is based on simultaneous excitation of standard and sample. It should be stressed that it is always highly recommended to use standards of chemical composition as close as possible to the analysed targets, e.g. synthetic having the same matrix (the composition of the main elements, J. L. Campbell *et al.*, 1987). In this study polished sections were used. The proton beam was always positioned on larger, homogenous areas. Under these conditions geological samples can be successfully measured with powdered standards as shown by a study of geological samples (P. J. Clark *et al.*, 1975).

RESULTS

BLACK SHALES

Ten samples of noble metal- and thucholite-bearing shale were analyzed. In the analyzed shales the proton beam was focused on the areas free of microscopically visible thucholite and opaque minerals. A typical PIXE spectrum is shown in Figure 1. The shales are characterized by a high U, Pb, Mo, As, Cu, Ni, Co, Fe, Ti and V content (Tab. 1, 2), present in the clay organic matrix. Up to 0.3 wt. % of Cu can be present in the clay-organic matrix (H. Kucha, 1985), but higher values (Tab. 1) are referred to small covellite specs. As, Co and minor Ni are presumably dispersed as submicroscopic di-arsenides and sulphoarsenides. V and part of the Ni are present as porphyrines (H. Kucha, 1985). No iron sulphides

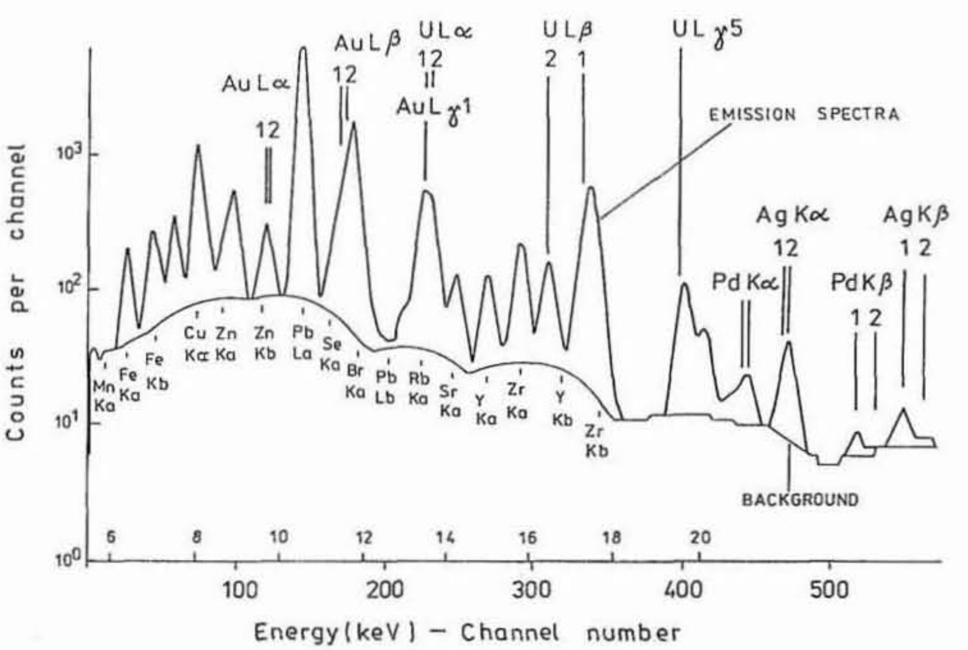

Fig. 1. A typical PIXE spectrum of a matrix of noble metals bearing shale; the matrix is free of thucholite and sulphide grains; sample 60

Typowe PIXE spektrum dla łupku zawierającego metale szlachetne; matryca uwolniona od thucholitu i siarczków; próbka 60

were observed and therefore Fe is assumed to be present in the clay-organic matrix in illite as well as Fe-organic compounds. The Ti content is unusually high and can be only partly explained by detrital TiO_2 polymorphs observed in the samples. It suggests that part of the Ti may be present in the structure of clay minerals.

Despite high Pb values (Tab. 1), no lead minerals were observed. The studied shales contain an increased concentration of Au and Pd (Tab. 1). Detectable amounts of Pt were also found in places. Analyzed shales also show significant amounts of Zr, Y, Rb, Se and Br. By EPMA other rare-earth elements were also found.

PIXE analysis (Fig. 1, Tab. 1) suggests that an increased concentration of Au and PGMs in the bottom part of black shale is related to an increased U content. This relationship marked by γ radiation has been proposed as a tracer for increased concentrations of noble metals in the Kupferschiefer (H. Kucha, 1982).

PIXE allows us to analyse black shale starting from ppm level (Tab. 3, 4) for most elements.

Table 1

Concentrations of minor and trace elements (ppm) in Kupferschiefer samples; for different matrices the minimum, maximum and mean volues are reported

Deposits	Fe	Co	Ni	Cu	As	Se	Y	Zr	Nb	Mo	Pd	Ag	Au	Pb	U
Black shales	2200*	380	90	2000	50	6.3	36	90	<12	38	<20	90	<40	80****	–
	32900**	2000	1400	51300	4900	30	340	240	<50	1080	70	2500	700	6700	3000
	14900***	1000	600	19400	1400	16	90	170	–	340	20	560	140	1300	800
Thucholites	3940	–	<14	650	11	<5	27	–	–	–	–	–	–	<130	100
	28700	600	900	97000	580	47	540	190	–	170	160	100	800	6400	38000
	10400	–	–	18300	300	22	140	40	–	–	–	–	–	1400	19600
Carbonate	5600	–	–	270	6	–	38	<6	–	15.4	–	–	–	65	–
Sulphide + carbonate	3450	730	120	2400	1200	–	70	–	–	33	–	270	–	15000	–
	12.6[%]	9100	1600	17500	12800	<20	320	<30	<130	3900	–	14500	–	89200	–
	35300	3600	630	10800	5100	–	160	–	–	1000	–	4500	–	41200	–
Thucholite + carbonate	3300	–	8	300	50	–	19	<14	<8	39	–		–	–	–
	4800	<400	430	54000	600	9.3	40	90	50	100	30	81	<13	90	6200
	4200	–	220	22900	280	–	29	38	17	67	–	26	–	–	2900
Sulphide	27300	22700	8300	32000	63000	80	<50	–	300	66000	–	1500	–	2600	–
Sandstone + sulphide	2660	190	20	1800	130****	–	–	<28	–	–	–	550	–	11900	–
	21800	2440	250	2800	3300	–	40	83	60	94	90	9140	–	26000	–
	9700	880	90	2140	1300	–	–	30	–	45	–	3800	–	17300	–
Phosphate	11.0[%]	–	–	16600	<55	2040	600	64	–	50	70	70	–	8400	–

* —minimum value, ** — maximum value, *** — mean value, **** — estimated value due to the large error of measurement

Table 2

Concentrations of minor and trace elements (ppm) in Kupferschiefer samples; for different matrices the minimum, maximum and mean values are reported

Deposits	Mn	V	Ti	Br	Rb	Sr	Bi	Zn	Cd
Black shales	360* 660** 490***	2450 5700 4000	4400 29300 13800	< 30 70 24	33 250 150	30 80 46	– – –	60 540 240	– 23 7
Thucholites	190 6150 3400	120 460 180	< 120 5900 1500	– 38 10	– 250 50	– 113 70	– 330 140	– 1500 550	– 26 –
Carbonate	6650	< 120	< 220	4.3	10	73	–	290	–
Sulphide + carbonate	n. a. n. a. n. a.	n. a n. a. n. a.	n. a n. a. n. a.	120 490 240	< 18 25 –	– 57 29	– < 320 –	< 18 120 30	– 220 80
Thucholite + carbonate	1790 5200 3700	< 90 420 160	180 1500 460	9.3 25 14	– 21 –	50 104 80	– < 50 –	20 300 100	– – –
Sulphide	n. a.	n. a.	n. a.	500	–	130	< 1000	230	–
Sandstone + sulphide	– 400 –	– < 280 –	– 1600 –	– 90 50	30 38 35	– 46 15	– – –	370 6300 3500	– 250 80
Phosphate	n. a.	n. a.	n. a.	–	–	540	–	–	–

n. a. — not analyzed; explanations as in Tab. 1

THUCHOLITE

Thucholite is polymerized and partly graphitized organic matter rich in U, Th and other metals. It is composed of two components:

I — anisotropic, highly reflectant component made up parallel domains of normal graphite and of graphite with Van der Waals thickness of the ring;

II — isotropic, low reflectant component which is not crystalline as indicated by electron diffraction study (H. Kucha, 1982).

EPMA study suggests that the isotropic, amorphous component has a higher concentration of metals than the anisotropic one. The size of the two thucholite components is about 100–300 μm, therefore PIXE with beam diameter of 3 mm could not resolve the two components and the reported concentrations of elements should be regarded as average values (Tab. 1, 2). The size of thucholite grains is 3–8 mm in diameter. Fifteen thucholite grains were studied.

Thucholite is rich in U, Cu, Pb and Fe (Tab. 1, 2). Microscope study indicates the presence of UO_2 and traces of Cu-Bi sulphides. No Fe, Pb or Ti minerals were found. According to EPMA study a significant amount of U is also present in the matrix of the

Table 3

Dedection limits for minor and trace elements (ppm) in Kupferschiefer samples; minimum and maximum values are reported

Deposits	Fe	Co	Ni	Cu	As	Se	Y	Zr	Nb	Mo	Pd	Ag	Au	Pb	U
Black shales	32* 3300**	28 1300	12 350	8.5 160	4 115	4 30	9 75	9 60	11 50	14 48	20 45	14 65	20 70	60 420	90 200
Thucholites	45 1800	– 500	14 160	10 80	10 28	5 14	7.5 34	15 36	– –	8 30	12 37	18 35	30 –	30 130	50 210
Carbonate	54	–	–	6	4	–	5	6	–	6	–	–	–	15	–
Sulphide + carbonate	53 270	47 460	21 160	14 85	60 270	– 20	50 240	– 30	– 130	24 150	– –	60 300	– –	140 880	– –
Thucholite + carbonate	38 1200	40 400	7 120	5 63	3 15	– 6	4.5 19	9 26	8 23	8 50	– 28	– 12	13 30	18 180	35 140
Sulphide	260 3900	230 1200	170 450	100 220	60 –	55 70	50 130	60 –	70 210	80 250	– –	130 480	– –	– 1700	– –
Sandstone + sulphide	45 50	36 90	18 30	12 18	45 66	– –	38 44	15 30	– 37	18 48	– 70	36 90	– –	50 200	– –
Phosphate	115	–	–	28	55	23	56	47	–	48	60	70	–	80	–

Eksplanations as in Tab. 1

Table 4

Dedection limits for minor and trace elements (ppm) in Kupferschiefer samples; minimum and maximum values are reported

Deposits	Mn	V	Ti	Br	Rb	Sr	Bi	Zn	Cd
Black shales	55* 120**	130 320	190 380	9 40	8 40	6 47	– –	10 310	15 19
Thucholites	40 180	70 230	120 360	6 14	25 40	5.5 14	50 90	10 170	– 21
Carbonate	50	120	220	3.5	4	4	–	5.7	–
Sulphide + carbonate	n. a n. a	n. a n. a	n. a n. a	20 120	18 80	16 25	– 320	18 44	70 340
Thucholite + carbonate	30 50	90 140	160 260	3 20	6 40	4 17	– 50	5 106	– –
Sulphide	n. a n. a	n. a n. a	n. a n. a	170 200	– –	36 100	– 1000	113 180	– –
Sandstone + sulphide	– 60	– 280	– 180	14 27	14 21	12 –	– –	14 18	– 80
Phosphate	n. a	n.a	n. a	–	–	40	–	–	–

n. a. — not analyzed; explanations as in Tab. 1

isotropic, amorphous thucholite component (H. Kucha, 1982). No Th was detected in the studied thucholite. An increased concentration of Au and Pd is of particular interests (Tab. 1, Fig. 2). Occasionally (in ppm) 130 Pt, 110 Ir, 14–70 Rh and 60 Ru were detected.

The average V and Mo concentration in thucholite is significantly lower than in the shale (Tab. 1, 2). An increased content of Y and Zr correlates with U (Tab. 1, 2).

Comparing concentration of metals in the clay organic matrix of the shale, which may be considered as a source of metals for thucholite, with the concentration of metals in thucholite an enrichment in U, Au, PGMs, Y and Bi observed (Tab. 1, 2). In a similar way a depletion in Zr, As, V and Ti is found in thucholite versus black shale matrix. This type of pattern may speak in favour of autooxidation of organic matter catalyzed by PGMs, Au and γ radiation of U as a mechanism of concentration of U, PGMs and Au in thucholite (H. Kucha, 1982).

MDLs in thucholite are generally better than in black shale matrix (Tab. 3, 4).

The Witwatersrand thucholite studied for comparison shows generally: more Fe, mainly due to dispersed pyrite, less Cu (1000–2300 ppm), less As (120–180 ppm), more Y (500–590 ppm), a similar Zr, Pb and U content. PGMs in Witwatersrand thucholite are below 15 ppm. Witwatersrand thucholite contains 700–1400 ppm Th while Kupferschiefer thucholite has a Th content below detection limit.

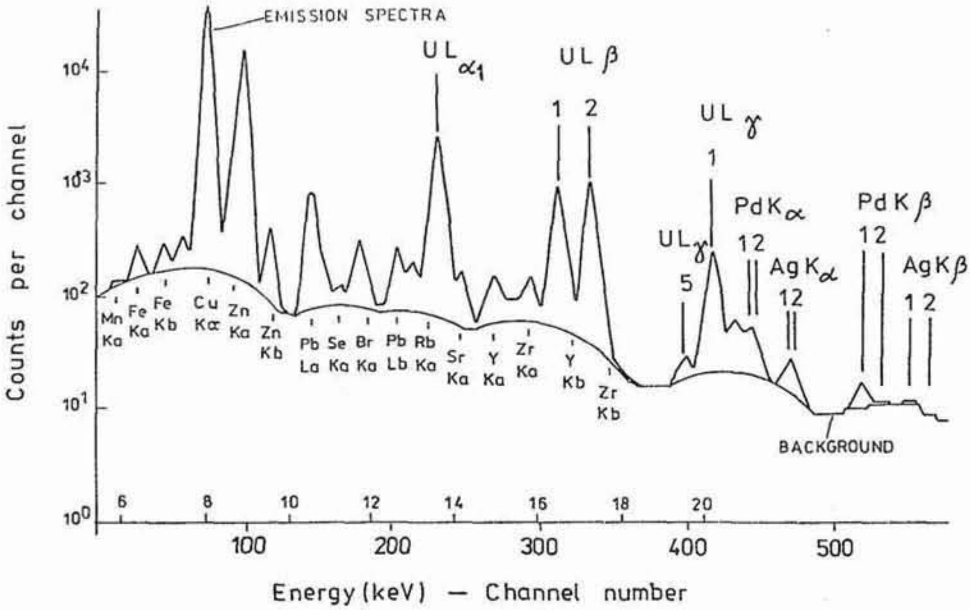

Fig. 2. A typical PIXE spectrum of a matrix of thucholite free of sulphide grains; sample 45C
Typowe PIXE spektrum dla thucholitu uwolnionego od siarczków; próbka 45C

CARBONATES

Carbonates frequently contain small but abundant sulphide grains. Carbonates also replace thucholite with resultant exolution of native gold, PbSe, Cu-Bi sulphides and Pd-arsenides (H. Kucha, 1981, 1982). For the above reasons the metal concentration was measured in the clean carbonate matrix. Only Mn, Fe and minor Zn, Cu, Pb and Sr were found to be present (Tab. 1, 2).

SULPHIDES IN CARBONATE MATRIX

The composition of six carbonate samples containing sulphide mineralization depends on the major mineral: pyrite, Ag-bearing chalcopyrite, galena and native silver. As, Ni and Co are bound to pyrite. Mo concentration is high and related to castaingite. Br content is high but no Br-bearing mineral was detected by optical or EPMA methods. Because a mixture of carbonate and sulphides forms a heavier matrix than organic or clay-organic matrix MDLs are in the order of several tens of ppm (Tab. 3, 4).

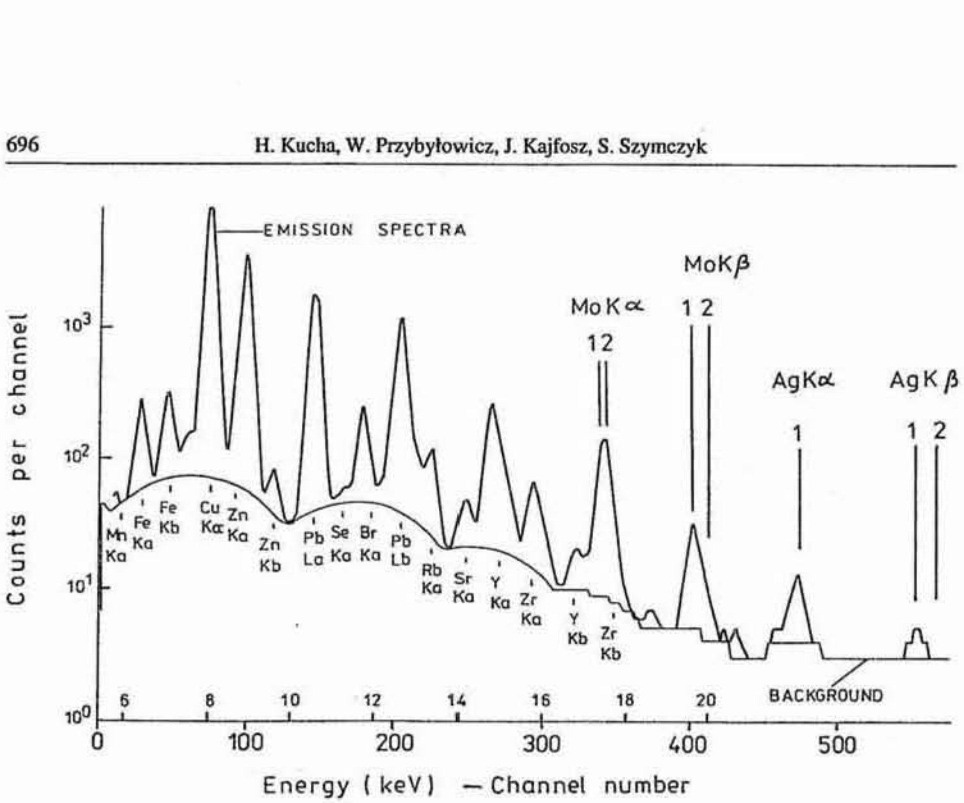

Fig. 3. A typical PIXE spectrum of sulphides composed of castaingite and Ag-bearing chalcopyrite; sample 110
Typowe PIXE spektrum dla siarczków złożonych z castaingitu i srebronośnego chalkopirytu; próbka 110

THUCHOLITE-CARBONATE

Thucholite replaced by carbonates is of particular interest, because during this process native Au and PGM minerals are produced (H. Kucha, 1982). To study the redistribution of elements during thucholite oxidation (replacement by calcite) nine thucholites replaced by calcite were studied. U, Pb, Ti and Fe show distinct depletion in this process (Tab. 1). Cu concentration increases which may indicate an external source of this metal (oxidized solutions from Rote Fäule?).

Pd and Au do not change in concentration compared to original thucholite. These two metals are enclosed as native gold, native Pd and Pd-arsenides into the matrix of replacive carbonate. Pt was always below the detection limit in analyzed thucholite-carbonate mixtures produced by replacement (oxidation) of the former by the latter.

Results obtained by PIXE are consistent with results obtained before by EPMA (H. Kucha, 1982). MDLs found in thucholite-carbonate are generally similar to those found in thucholite itself (Tab. 3, 4).

SULPHIDES

An example of sulphide (Fig. 3) is represented by castaingite rich in As (Tab. 1, 2). It also contains a high amount of Co, Ni, Ag and Pb. A high Br content may be referred to

KCl inclusions present in this castaingite. Re content is high — 1300 ppm. Also several to a hundred ppm of W are present. PIXE also indicates 80 ppm of Se which was not detected by EPMA.

SULPHIDES IN SANDSTONE

Six samples of sandstone mineralized with galena, chalcopyrite, sphalerite and silver amalgams were studied (Tab. 1, 2). Major elements conform with the above listed minerals. 90 ppm Ni and 40 ppm Mo, not detected by EPMA are indicated (Tab. 1, 2). The average Hg content is 320 ppm.

MDLs for these type of samples are listed in Table 3 and 4.

PHOSPHATE

Fe-Ca phosphate was studied by PIXE for REE and PGM traces because EPMA study revealed inclusions of clausthalite, native gold and mooihoekite. PIXE indicates 70 ppm Pd, 600 ppm Y, 700 ppm Ce (Tab. 1, 2). La is also present.

CONCLUSIONS

A PIXE test performed on Kupferschiefer samples revealed several elements not expected in this type of matrix. It indicated Ti, Zr and REE in uranium — rich organic matter. Also a significant amount of Br was found in organic matter. The presence of Au and PGMs related to thucholite has been confirmed.

MDLs of PIXE depend on the matrix. In light matrix they are in the order of ppm, in heavy matrix in the order of tens of ppm. MDLs also depend on the element composition of the target. In the case of peak coincidences or proximity of a major disturbing peak the MDL may even be in the order of 200–300 ppm. However, in the studied samples under the applied analytical conditions the MDLs depended first of all on emission efficiency, being best for elements of $Z = 22$ to 47, where K_α lines of high efficiency can be used.

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BADANIA CECHSZTYŃSKICH ŁUPKÓW MIEDZIONOŚNYCH METODĄ PIXE

Streszczenie

Opisano wyniki badań metodą PIXE próbek z cechsztyńskich łupków miedzionośnych. Mierzono zarówno zawartość pierwiastków, jak też poziomy ich wykrywalności w preparatach polerowanych (*thick target*). Najlepsze wykrywalności uzyskano w próbkach o lekkiej matrycy, tj. w węglu organicznym (kerogen-thucholit) oraz w ilasto-organicznej matrycy łupku czarnego. Najniższe poziomy wykrywalności zaobserwowano w siarczkach metali ciężkich.

Zaletą metody PIXE w stosunku do innych metod analitycznych jest:

— szybka i nieniszcząca analiza wszystkich pierwiastków począwszy od $Z = 18$ w badanych preparatach;

— relatywnie niskie poziomy wykrywalności w granicach od kilku do kilkudziesięciu ppm.