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Geochemistry of the Kupferschiefer, Poland

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With 11 figures and 4 tables

Zusammenfassung

Die häufigsten Metalle, die in den Sulfiden des Kupferschiefers vorkommen, sind Kupfer, Blei und Zink. Diese Metalle sind in der Reihenfolge Cu-Pb-Zn an drei bestimmte Zonen um die »Rote Fäule« gebunden.

Die Kupfer-führenden Zonen sind reich an Übergangsmetallen wie Ag, Ni, Co, V und Mo, deren Konzentrationen zwischen 600 und 1500 ppm schwanken und die hauptsächlich in bodennahen Bereichen des Schwarzschiefers angereichert sind. Dabei tritt Re in Verbindung mit Mo auf und das Re-Mo Verhältnis in Cu-, Pb- und K-Castaingiten ist ungefähr 1:70.

Gold, Platin-Gruppen-Metalle (PGM) und Uran, deren Konzentrationen zwischen geringen Spuren und mehreren 100 ppm liegen, findet man in Kupfer-führenden Schichten in der Nähe von Kontakten zu Blei-führenden Zonen. Katalytische Autooxidation und Dehydrogenisierung organischen Materials sind die dominierenden Mechanismen, die die Anreicherung der Übergangsmetalle steuern. Die Metalle liegen als Minerale oder gebunden an organische Substanz und Thucholit vor.

In den Kontaktbereichen der Blei- und Kupferzonen findet man erhöhte Werte von Ag (100–1500 ppm) und Hg (5–800 ppm). Der Durchschnittswert für Hg im Schwarzschiefer beträgt 61 ppm.

Ein natürliches Gas, das aus dem den Kupferschiefer unterlagernden Rotliegenden gefördert wird, enthält als Aerosole bedeutende Mengen an Pb, Cu, Mn, Fe, Ag und Hg. Somit ist es wahrscheinlich, daß das Rotliegende entweder als Quelle der Metalle des Kupferschiefers oder zumindest als Durchgangsstation der Metallführenden Lösungen anzusehen ist. Das Vorkommen von K-Castaingit-Verwachsungen mit Silvinit (KCI) spricht für K-reiche Solen als mineralisierende Lösungen.

Abstract

Cu, Pb and Zn are the main metals occurring in sulfides in the Kupferschiefer. They are arranged in the three distinct zones around »Rote Fäule«, in the order Cu, Pb and Zn.

Copper zones are enriched in transition metals, i.e. Ag, Ni, Co, V and Mo ranging from 600 to 1500 ppm; they are concentrated especially in the bottom part of black shale. Re is associated with Mo; the Re: Mo ratio in Cu-, Pb- and K-castaingites is about 1:70.

In copper zones, near the contact with lead zones, Au, platinum group metals (PGM) and U are concentrated, ranging from traces to several hundred ppm. The main mechanism of concentration of transition metals was catalytic autooxidation and dehydrogenation of organic matter. The noble metals form either independent minerals or are present in organic matter and thucholite.

In the lead zones, at the contact with Cu zones, an increased content of Ag (100–1500) and Hg (5–800) ppm is present. The average Hg content for the black shale of the zone is 61 ppm.

A natural gas, exploited from the Rotliegendes beneath the Kupferschiefer, carries, in aerosols, significant amount of Pb, Cu, Mn, Fe, Ag and Hg. This suggests the Rotliegendes as a pathway or as a source of metals for the Kupferschiefer. The presence of K-castaingite intergrown with silvinite (KCl) may suggest K-dominated brines as the mineralizing fluids.

Résumé

Le Cu, le Pb et le Zn sont les métaux principaux des sulfures de la formation des Kupferschiefer. Ils sont distribués autour de la «Rote Fäule» en trois zones distinctes, dans l'ordre: Cu – Pb – Zn.

Les zones à Cu sont enrichies en métaux de transition (Ni, Co, V et Mo) qui y présentent des teneurs de 600 à 1500 ppm; ces métaux sont concentrés spécialement dans les parties inférieures des schistes noirs. Le Re est associé au Mo, avec un rapport Re/Mo de l'ordre de 1,70 dans les castaingites à Cu, Pb et K.

Dans les zones à Cu, près du contact avec les zones à Pb, on observe une concentration de Au, de U et des métaux du groupe du Pt, avec des teneurs qui vont des traces à quelques centaines de ppm. Le mécanisme principal de la concentration des métaux de transition a été l'auto-oxydation et la déshydrogénation catalytiques de la matière organique. Les métaux nobles sont sous la forme de minéraux indépendants, ou sont contenus dans la matière organique et la tucholite.

Dans les zones à Pb, il existe une concentration en Ag (100–1500 ppm) et en Hg (5–800 ppm) au contact avec les

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zones à Cu. La teneur moyenne en Hg des schistes noirs est de 61 ppm.

Un gaz naturel, exploité à partir des Rotliegende situés sous les Kupferschiefer, renferme, sous forme d'aérosols, des quantités appréciables de Pb, Cu, Mn, Fe, Ag et Hg. Les Rotliegende pourraient donc être soit la source, soit le chenal des métaux contenus dans les Kupferschiefer. La présence d'intercroissances de castaingite potassique et de sylvinite (KCl) suggère que les fluides minéralisants ont pu être des solutions potassiques.

Краткое содержание

В сульфидах сланцевых медных месторождений наиболее часто встречаются медь, свинец и цинк. Эти элементы раслолагаются в том же порядке в трех известных зонах вокруг «Rote Fäule».

Зоны, вмещающие медь, обогачены переходными элементами, как напр.: Ag, Ni, Co, V и Mo, концентрация которых колеблется между 600 и 1500 ppm; они особенно обильны в черном сланце в регионах близких к подошве. При этом Re появляется связанным с молибденом, а соотношение Re/Mo в медных, свинцовых и калиевых кастэйнгитах составляет примерно 1:70.

Золото, металлы группы платины и уран, концентрации которых колеблются от следов до нескольких сот ppm, находят в слоях, вмещающих медь вблизи контактов с зоной, вмещаюей свинец. Каталитическое автоокисление и дегидрогенизация органического материала являются главными механизмами накопления элементов переходной группы. Они находятся в виде минералов, или связаны с органическими веществами и тухолитами.

Контакт зон свинца и меди имеет повышенные содержания серебра (100–1500 ppm) и Hg (5–800 ppm). В среднем в черном сланце содержание ртути составляет 61 ppm.

Природный газ, выделяющийся из красного лежня, подстилающего медь содержащий сланец, содержит аэрозоли со значительными количествами свинца, меди железа, серебра и ртути. Кажется вероятным, что красный лежень является или основным источником элементов, найденных в меднорудном сланце, или, по-крайней мере, играет роль «пересадочной станции» для растворов, несущих металлы. Месторождения калиевого кастэйнгита и его сращения с сильвинитом KCl говорят о том, что богатые калием золи являлись минерализующими растворами.

Introduction

Mining operations at four mines Lubin, Polkowice, Rudna and Sieroszowice (Fig. 1) produce per annum about 300 000 T Cu, 12 000 T Pb, 700–800 T Ag, 280 T Ni and 0.2–0.3 T Au. Some platinum and palladium are also recovered. The recovery of noble metals does not exceed 20–25%. Quantities of V, Mo and Co in the ore are similar to those of silver but none of these metals is produced.

Materials and methods of investigation

This study is based on about 3000 polished samples from Kupferschiefer exposed in mines Lubin, Polkowice, Rudna and Sieroszowice.

A lateral distribution of metals (Fig. 1) is based on channel samples analysed by Geological Survey of the mines.

Channel samples for Cu are collected in a regular 15 x 15 m network. The individual sample length is 10 cm. Based on this an average for sandstone, black shale and dark dolomite were calculated. The Cu concentration is analysed by synchrotron radiation with photons of 15 MeV energy. The appropriate nuclear reaction affects $_{63}$Cu:

$$_{63}\mathrm{Cu}(\gamma, n) \longrightarrow {}_{62}\mathrm{Cu} \xrightarrow[9.8\ \mathrm{min}]{\beta +} {}_{62}\mathrm{Ni}$$

This reaction permits an automatic measurement of Cu starting from 0.001 wt.% with accuracy ± 2% of measured value.

Channel samples for Ag, Pb and Zn are collected in a regular network 45 x 45 m and analysed with atomic absorption spectrometry (AAS).

Channel samples for other elements are collected in a regular 150 x 150 m network and analysed either by AAS or induced coupled plasma spectrometry (ICP »Baird«).

Samples from noble metals bearing shale were analysed with AAS. In order to provide sufficient detection limits 10 g samples were used. Pulverized samples were decomposed in a boiling mixture composed of 3 parts of perchloric acid and 1 part of nitric acid. In order to trap volatile elements (Hg) and volatile organic compounds carrying some of analysed metals a decomposition of samples was done in a test tube supplied with a cooling outlet system. Trapped volatile organic compounds were reintroduced into the test tube. Main metals found in the trapped volatile organic substance were As, Cu and Se but some Pt, Bi, Hg and probably traces of Au were also detected. A complete sample decomposition required 24–48 hours depending on the organic matter content in the sample. The following spectral lines were used (nm): Ag 328.1, Au 242.8, Pd 247.6 and Pt 265.9.

Electron microprobe analyses were made at conditions described in KUCHA (1982).

PIXE analyses were carried out at the Institute of Nuclear Physics in Cracov, using samples tested before by electron microprobe. The proton energy was about

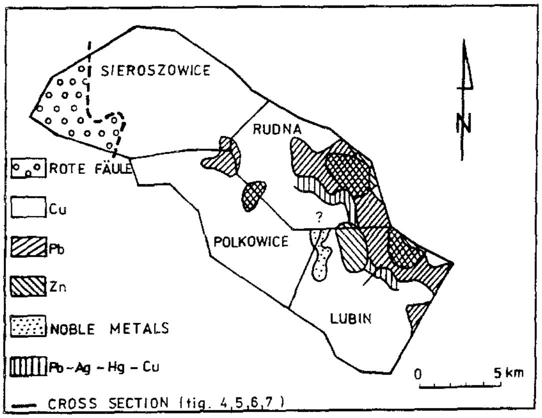

Fig. 1. A distribution of mineralization in the area of the four mines under operation. Noble metals bearing shale is defined as a few mm thick bottom part of the black shale where Au content exceeds 1 ppm.

2.6 MeV and the beam intensity about 5 uA. The beam diameter on the target was about 3–4 mm which allowed focusing on a selected area of polished sample. The X-ray spectrum was recorded by ORTEC Si (Li) semiconductor detector with a resolution about 200 eV.

Micro-PIXE analyses were made with the Heidelberg proton microprobe using the following conditions: proton energy 3 MeV, 195 μm thick external Al absorber and beam spot size about 3 x 3 μm (PRZYBYŁOWICZ et al., 1989).

Sulfur valence was measured by ARL SEMQ probe at 20 kV in the Institute of Mineralogy and Petrology, Mining University, Leoben, Austria. In order to determine the S valence the PET spectrometer was calibrated using technique developed in the former study (KUCHA et al., 1989).

Stratigraphy

The Precambrian and Lower Paleozoic strata of the Fore-Sudetic monocline constitute the crystalline basement composed of the 3 main rock types: 1) weakly metamorphosed sandstones, arkoses, and shales, 2) strongly metamorphosed schists with sericite, chlorite, biotite, vermiculite, garnet and quartz; gneisses, granitoids, granites; and 3) effusive rhyolites, dacites, diabases, trachytes, rhyodacites, basalts, mugearites, hawaiites and tephrites (SIEMASZKO, 1978). In the western part of the Fore-Sudetic monocline lamprophyres are common. The rocks discussed have been subjected to secondary alteration: albitization, chloritization, silicification, carbonatization, haematitization, zeolitization and serpentinization (HEFLIK & KRZYCZKOWSKA, 1975; SIEMASZKO, 1978).

The Rotliegende rests discordantly on the crystalline basement. At the base it comprise eruptive rocks and pass gradually from the basal conglomerates through red-brown sandstones and melaphyre-porphyry conglomerates to white sandstones at the top. Horizontal permeabilities in the Rotliegendes are 1–2 orders of magnitude higher than the vertical ones (KUCHA & PAWLIKOWSKI, 1986).

The Zechstein sediments start with a 0–0.25 m thick white sandstone and pass through different types of shales (Table 1) and carbonate beds to the salt deposits. The Zechstein evaporites dip 3–6° to the NE at the Fore-Sudetic monocline. Further to the north, the dip increases and the salt bearing Zechstein reaches a depth of more than 6 km in the central part of the basin (POBORSKI, 1975). The salt bearing formations attain a thickness of several hundred meters at the peripheral areas and up to 1500 m in the central parts (OSIKA & POBORSKI, 1970). The evaporites are intensely deformed forming over 50 salt domes and pillows. The Zechstein is overlain by the Bunter Sandstone of the Lower Triassic, rock salts of Keuper and by thick Tertiary and Quaternary deposits.

Mineralized Lithologies

The main mineralized lithologies in the mining area (Fig. 1) are: white sandstone, black shale and dark dolomite.

The main detrital minerals of the white sandstone are quartz ca. 90%, feldspars ca. 8% and pieces of igneous and metamorphic rocks ca. 2%. The sandstone is cemented by: i) sulfides and carbonates in its top part, ii) illite and minor kaolinite, iii) anhydrite and gypsum and iv) locally by apatite and β-boracite. The top part of the sandstone may be often developed as an almost pure, massive chalcocite with phantoms of detrital grains. A replacement of quartz grains was suggested as a reason for such massive chalcocite layers at the 10–20 cm top of the white sandstone (BANAŚ et al., 1982). However, most of these »quartz« grains when studied by microprobe appeared to be cleavage-free Cu-bearing feldspars (KUCHA, 1985). This, in turn, suggests that in places the top part of the white sandstone was developed as a feldspatic sandstone before its replacement by massive chalcocite at a later stage. Such replacement affected feldspars causing their transformation into illite, and excess SiO_2 was precipitated as overgrown quartz (KUCHA, 1985). The idiomorphic quartz often contains a detrital core that is coated by Fe-oxides.

Heavy metal-bearing feldspars have been found only in the mineralized upper part of the white sandstone. Feldspars from the non-mineralized white sandstone are base metal-free, and feldspars from the Rotliegendes contain only up to 2.5 wt.% of Fe.

The 0 and 1 m thick black shale either directly overlies white sandstone or is separated from it by a dolomite bed 0 to 20 cm thick. The shale is locally absent and an organogenic limestone (dolomite) occurs in its stead. The main minerals of the black shale are illite, glauconite, carbonates, detrial and secondary overgrown quartz, phengite and 0.3 to 30 wt.% of organic matter (Table 1). Gpysum is seen on bedding planes of the shale as small flat rosettes. Phosphates and detrital feldspars are also important constituents of the shale.

A spatial distribution of the shale was controlled by paleorelief, off-shore deep shelf is represented by black shale 0.3–0.5 m in thickness, shallow shelf environment deposited red shales (with red stains) 0 to 0.6 m in thickness. The near shore environment introduced gray shales 0.4–1.0 m thick (OSZCZEPALSKI, 1986).

The shale is usually referred to as copper-, lead-, zinc-, noble metal-, thucholite-bearing or glauconitic according to the dominant mineral (Table 1).

The black shale passes transitionally into dark dolomite coloured by 0.5–4 wt.% of organic matter. The dolomite may be a few meters in thickness. The bottom 1–2.5 m of dolomite contains 1–4 wt.% Cu, 0.5–5 wt.% Pb and 0.9–8 wt.% Zn in the Cu-, Pb- and Zn-bearing areas respectively. Often the dark dolomite is rich in gypsum and anhydrite with corresponding decrease in the organic matter content.

The mineralization

Economic grade Cu-ore is present in white sandstone – ca. 50% of the Cu reserves, in black shale – ca. 20% of the Cu reserves, and in dark dolomite – ca. 30% of the Cu reserves. The average thickness of the mineralized horizon is about 4 m. The lateral zoning patterns are oriented radially outwards from the Rote Fäule in the following order: haematite-chalcocite-bornite-chalcopyrite-galena-sphalerite (RYDZEWSKI, 1976). Zoning patterns studied in more detail in the mining area (Fig. 1) show that a lateral separation of Cu, Pb and Zn is never so perfect. Zn and Pb often overlap and in Pb-zones although PbS dominates as a mineral, where it is always associated with a significant amount of chalcopyrite.

The vertical zonation from the bottom upwards is: barren haematite-dispersed pyrite with minor chalcopyrite-copper sulfides-galena and chalcopyrite-sphalerite and pyrite-pyrite. Cu, Pb, Zn and pyrite may partly overlap (Fig. 2, 3, 4, 5, 6) but usually are developed as clear horizons and are independent of changes in the lithology. The mineralized areas with shale-free sections provide the most spectacular evidence of this fact (KUCHA & PAWLIKOWSKI, 1986). The mineralization is discordant with respect to time lines.

Geochemistry of copper

Typical copper mineralized sections are composed of white sandstone and bituminous shale which gradually passes into clay-rich dark dolomite. Cu in the shale is associated with high concentrations of the transition

Shale Thickness (m)	Cu	Pb	Zn	Hg	Ag	Au	Pd	Pt	N
Pitchy 0—0.2	1.8—39.1 7.1	0.04—0.5 0.1	0.8— 0.1 0.06	1— 53 15	120—3500 286	≦0.6— 10 1.5		0.01— 0.9 0.1	39
Dolomitic 0—1.0	0.2—15.0 2.3	0.2— 0.6 0.3	0.04—0.1 0.06	1— 20 5	50—1000 89	0.01— 0.1		0.01— 0.2 0.05	84
Glauconitic 0—0.3	4.0— 5.8 4.7	ca 0.1	ca.0.05		44— 280 98	0.01— 0.7 0.08			5
Pb-bearing 0—0.5	0.2— 5.2 1.2	0.5 —15.8 3.8	0.8— 1.8 1.1	3— 27 8	60— 280 172	0.01— 0.3 0.18			24
Zn-bearing 0—1.0	0.2— 0.6 0.4	0.5 — 2.1 0.8	0.6—10.2 2.5	4— 48 9					17
Pb-Ag-Hg-Cu 0—0.3	0.4— 1.2 1.0	1.8 — 8.9 3.8	0.6— 3.1 1.0	9— 800 61	100—1500 236	≦0.1 — 2 1	0.01— 0.2 0.09	0.04— 0.1 0.07	9
Noble metals 0—0.1	0.2— 1.2 0.8	ca 0.1	ca. 0.1	8—1500 174	310—5780 1222	1 —3000 40	2 —1000 37	2 —340 18	31
Thucholite 0—0.02	0.1— 1.4 0.8	ca 0.2	ca. 0.05	9— 800 39	30— 420 286	1 — 200 31	2 — 100 21	2 — 80 15	5

Tab. 1 Concentration of heavy metals in Zechstein shales. Upper figure – range, lower figure – average. Cu, Pb and Zn wt.%, Hg to Pt ppm, N – number of analyses.

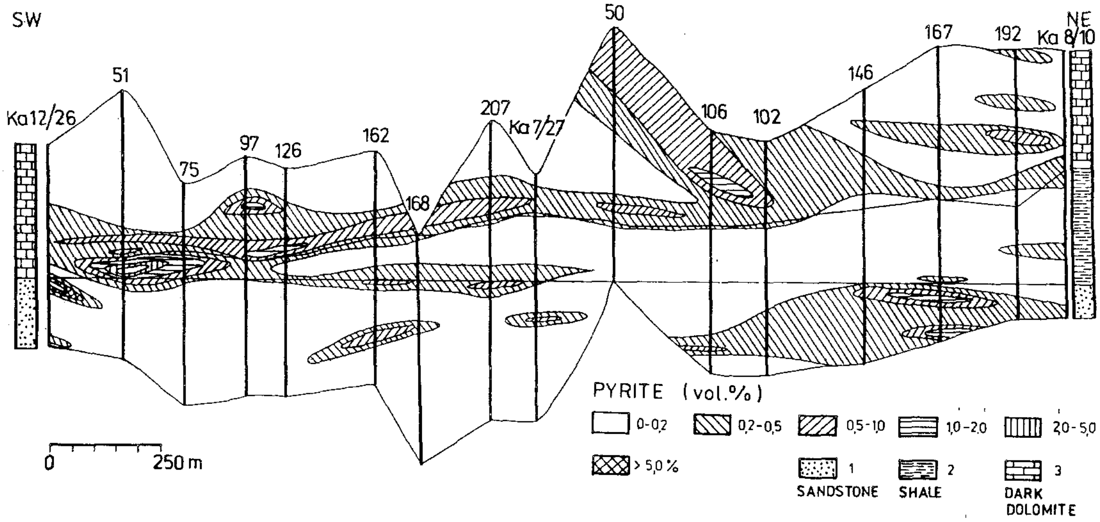

Fig. 2. A distribution of pyrite in the Lubin mine cross-section indicated on Fig. 1.

metals V, Mo, Ni, Co and As. Their content in the very bottom part of the shale may reach 5000 ppm with copper as high as 39.1 wt.% (Table 1). Such a high concentration of transition metals exactly at the redox interface suggests that the transition metals were concentrated as catalysts of oxidation and dehydrogenation of organic matter (KUCHA, 1981, 1982). Concentration of the transition metals in black shale is 1 to 2 orders of magnitude higher than in the overlying dark dolomite.

In the shale-free areas the top part of the sandstone is cemented with anhydrite and below it up to 40 m of sandstone may be mineralized with economic grade chalcocite mineralization. However, in such sandstone a concentration of transition metals does not go beyond a few ppm. This again suggests that transition metals in Kupferschiefer were concentrated as catalysts of the redox reactions.

Copper and pyrite are present separately, but in the glauconitic (phengitic) shale where pyrite, chalcopyrite and bornite are replacing Cu-phengite (KUCHA, 1985), pyrite and copper overlap (Fig. 2, 3). In Pb and Zn areas copper is present in the very bottom part of the black shale (Figs. 3, 4, 6) as chalcopyrite and bornite.

The main copper minerals are: chalcocite, digenite, djurleite, bornite, chalcopyrite and covellite with minor amounts of tennantite, anilite Cu_7S_4, idaite

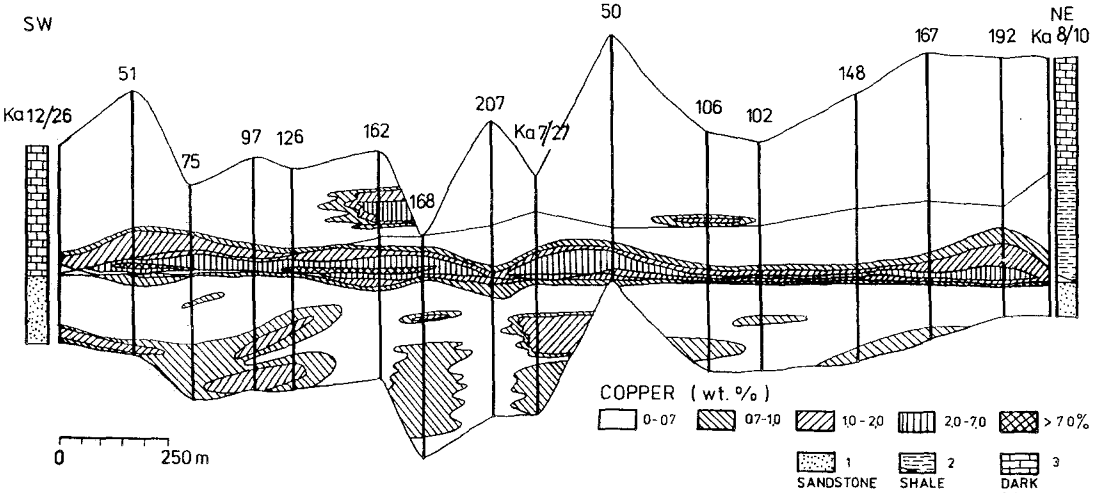

Fig. 3. A distribution of Cu in the Lubin mine cross section shown on Fig. 1.

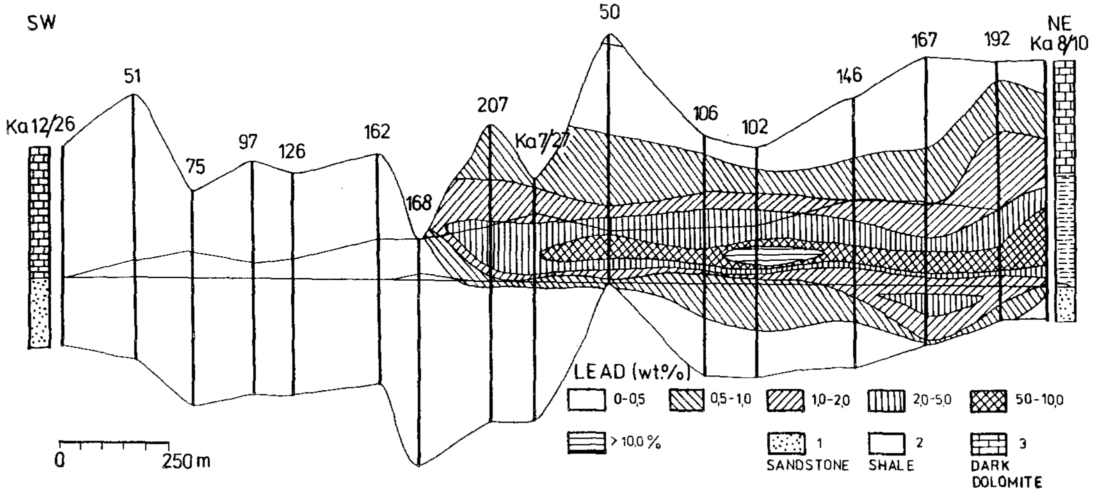

Fig. 4. A distribution of Pb in the Lubin mine cross-section shown on Fig. 1.

Cu_5FeS_6, luzonite Cu_3AsS_4, mooihoekite $Cu_9Fe_9S_{16}$ and haycockite $Cu_4Fe_5S_8$. The main copper-bearing minerals are: pyrite together with rare villamaninite (Cu, Ni)S_2, pyrite formed by a replacement of thiosulphates, Cu-calcite, Cu-glauconite (Cu-phengite, KUCHA, 1985), detrital feldspars and recrystallized, overgrown muscovite (Table 2). Heavy metal-bearing rock forming minerals are heavily replaced by respective sulfides of Cu, Pb, Zn, Ni and Mo. It has been suggested that 25–40% of heavy metals might have been concentrated initially in the presulfide form in the structure of the rock forming minerals (KUCHA, 1985). Also organic matter can contain significant amounts of copper (Table 2). The Pearson correlation coefficient Cu–$C_{org.}$ is 0.73 (HARANCZYK, 1961). The content of Cu and Ag increases in the Kupferschiefer with an increasing oxidation of extractable organic matter measured as a ratio of phenantrene/sum of methylphenantrenes (PÜTTMAN et al., 1988). The sulfide-organic matter relationship suggests that metals were concentrated as catalysts of oxidation and desulfurization of organic matter (KUCHA, 1981, 1982). This would provide an excellent general mechanism accounting for the correlation of heavy metals with organic matter, that does not rely on the formation of direct organometallic compounds. Vanadium is an exception from this general rule, as most of this metal is present in the form of metal por-

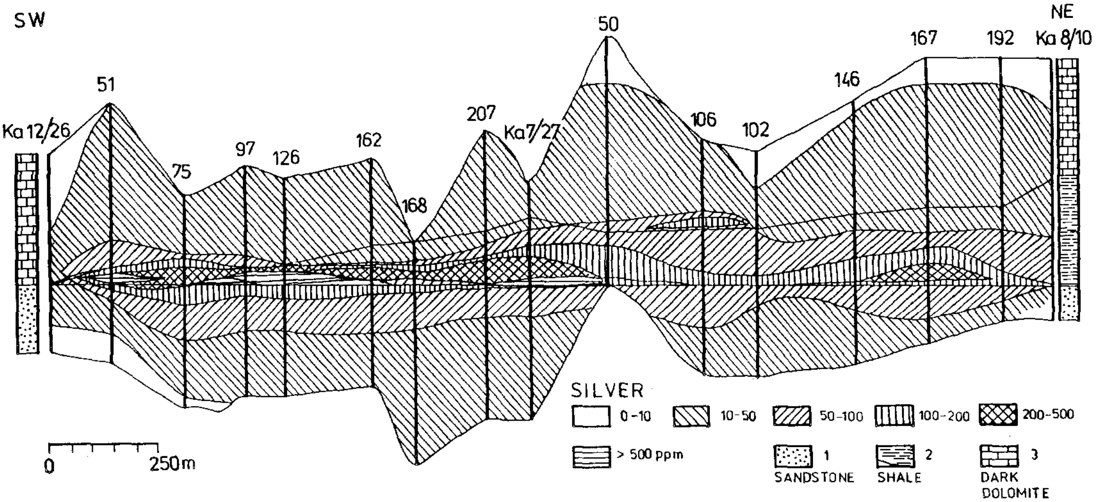

Fig. 5. A distribution of Ag in the Lubin mine cross-section shown on Fig. 1.

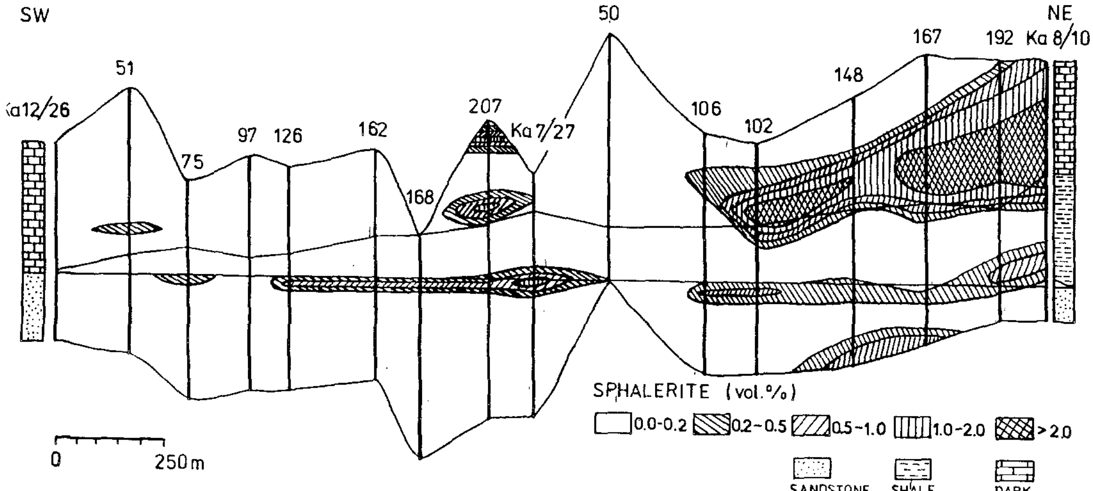

Fig. 6. A distribution of ZnS in the Lubin mine cross-section shown on Fig. 1.

phyrins (KUCHA et al., 1983). Suggested concentration of metals as catalysts of oxidation, desulfurization and dehydrogenation of organic matter can provide an explanation for a good correlation between oxidation of organic matter and concentration of metals (PÜTTMAN et al., 1988).

Geochemistry of lead

In the copper areas a lead horizon 0.3–1.5 m thick rests directly on the Cu-horizon or is separated from it by a barren carbonate interval. The Pb-horizon in turn is overlain by a Zn-horizon (KUCHA & PAWLIKOWSKI, 1986). A typical host rock of this lead mineralization is Ca-dolomite containing average 1.41 wt.% Pb (number of analyses 35). The dominant mineral is galena with pyrite, framboidal pyrite, minor chalcopyrite and sphalerite. A discordance of the Pb-horizon to the stratigraphy is stronger than in the case of the Cu-horizon.

A typical Pb-mineralized black shale is a dark-grey dolomitic shale with an average 3.8 wt.% Pb (Table 1),

Mineral	S	Fe	Co	Ni	Cu	Zn	As	Ag	Pb	N	Method
Framboidal pyrite	53.36	45.64	0.17	0.08	0.19	0.10	0.20	≦0.04	0.20	10	EPMA
Pyrite	52.06	42.97	1.92	0.51	2.48	0.10	2.40	≦0.04	0.20	70	EPMA
Pyrite with thiosulphate inclusions	46.74	35.22	3.26	0.59	1.77	0.05	2.46	0.51	1.11	39	EPMA
Sphalerite	31.50	0.65	≦0.04	≦0.04	0.34	66.20	≦ 0.05	≦0.04	≦0.08	33	EPMA
Tennantite	28.56	1.80	≦0.04	≦0.04	43.49	5.39	18.48	≦0.04	≦0.05	14	EPMA
Soluble organic matter	0.30	0.30	0.01	0.10	0.03	0.05	0.11	0.01	0.08	7	AAS
Thucholite	0.20	0.62	0.05	0.11	0.91	0.07	1.04	0.02	0.13	34	EPMA, PIXE
Fe-calcite	0.04	3.01	0.08	0.08	0.05	0.10	0.19	≦0.03	0.20	10	EPMA
Cu-calcite	0.04	0.32	0.08	0.08	1.28	0.15	0.19	≦0.03	0.20	14	EPMA
Dolomite	0.04	0.71	0.08	0.08	0.08	0.44	0.19	≦0.03	0.61	20	EPMA
Detrital feldspars	0.04	0.08	0.29	0.25	0.87	0.71	0.24	≦0.03	1.00	35	EPMA
Detrital illite	0.04	0.80	0.08	0.08	0.32	≦ 0.04	≦ 0.04	≦0.03	≦0.06	15	EPMA
Glauconite	0.04	6.39	0.08	0.08	1.54	0.10	0.19	≦0.03	0.10	10	EPMA
Overgrown muscovite	0.04	0.50	0.08	0.08	0.90	≦ 0.04	0.19	≦0.03	≦0.05	10	EPMA

≦ – dedection limit of microprobe

Tab. 2 Geochemistry of major minerals and mineral substances from Kupferschiefer, Poland (wt.% average, N – number of analyses).

containing mixed illite-montmorillonite aggregate (KUCHA, 1982). A typical lead mineralized area is separated from the Rote Fäule by a copper-bearing zone (Fig. 1). The highest Pb contents are found in the middle of black shale (Fig. 4). An overlying pyrite horizon partly overlaps with Pb (Figs. 2, 4). The Pb concentration in white sandstone is low. Only occasionally higher Pb concentrations are found in the top part (Fig. 4) and in this case galena is associated with pyrite.

The main Pb mineral is galena. The main Pb-bearing minerals are dolomite, pyrite with thiosulphate relics and feldspars (Table 2). Also thucholite may contain significant amounts of radiogenic Pb (Table 3).

A high Pb content in pyrite with thiosulphate relics is genetically significant suggesting involvement of thiosulphates in accumulation and redistribution of metals in Kupferschiefer. Lead complexes with thiosulphate are insoluble in water (KNEEN et al., 1972). This explains a high Pb content in pyrite formed after thiosulphate precursor (Table 2). A similar behaviour of lead at the presence of thiosulphates was found in carbonate-hosted Zn-Pb deposits of Ballinalack (KUCHA, 1988). All analysed compounds with mixed sulfur valences contain a high or an increased Pb content (KUCHA, 1988; KUCHA et al., 1989). It seems that admixture of lead in thiosulphates of Fe and Zn decreases solubility in water of these compounds and increase their stability in a solid state. The discussed compounds have an increased As and Ni content (Table 2, KUCHA, 1988; KUCHA et al., 1989). A preliminary study of natural thiosulphate relics preserved in sulfide bands on the microscopic heating stage suggests that these compounds are thermally stable up to 200–350 °C depending on the chemical composition. At higher temperatures they disproportionate exsolving sulphate and sulfide.

A possible involvement of thiosulphates in the formation of Mississippi Valley deposits has been suggested by SPIRAKIS (1986).

Geochemistry of zinc

In the Cu-areas the Zn-horizon is above the Pb-horizon. Its thickness ranges from a few cm to 1 m with average 0.4 m containing 1.27 wt.% Zn average (number of analyses 35).

In the Pb-areas the zinc horizon overlies the lead (Fig. 6) but typically both metals partly overlap (Fig. 4, 6). In such sections Pb is preferentially hosted by dolomitic shale and Zn is preferentially hosted by argillaceous dolomite.

In the Zn-areas black shale hosting sphalerite mineralization is rich in MgO and CaO. The average Zn content is 2.5 wt.%. Only little Zn is present in sandstone (Fig. 6).

Sphalerite is a major Zn mineral. It contains 0.65 wt.% Fe and 0.61 wt.% Cd (Table 2). The main Zn-bearing minerals are fahlore containing 5.39 wt.% Zn, dolomite and detrital feldspars (Table 2).

Geochemistry of silver

An average silver content in black shale equal to 132 ppm is higher than in white sandstone and in dark dolomite – 61 and 58 ppm respectively. The richest Ag shales are: bituminous, Pb-Cu-Ag-Hg and noble metals bearing (Table 1). The last shale, concerning the total Ag reserves, is not significant as it occupies only a limited area (Fig. 1). The richest Ag in the Kupferschiefer (with average Ag content above 100 ppm) is present in the Lubin and Sieroszowice mines. A high Ag content is also present in Pb-Ag-Hg-Cu shale separating Cu- and Pb-areas (Fig. 1). Silver distribution in the ore zone (Fig. 5) is similar to that of copper (Fig. 3) – the highest Ag values are present in the black shale especially in its bottom part and in the top part of the white sandstone.

Main silver minerals are stromeyerite, native silver and silver amalgams. About 25% of the total silver is present as native or amalgam. The main Ag-bearing minerals are: bornite containing up to 25 wt.% chalcopyrite, mooihoekite, haycockite, locally chalcocite as well as pyrite with thiosulphate relics (Table 2). The last mineral is very common and plays a significant role in the distribution of silver.

In the top part of white sandstone pyrite is ubiquitous as a cement of detrital grains. Framboidal pyrite cemented with other sulfides is common. Often only a thin external rim (wall of bacterial cell?) is composed of pyrite and the inner part is filled with low reflectant compound (Fig. 7). These micron sized rims of pyrite may form around cell walls of sulphate reducing bacterias, especially these which secrete reduced sulfur outside cell walls. Pyrodictium, a disc-shaped sulphate reducing bacteria, may be suggested as an attractive candidate, which can optimally metabolize sulfur at temperatures as high as 105 °C (STETTER et al., 1983).

Chemical analyses of such a mineral assemblage fall remarkable short to 100% (Table 4, Fig. 7). The main elements are S, Co, As, Ag and sometimes Pb. Compounds cementing framboids (Fig. 7) show the presence of the S^{6+} (Fig. 8) suggested by S^{6+} satellite (KUCHA et al., 1989). The SKα peak shift is equal 0.13 eV at point 120/P1 (Table 4) which means that 1/4 of the total sulfur is S^{6+}. At the microarea 120/P2 (Table 4) the SKα shift is equal to 0.21 eV which requires that

	V	Ti	Br	Y	Zr	Mo	Pd	Ag	Au	Pb	U	N
Noble metals bearing shale	4000	13800	24	90	170	340	20	560	40	1300	800	10
Thucholite	180	1500	10	140	40	170	60	100	80	1400	19600	15
Thucholite replaced by calcite	460	460	14	29	38	67	30	26	13	90	2900	10

Tab. 3 Geochemistry of the matrix of noble metals bearing shale and thucholite free of visible sulfides and native phases by PIXE (ppm, average, N – number of analyses).

Number	S	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Pb	Total
120/P1	17.24	6.38	17.19	2.74	8.56	0.13	12.65	≦0.03	17.15	4.35	86.38
120/P2	21.46	8.53	16.65	2.24	1.61	0.14	15.11	0.06	5.88	12.93	84.92
120/P3	22.79	5.19	14.47	2.04	3.98	0.16	16.13	≦0.03	11.83	4.37	80.96
120/P4	23.77	10.51	13.72	1.69	1.02	0.10	13.95	≦0.03	2.82	2.10	69.69
120/P5	23.96	6.95	19.47	2.75	1.19	0.41	22.79	0.05	11.99	0.75	90.31
120/P6	25.04	8.49	20.36	2.67	1.88	0.40	25.37	≦0.03	4.09	2.37	90.66

Tab. 4 Microprobe composition of framboidal pyrite cemented with thiosulphates (wt.%).

3/10 of the total S is S^{6+} (KUCHA et al., 1989). Therefore it may be concluded that the investigated mineral intergrowths (Fig. 7) are composed of pyrite and thiosulphate of Co-Ag-As-Fe. In the last substance a concentration of thiosulphatic sulfur ($S_2O_3^{2-}$) varies from 1/2 to 3/5 of the total sulfur present. In reflected light the higher the S^{6+} amount in the microarea, the lower the reflectivity observed.

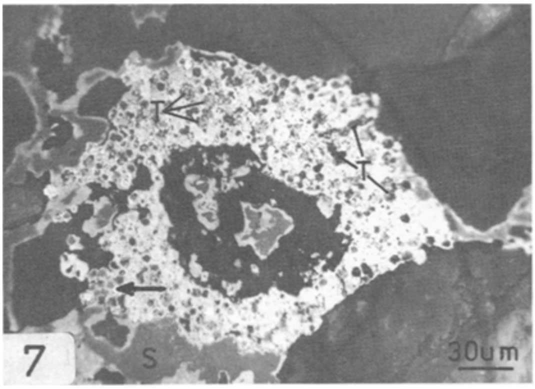

Fig. 7. Microphotograph of mineral assemblage composed of framboidal pyrite cemented with Co-Ag-As-Fe thiosulphate (T) and sphalerite (S) forming a filling cement in the top part of white sandstone. Thiosulphate is cementing individual pyrite framboids or is forming the inner part of circular bodies rimmed by a thin pyrite wall (arrowed). These forms a few μm in size are interpreted as an individual bacterial cells, where the inner part is filled by thiosulphate and the cell wall is composed of pyrite. Reflected light, sample 120/P, Lubin mine.

A distribution of silver in the ore horizon is similar to that of copper (Fig. 3, 5). The copper distribution was controlled by the redox reactions involving oxidation of organic matter catalysed by Cu and other transition metals (KUCHA, 1981, 1982). A similar explanation cannot be used for the Ag distribution despite its similarity to the Cu pattern (Fig. 3, 5), because Ag has always valence +1. Concerning a widespread presence of thiosulphate relics containing an increased (Table 2) or a high Ag content (Table 4) the silver distribution was proabably controlled by a stability of the $S_2O_3^{2-}$anion. Ag thiosulphates are soluble in water (MANN, 1984), but at the redox interface they would be reduced and silver could be immobilized as an insoluble sulfide. This can produce a distribution pattern (Fig. 5) with the highest Ag values present at the redox interface in the very bottom part of black shale. This way a distribution of Cu and Ag would be similar despite different factors controlling a mobility of the two metals discussed.

Silver amalgams in black shale are later than silver sulfides. Amalgams form reaction rims surrounding Ag-bornite containing 20 wt.% Ag (Fig. 9). In the top part of white sandstone silver amalgams replace silver chlorides (Fig. 10). In both cases Ag-sulfides and Ag-chlorides are older. It suggests that Hg came later probably from a separate source. A natural gas present in the Rotliegendes beneath the Kupferschiefer contains up to 2 mg of Hg per 1 m^3. It also carries significant

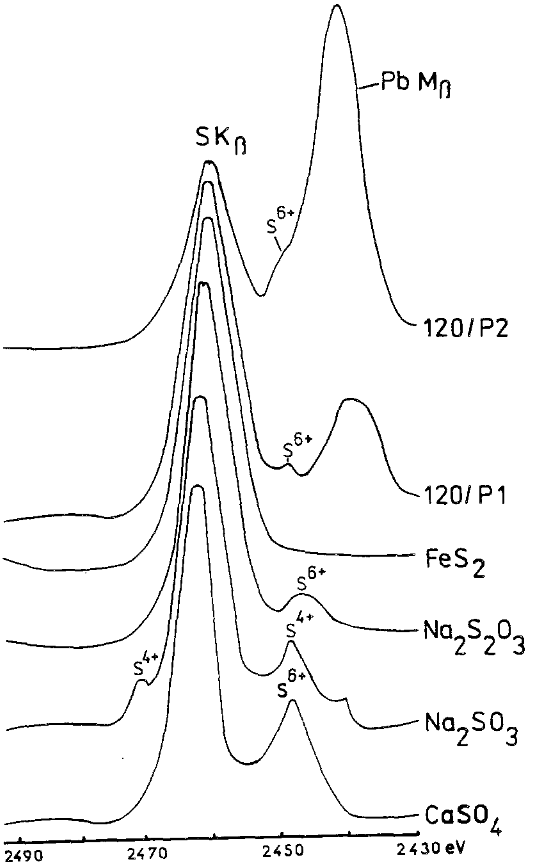

Fig. 8. Emission spectra of the SKβ line in synthetic compounds compared with these of Co-Ag-As-Fe thiosulphate (Fig. 7, Table 4). Sulphate has one S^{6+} satellite, sulfite two S^{4+} satellites on either side of the main Kβ peak, thiosulphate one S^{6+} satellite and a double main SKβ peak. 120/P1 shows S^{6+} satellite and 120/P2 S^{6+} satellite and a double SKβ peak.

amounts of Pb and Cu and minor amounts of Ag as well as some Pd in aerosols and/or gaseous organometallic compounds. Therefore such a gas may be a source of Hg producing amalgams in reaction with earlier Ag sulfides and chlorides (Fig. 9, 10). Mercury is probably mantle derived during Triassic rifting. This may explain the presence of Hg in natural gas trapped below the impermeable Kupferschiefer and the absence of Hg in natural gas deposits known above the Kupferschiefer barrier.

Noble metals

An increase in the content of noble metals is present in the western part of Lubin mine and in the eastern part of Polkowice mine (Fig. 1). This area is enveloped by a larger patchy area of γ anomaly extending from the central part of Polkowice mine to the western part of Lubin mine. The most extensive γ anomaly directly envelopes noble metals bearing area (PRZYBYLOWICZ et al., 1989). The uranium content varies from 12.8 to 163 ppm, with 42.5 ppm average. Th content is very low and changes around a few ppm (PRZYBYLOWICZ et al., 1989). The main U-bearing substance is thucholite. Within the γ anomaly the thickness of black shale is strongly reduced or the shale is facially replaced by organogenic limestone (KUCHA, 1981), copper content is often below cut off limit (1 wt.% Cu), and the shale usually rests directly on sandstone with red stains free of copper mineralization (PRZYBYLOWICZ et al., 1989).

So called noble metals bearing area (Fig. 1) is outlined as an area containing above 1 ppm Au in the bottom few mm of the black shale. This is the N-S extending area about 3 km long and several hundred meters wide (Fig. 1). The content of pay metals within the area is very variable. The lithology is also very variable and often black shale is replaced by organogenic limestone. This area also contains ubiquitous thucholite. Noble metals were accumulated in a few bottom mm of black shale as catalysts of oxidation of organic matter in the area where higher γ radiation of uranium (thucholite) enhanced autooxidation process (KUCHA, 1981, 1982). A principal role of γ radiation relays on the very strong enhacement of the formation of peroxides and peracids, by means of which organic matter isoxidized (WATERS, 1963). The role of transition metals is similar and the best catalysts are amongst PGM's. In the course of catalytic oxidation the involved transition metal catalysts may be immobilized in one of their valence stages (WATERS, 1963). In the discussed

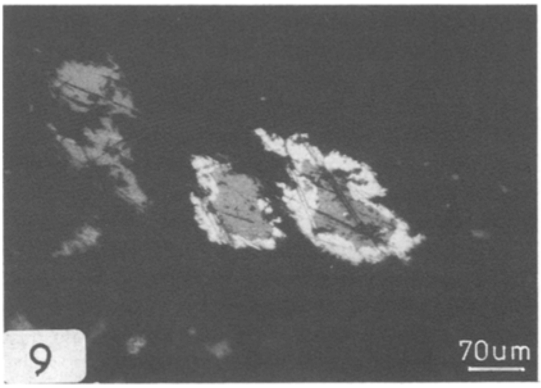

Fig. 9. Microphotograph of silver bornite (light grey) surrounded by replacive rim of Ag-amalgam (white). Black shale matrix is black. Reflected light, sample 110/C, Pb-Ag-Hg-Cu shale. Reflected light, oil, sample 120/U, Lubin mine.

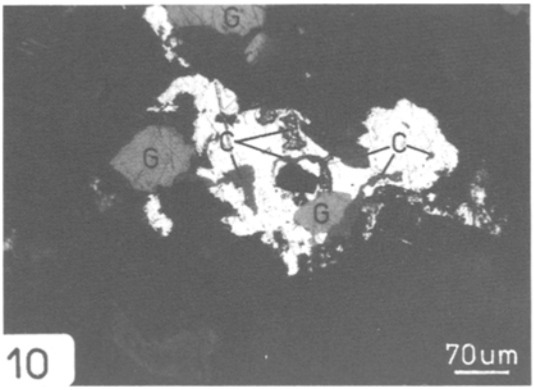

Fig. 10. Microphotograph of silver amalgams (white) replacing AgCl (C). Galena (G) is also present. The top part of white sandstone below Pg-Ag-Hg-Cu shale. Reflected light, oil, sample 120/U, Lubin mine.

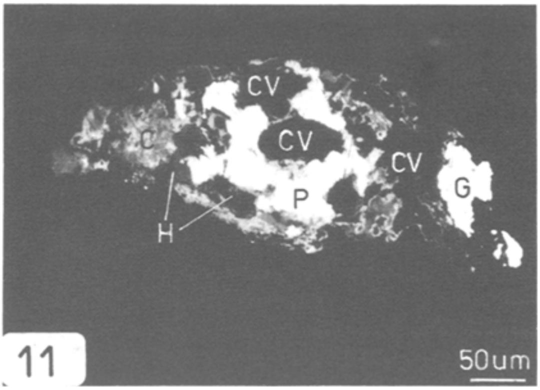

Fig. 11. Microphotograph of a typical noble metal assemblage in noble metal bearing shale: castaingite (C), low reflectant palladium hydride of arsenic (H), Pd_3As_5 (P), covellite (CV) and gold (G). The shale matrix is black. Reflected light, oil, sample 60/A, Lubin mine.

case native phases, arsenides and sulfides are suggested as such immobile (insoluble) forms of metal catalysts. The γ radiation of U and catalytic oxidation of the organic matter by the transition metal catalysts are acting in concert and enhancing each other. Therefore they may succeed to accumulate a significant metal concentration even from very poor solutions. Such a mechanism explains Au, Pt, Pd and U concentration at the redox interface.

Au, Pd and Pt content in the noble metal bearing shale is very variable (Table 1). However as a rule higher pay metals content is always associated with high Ag values. The average Au and Pd concentration is similar, Pt content is half as much. The noble metals shale has thickness of 0.0 to 0.1 m only. The smaller the thickness of the shale the higher the pay metals content.

The matrix of noble metals shale and the matrix of thucholite studied by PIXE (Table 3) shows that pay metals are associated with a high Ti, U and Pb content. Also the content of Zr and Y is high. During replacement of thucholite by calcite the metals are partly mobilized, but a significant part of Pd and Au is precipitated in the form of native metals or arsenides and a part of lead as PbSe (KUCHA, 1981).

In the noble metals bearing shale Au is present as a continuous Au–Ag series starting from a maximum 75 wt.% of gold. Sometimes a two-phase gold is present, where in the silver rich matrix, smaller rounded Au-rich grains occur. The Au content in the noble metal bearing shale in which the matrix is free of microscopic Au grains is 40 ppm (Table 3). A part of gold detected by PIXE in the matrix may be partly connected with microinclusions of electrum hidden below the sample surface. This may be suggested by the presence of Au together with Ag (Table 3). Indeed, a very recent survey of the shale matrix by Micro-PIXE (average of 14 microareas) gives 20 ppm Au with no Ag detected (PRZYBYŁOWICZ et al., 1989). The absence of Ag may strongly suggest that these Ag-free gold peaks are not connected with native Au and may be truly bound in the organic matrix of the noble metal bearing shale.

Similar reasoning does not apply to Pd, because a high As content always accompany Pd in the shale matrix. This was shown by both the PIXE and the Micro-PIXE.

The palladium content in the noble metals bearing shale matrix is 20 ppm (Table 3). Pd forms the following minerals: palladium, sobolevskite, several Pd-arsenides, sulfo-arsenides and palladium hydrides of arsenic. The last minerals have reflectivities of 18 to 30% and tarnish quickly in the air. The Pd content in Ni- and Co-arsenides from the noble metal bearing shale reaches 5.50 wt.% (KUCHA, 1984).

Platinum does not form minerals. Its content in noble metal bearing shale matrix reaches occasionally 130 ppm but usually is below detection limit of PIXE. The Pt content in a microarea of thucholite may reach 1.06 wt.% (KUCHA, 1982). Generally Pt stays dispersed in organic matter.

A typical noble metals assemblage from black shale is composed of: native gold, Pd_3As_5, castaingite, palladium hydrides of arsenic and covellite (Fig. 11) set in the matrix of black shale.

An average Au content in black shale, excluding noble metal bearing area (Fig. 1), measured by ICP spectrometry is 0.115 ppm (BANAŚ & KIJEWSKI, 1987). Au content rarely exceeds 4 ppm and in general correlates positively with uranium and silver (PRZYBYLOWICZ et al., 1989).

Geochemistry of Molybdenum

The average concentration of Mo in black shale is about 200 ppm. In the very bottom part of the shale the molybdenum concentration may reach 5 wt.%. Polkowice and Sieroszowice mines have a higher Mo content than the two others mines.

The main Mo minerals are: castaingite – $CuMo_2S_5$, $CuMoS_3$, Pb- and K-castaingite paragenetic with silvinite (KCl) and molybdenite. Mo sulfides are the main rhenium carriers. The Re:Mo ratio in molybdenite is 1:50, and in castaingite 1:70. An average Mo content in the matrix of noble metal bearing shale is 340 ppm (Table 3).

Organic matter and Mo-feldspars can contain up to 0.7 wt.% Mo (KUCHA, 1985).

Genetic remarks

The Kupferschiefer, being itself strongly reducing, separates the two most contrasting types of rocks which may be found in the sedimentary column. Below the Kupferschiefer a thick Rotliegendes aquifier composed of haematite-rich siliciclastics, pyroclastics, eruptive rocks and their conglomerates forms an oxidized permeable pile resting directly on the crystalline basement. Above the Kupferschiefer, a few dozen meters thick carbonate sequence separates black shale from thick evaporites, one of the least permeable rocks rich in sulphatic sulphur. It is suggested that the sulfide mineralization rich in transition metals resulted from a large scale transfer of gases, liquids, elements and heat between thick evaporitic sequence and underlying rocks across the Kupferschiefer. High Hg contents in a natural gas deposits below the Kupferschiefer trap and the epigenetic relation of Ag-amalgams to Ag-sulfides and Ag-chlorides (Fig. 9, 10) may suggest, that this large scale mass transfer included also mantle derived fluids and gases. This mass transfer was probably driven by the Triassic rifting and related high heat flow from one side (JOWETT, 1986; SPECZIK & PÜTTMANN, 1987), and the Triassic salt doming and related formation of geopressed brines from the other side (KUCHA & PAWLIKOWSKI, 1986).

The most important local factor controlling the mineralization was the redox interface developed between black shale and the Rotliegendes aquifier (KUCHA, 1981, 1982). It controlled accumulation of transition metals as catalysts of oxidation, dehydrogenation and desulfurization of organic matter. Ubiquitous thiosulphate relics suggest that $S_2O_3^{2-}$ complex played a crucial role in metal accumulation and redistribution in the ore zone.

Underlying red sediments of the Rotliegendes may be suggested as one of major, potential sources of metals for the Kupferschiefer epigenetic mineralization (SVERJENSKY, 1987), deposited by migrating brines. Such brines are capable of remobilizing and depositing of the metals found in the Kupferschiefer concerning all: the style, quantity and zonation patterns observed.

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