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PLATTNERITE FROM KUPFERSCHIEFER, POLAND, AND ITS MEANING FOR MINERALIZING CONDITIONS

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Abstract: Plattnerite forms spectacular myrmekitic intergrowths with banded chalcopyrite. It is directly intergrown with chalcopyrite, anglesite and less often cerussite. Simultaneous precipitation of PbO_2, $PbSO_4$ and $PbCO_3$ requires a high activity of S and Eh values close to these found in the surficial environment. Alternatively, PbO_2 was formed from Cu-Fe-Pb oxysulphide precursor, which broken down after precipitation into a fine mixture of hematite, plattnerite, anglesite, and minor cerussite all encompassed by banded chalcopyrite.

The first possibility requires surficial fluids penetrating orezone and mixing with local reducing solutions. The second one can be reconciled with Eh–pH conditions of the Rotliegendes brines interacting with a local reducing solutions.

Abstrakt: Plattneryt tworzy spektakularne zrosty myrmekitowe z pasiastym chalkopirytem. Minerał ten jest bezpośrednio zrośnięty z chalkopirytem, anglezytem i rzadziej z cerussytem. Równoczesna precypitacja PbO_2, $PbSO_4$ i $PbCO_3$ może nastąpić tylko w przypadku wysokiej aktywności S i wysokich wartości Eh, zbliżonych do panujących w warunkach powierzchniowych. Druga możliwość powstania opisanych struktur to utworzenie PbO_2 z prekursora oksysiarczkowego Cu-Pb-Fe, który rozpadł się po strąceniu na mikroskopową mieszaninę hematytu, plattnerytu, anglezytu z mniejszą ilością cerussytu zcementowaną pasiastym chalkopirytem.

Pierwsza z wymienionych możliwości wymaga penetracji strefy złożowej przez roztwory powierzchniowe i ich mieszania się z lokalnymi redukcyjnymi roztworami. Druga możliwość mogła mieć miejsce w warunkach mieszania się dwu rotworów: jednego, będącego w równowadze z solankami porowymi Czerwonego Spągowca i drugiego, będącego lokalnym roztworem redukcyjnym.

Key words: plattnerite, myrmekite, mixing, two fluids, oxysulphide, Eh–pH conditions, Fore-Sudetic Monocline.

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INTRODUCTION

The crystalline basement of the Fore-Sudetic Monocline comprises Cambrian, Silurian and Carboniferous deposits represented by the three major rock types: 1) weakly metamorphosed sandstones, arkoses and shales, 2) strongly metamorphosed schists with sericite, chlorite, biotite, garnet and quartz, 3) volcanic rhyolites, dacites, diabases, trachytes, basalts, mugearites, hawaiites and tephrites (Siemaszko, 1978). In the western part of the Fore-Sudetic Monocline lamprophyries occur. The rocks described were a subject of secondary alterations: albitization, chloritization, silicification, hematitization, zeolitization and serpentinization.

The Rotliegendes rests discordantly on crystalline basement. At the base it is composed of eruptive rocks and passes gradually from the basal conglomerates through red-brown sandstones and melaphyre-porphyry conglomerates into white sandstones at the top. The white sandstone is 0 to 80 m thick and its upper 0 to 20 m thick part is cemented with carbonates, illite, anhydrite, gypsum and in the mining district by copper sulphides.

The Zechstein sediments commence with a thin, 0 to 0.25 m thick, white sandstone bed originating from redeposited and decoloured red sandstone of the Rotliegendes (Kucha & Pawlikowski, 1986; Kucha, 1990; 1995). Locally the white sandstone bed discussed contains Zechstein fauna (Kłapcinski, 1964). However, in some sections the red sandstone of the Rotliegendes has not been decoloured and therefore the overlaying shales rest locally directly on it. The 0 to 1 m. thick black shale sequence either directly overlies the white sandstone (locally red sandstone) or is separated from it by a dolomite bed 0 to 0.2 thick. The shale is locally absent over sand bars and organic limestone (dolomite) occurs in its stead. The main minerals of black shale are illite, carbonates, detrital and overgrown secondary quartz, 0.3 to 30 wt.% of organic matter, glauconite, phen-

Table 1

Stratigraphic division of the Zechstein sediments in the Lubin area (after Kłapciński, 1964)

Epoch	Period	Rock types	Thickness (m)
UPPER	ALLER Z_4	Brown-red shales and claystones with intercalations and lenses of gypsum	18–34
		Grey anhydrite and gypsum	0.5–1.5
		Brown-grey shales and siltsones with intercalations and lenses of gypsum	2.5–5.0
		Grey limestones (locally)	1–7.5
	LEINE Z_3	Hiatus	
	STRASSFURT Z_2	Grey anhydrites (basal)	0–37
MIDDLE		Grey dolomites with thin interbeddings of anhydrite	0–6
		Grey claystones and shales (H_2S-bearing)	0–10
	WERRA Z_1	Grey anhydrites (upper)	60–88
		Anhydrite and claystone breccias	0–5
		Grey anhydrites (lower)	0–25
LOWER		Grey dolomitic limestones and calcareous dolomites	25–78
		Dark grey claystones and shales	0–20
		Dark grey dolomites, limestones and marls (Cu-bearing)	1.5–3.5
		Dark grey dolomitic shales (Cu-bearing)	0.50–0.86
		Grey boundary dolomite (Cu-bearing)	0–0.2

gite and sulphides. Gypsum is often seen as flat small rosettes on bedding planes of the shale. Phosphates and detrital feldspars are also important constituents of the mineralized shales. Black shales pass gradually into dark, argillaceous dolomites coloured by 0.5 to 4.5 wt. % of organic matter. Dolomites are often rich in gypsum and anhydrite with corresponding decrease in organic matter content. The bottom, 1–3.5 m thick part of the argillaceous dolomites is mineralized with 1 to 4 wt.% of Cu. Towards the top of the Z1 Cyclotheme Werra (Table 1) argillaceous dolomites pass through calcareous dolomites and dolomitic limestones into anhydrites capped by rock salts.

The Z2 stage is marked by regression of sea and begins with a black shale similar to the Kupferschiefer except that it is not mineralized with copper sulphides. It is succeeded by a typical evaporitic sequence towards the top (Table 1).

The Z3 stage is marked in Poland by ingression of sea at the beginning, but towards the Z3/Z4 boundary the sea retreated marking a significant period of weathering of the Zechstein evaporates. In the area of Lubin the Z3 is entirely absent (Table 1, Kłapcinski, 1964). The Zechstein sediments are succeeded by Lower Triassic red sandstones (Bunter Sandstone). However, in the Lubin area the Bunter Sandstone is locally absent and the Zechstein is directly covered by other Triassic sediments (Karnkowski, 1980).

Economic grade Cu-ore is present in white sandstone – ca 50% of the Cu reserves, in black shale – ca 20%, and in dark dolomite – ca 30%. The average thickness of the mineralized horizon is about 4 m, but may reach up to 25m in the Rudna mine. The lateral zoning patterns are oriented radially outwards from Rote Fäule in the following order: hematite-chalcocite-bornite-chalcopyrite-galena-sphalerite-pyrite (Rydzewski, 1976). The vertical zonation from the bottom upwards is as follows: barren hematite-dispersed pyrite with minor chalcopyrite-copper sulphides-galena-sphalerite-pyrite. There are four types of epigenetic hematite in the ore zone (Kucha, 1995), each associated with different metals. Cu-, Pb-, Zn-, and pyrite-horizons may partly overlap but usually they are developed as distinct units independent from changes in lithology (Kucha, 1990). The mineralization is discordant to time lines.

The average content of lead in different rock types shows large variations (wt.%/number of analyses): barren sandstone 0.015/15, anhydritic sandstone 0.018/49, mineralized sandstone 0.050/150, black Cu-shale 0.53/270, mineralized dolomite 0.11/196, and barren dolomite 0.39/35. However, in the Pb-shale the concentration of Pb may locally reach 12.88 wt.%, and in the independent Pb-horizon located above the Cu-layer the Pb content changes from 1.33 to 2.26 wt.%, while the horizon thickness varies between 0.50 and 1.85 m.

MATERIALS AND METHODS

The samples from Lubin, Rudna and Polkowice mines were studied by reflected light microscopy, SEM and electron microprobe. All the samples were freshly polished before analyses.

Electron microprobe analyses were made in the Institute of Mineralogy and Petrology, Mining University Leoben, Austria, with an ARL SEMQ probe at 20kV and probe current 120 μA. The following spectral lines and synthetic standards were used: S Kα i Fe Kα (FeS_2, Fe_2O_3, PbS), Co Kα, Ni Kα, Cu Kα (100%, $Cu_{10}Fe_2As_4S_{13}$), Zn Kα, Ge Kα, As Kα and Lα (As 100%, $Cu_{10}Fe_2As_4S_{13}$), Se Kα, Rh Lα, Pd Lα, Cd Lα, Sn Lα, Sb Lα, Te Lα, Re Lα, Pt Lα, Au Lα and Mα, Hg Lα, Pb Mα (PbS), and Bi Mα. All the analyses were ZAF corrected.

Sulphur valencies were determined in the Institute of Material Sciences, Katholieke Universiteit Leuven, with a Jeol 733 microprobe automated with a Tracor Northern software package, using an accelerating voltage of 20 kV with a beam spot size of 15 μm. The spectrometer with a PET crystal was calibrated using the following sulphur standards: $CaSO_4$, $CaSO_3$, $Na_2S_2O_3$, S, FeS_2 and FeS. Cubic FeS_2 was used as a zero reference point determined directly before and after a given microarea was tested. When the drift of the zero reference point was smaller than one standard deviation (one σ) the measurement was accepted. The sulphur valency was calculated by procedures developed for the electron microprobe (Kucha *et al.*, 1989).

SEM analyses were made at Afdeling Fysico-chemische Geologie, KU Leuven, Belgium with a JEOL JSM-6400 scanning microscope equipped with a Link EXL-10/EDS system at 20 kV.

MODE OF OCCURRENCE

Plattnerite occurs in mineral assemblages composed of banded chalcopyrite, hematite, bornite, galena, oxysulphides and dolomite (Fig. 1–3). In reflected light microscope plattnerite appears dark against chalcopyrite and bornite and has reflectivity in air about 7%. It forms direct fine, myrmekitic intergrowths with banded chalcopyrite (Fig. 1), bornite (Fig. 2), but its contacts with galena are sharp and straight (Fig. 3). Some dark, myrmekitic grains set in the banded chalcopyrite matrix are in fact a mixture of plattnerite and anglesite and/or oxysulphides (Fig. 1). Rarely some part of plattnerite occurring in bornite (Fig. 2) is intergrown with both anglesite and cerussite.

The plattenrite studied contains significant amounts of (wt.%): S ≤0.04 – 0.69, Fe 0.97–1.49 and Cu 3.38–6.32. The stoichiometry of plattnerite is close to PbO_2 (Table 2).

Table 2

Chemical composition of plattnerite from Kupferschiefer (wt. %/mol)

	S	Fe	Cu	Ag	Pb	$O_{diff.}$
13813	0.06 0.0043	0.99 0.0346	3.38 0.1037	≤0.04	81.72 0.7693	13.91 2.0000
13814	1.27 0.0791	1.49 0.0532	6.32 0.1983	≤0.04	74.85 0.7210	16.03 2.0000
13817	≤0.04	0.97 0.0368	3.61 0.1199	≤0.04	80.21 0.8167	15.17 2.0000
13817a	≤0.04	0.99 0.0411	3.38 0.1235	0.12 0.0026	81.72 0.9157	13.78 2.0000
13817b	0.69 0.0532	1.46 0.0644	3.84 0.1485	≤0.04	80.95 0.9602	13.02 2.0000
13818	0.69 0.0527	1.46 0.0628	3.84 0.1482	≤0.04	80.95 0.9590	13.04 2.0000

Analysed but not detected: Co ≤0.01, Ni ≤0.01, Se ≤0.04, Bi ≤0.09

Cerussite has stoichiometry close to $PbCO_3$ (Table 3). It contains significant admixture of (wt.%): Ca 0.34–0.56, and Cu 0.97–1.05. It can be easily distinguished from plattnerite and anglesite since it is brighter in reflected light and displays a strong bireflectance and optical anisotropism.

Anglesite (Table 3) from the studied mineral assemblage also contains significant admixture of Ca, Fe and Cu.

Hematite may be rich in Cu – up to 5.98 wt.% (Kucha, 1980), S up to 1.69 wt.% (Table 4) and sometimes also in Pb. As indicated by iron content (Table 4) the composition of the hematite studied correspond to Fe_2O_3 as well as to $\beta Fe_2O_3 \cdot H_2O$.

Table 3

Chemical composition of cerrusite and anglesite occuring together with banded chalcopiryte, hematite, oxysulphides and plattnerite (wt. %/mol)

	S	Ca	Fe	Ni	Cu	Ag	Pb	
13818a	0.19 0.0142	0.56 0.0336	0.31 0.0133	0.02 0.0008	1.05 0.0397	≤0.04	78.71 0.9126	$PbCO_3$
13818b	≤0.04	0.34 0.0208	0.30 0.0132	0.04 0.0017	0.97 0.0374	≤0.04	78.37 0.9270	$PbCO_3$
13817C	11.37 1.0000	0.31 0.0218	1.11 0.0561	≤0.01	3.21 0.1425	≤0.04	64.31 0.8753	$PbSO_4$
13817C	10.09 1.0000	0.14 0.011	0.27 0.0154	≤0.01	0.41 0.0205	≤0.04	67.84 1.0405	$PbSO_4$

Banded chalcopyrite may contain up to 1 wt.% of Pb (Kucha & Piestrzynski, 1991). The bornite studied contains the amount of Mn well above microprobe detection limit (Table 5), and it seems that Mn occurs in the structure in the sulphidic form.

Table 4

Chemical composition of chalcopyrite and bornite from oxysulphide-hematite-plattnerite assemblage (wt. %/mol)

	S	Mn	Fe	Cu	Ag	Pb	Total
138H1	34.50 2.0000	≤0.02	29.44 0.9799	33.25 0.9727	≤0.04	0.74 0.0066	98.05
66C3	25.68 4.0000	0.14 0.0127	12.79 1.1438	60.71 4.7722	0.38 0.00176	0.70 0.0169	100.40
66D1	25.40 4.0000	0.21 0.0193	12.66 1.1447	61.74 4.9067	0.10 0.0047	0.15 0.0037	100.26

The mineral assemblage discussed forms large crustifications in fractures within the boundary dolomite. The sequence of crystallization was as follows (Fig. 1–3):

1) galena **(g)** forming clean euhedral crystals growing on dolomite forming walls of fractures. Chemically it is pure PbS and no admixtures have been detected by microprobe analyses.

2) the first chalcopyrite band **(cp)** contains only minor minute inclusions of oxysulphides seen as dark spots in reflected light (Fig. 1).

3) distinctly banded chalcopyrite with large myrmekitic inclusions of plattnerite and minor plattnerite-anglesite (cerussite, oxysulphides) **(cp+p)** (Fig.1). This myrmekitic texture occurs also as spectacular rosettes of plattnerite (anglesite, oxysulphides) set in the chalcopyrite matrix (Fig. 3).

4) distinctly banded chalcopyrite with fine myrmekitic inclusions of oxysulphides **(cp+ox)**. The oxysulphides were identified as Cu-Fe (Pb) thiosulphates and sulphites (Kucha and Piestrzyński, 1991).

5) distinctly banded chalcopyrite with fine, syntaxial inclusions of hematite **(cp+h)** and minor oxysulphides

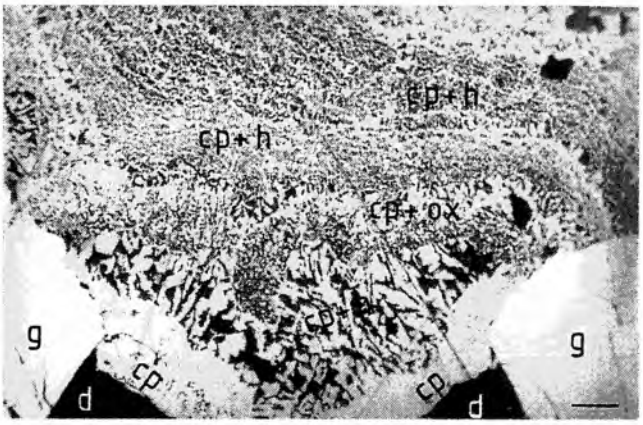

Fig. 1. Microphotograph of : 1) galena (g), 2) chalcopyrite with myrmekitic inclusions of oxysulphides (cp), 3) chalcopyrite with large myrmekitic inclusions of plattnerite, plattnerite-anglesite (cerussite, oxysulphides) (cp+p), 4) chalcopyrite with myrmekitic inclusions of oxysulphides (cp+ox), 5) chalcopyrite with syntaxial inclusions of hematite (cp+h). Reflected light, sample 138, Lubin mine, scale bar 50 μm

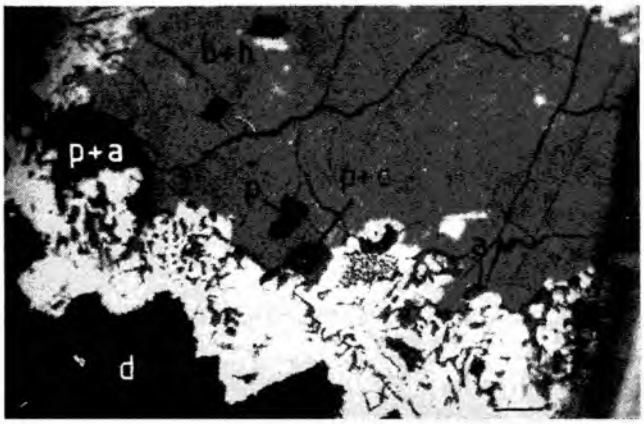

Fig. 2. Microphotograph of bornite with dispersed fine hematite (b+h) containing larger inclusions of plattnerite (p), anglesite (a), and cerussite (c). Plattnerite is located mainly at the bornite (grey) – chalcopyrite (light) border. Dolomite is black (d). Reflected light, sample 138, Lubin mine, scale bar 50 μm

6) bornite **(b+h)** with dispersed very fine hematite containing larger inclusions of plattnerite **(p)**, occasionally intergrown with anglesite **(a)** and rarely cerussite **(c)**. Plattnerite, anglesite and cerussite occur mainly at the bornite-chalcopyrite border (Fig. 2).

DISCUSSION

Myrmekitic intergrowths of ore minerals, mainly these including intergrowths of sulphides with metal oxides, carbonates, sulphates and oxysulphides may help to decipher Eh–pH conditions of mineral formation. Myrmekitic textures arise as "a result of the simultaneous formation of myrmekitic intergrowths in one independent process" (Ramdohr, 1975). In the case studied, the mineral assemblage

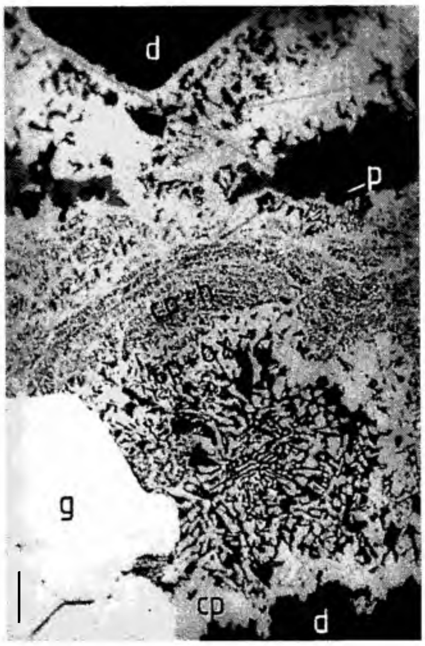

Fig. 3. Microphotograph of galena (g) and banded chalcopyrite with spectacular rosette of plattnerite (cp+p), overgrown by chalcopyrite with myrmekitic inclusions of oxysulphides (cp+ox), chalcopyrite with syntaxial inclusions of hematite (cp+h), bornite + hematite (b+h), plattnerite (p), and anglesite (a). Reflected light, sample 138, Lubin mine, scale bar 50 μm

containing myrmekitic intergrowths (Fig. 1–3) crystallised in the following order:

1) galena (g) and minor chalcopyrite overgrowing on the surfaces of fractures in the boundary dolomite (Fig. 1–3). Sulphides were precipitated from local reducing fluids as pure, stoichiometric PbS and minor $CuFeS_2$.

2) the first chalcopyrite band (cp) with minor inclusions of oxysulphides (Fig. 1). Simultaneous precipitation of $CuFeS_2$ and Cu-Fe oxysulphides can take place close to the sulphide-sulphate fence at pH about 8–9 and Eh about 0.0 – –0.3, and a sum of dissolved S changing between 10^{-1} and 10^{-4} mol. This assumption may be in a good agreement with the parameters displayed by present-day Rotliegendes brines having pH of about 6.3 (Bojarska *et al.*, 1978) and significant concentration of Fe, Pb, Cu etc. (Lubaś, 1986). Such brines could have percolated through the fractures in dolomite, mix with a local reducing fluids of the Kupferschiefer, and precipitate the observed (Fig. 1–3) banded chalcopyrite with small inclusions of oxysulphides. The fractured host dolomite probably caused an increase of pH of the inflowing fluids up to 9.

3) distinctly banded chalcopyrite with large, myrmekitic inclusions of plattnerite, anglesite (cerussite) and oxysulphides (cp+p) (Fig. 1–3). Simultaneous precipitation of chalcopyrite and plattnerite cannot be achieved at the same time from the same fluid. Direct intergrowths of $CuFeS_2$, $PbSO_4$ and $PbCO_3$ can occur under conditions close to Eh = –0.2 and pH = 8 (Fig. 4). However, the enclosure of PbO_2 into the assemblage would require to assume an influx of an extra fluid close in its parameters to the surficial fluids. Therefore to reconcile the observed mineral intergrowths it

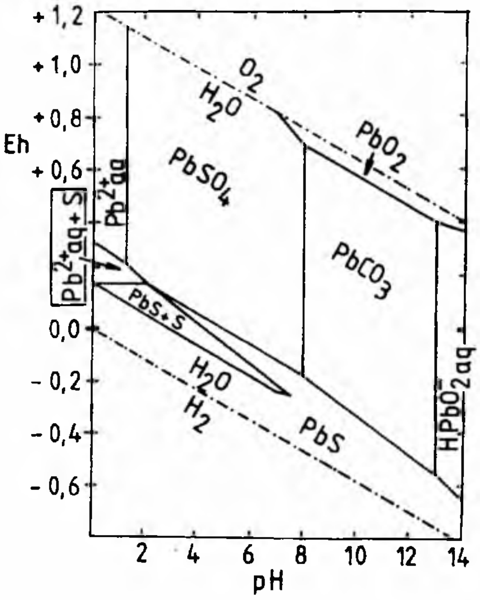

Fig. 4. Stability diagram of lead compounds in water at 298 °K, 1 atm of the total pressure, and P_{CO_2} equal to 10^{-4} atm. A sum of dissolved sulphur equals to 10^{-1} mol. Boundaries between solids are provided at the total activity of ions equal to 10^{-6} (after McIntire, vide Garrels & Christ, 1965)

posed to the surface environment: i) during the Z_3 stage due to the sea regression (Table 1), ii) during the deposition of Bunter Sandstone overlying locally Zechstein sediments, and iii) during the deposition of Tertiary sediments resting locally on the Zechstein deposits. The best choice seems to be the Bunter Sandstone time because at this period there was a possibility to generate geopressed, warm, metalliferous fluids in the Lower Permian sediments (Kucha & Pawlikowski, 1986; Jowett, 1986), which could mix with local, saline fluids descending from the surface. There are numerous observations indicating a descend of fluids from overlying evaporates (Mayer & Piestrzyński, 1982) and their mixing in the orezone with local fluids (Kucha, 1985, Kucha & Pawlikowski, 1986).

4) banded chalcopyrite with myrmekitic inclusions of Cu-Fe oxysulphides (cp+ox) (Fig. 1). Myrmekite of chalcopyrite + oxysulphides is a common phenomenon in the orezone (Kucha & Piestrzyński, 1991). Such a mixture can form at the sulphide-sulphate fence from one local fluid where precipitation of sulphides and oxysulphides can alternate to form syntaxial, myrmekitic intergrowths of both. Such phenomena are commonly observed in MVT deposits (Kucha, 1988; Kucha & Stumpfl, 1992; Kucha & Viaene, 1993) and in Kupferschiefer as well (Kucha, 1990; Kucha & Piestrzyński, 1991), where base metal thiosulphates and sulphites were identified.

5) banded chalcopyrite with hematite (cp+h) with or without accompanying oxysulphides (Fig. 1, 3). This microtexture can be produced by mixing of local, reduced fluids with those ascending from the Rotliegendes. The latter brines are in equilibrium with hematite cement and feldspars. Re-eqilibration of these fluids in fractures in dolomite probably increased pH up to 8–8.5, safeguarding a stability of oxysulphides (Kucha & Viaene, 1993). Chalcopyrite-hematite intergrowths are wide-spread in the orezone, and are observed in sandstone, black shales as well as in mineralized dolomite (Kucha, 1995).

6) bornite (b+h) with finely dispersed hematite and larger inclusions of plattnerite, anglesite and cerussite (Fig. 2). Myrmekite of bornite+hematite is a common phenomenon in the orezone (Kucha, 1980, 1995). This microtexture was probably formed at conditions close to Eh = –0.2 and pH = 8.5 to satisfy minor element composition of bornite containing some Mn and hematite containing copper (Table 4, 5; Kucha, 1980). However, the formation of bornite+ plattnerite myrmekite requires mixing of two fluids, one oxidising (Garrels & Christ, 1965; Sangameshwar & Barnes, 1983) descending from the surface to form PbO_2 and another local, reducing to precipitate bornite.

The discussed myrmekitic microtextures are common in the orezone, and therefore their presence may suggest that conditions responsible for the origin of such textures were also responsible for the formation of the Kupferschiefer ores. Consequently, these microtextures can occur due to mixing of at least two different fluids: local reducing being in equlibrium with the Kupferschiefer, and external, inflowing oxidizing ones. This may suggest three combinations of fluids:

1) near surface, oxygenated fluids descending to the orezone during periods of exposure of the Zechstein sediments to the surface environment and to the weathering process. Such descending fluids can mix up with local, reducing fluids to produce myrmekitic and syntaxial microtextures of sulphide and oxides, including highly oxygenated plattnerite (Fig. 4).

2) high pH, Ca-rich, saline fluids descending from the overlying evaporates due to transformation of gypsum into anhydrite, whereby conversion of $1m^3$ of gypsum releases 400 kG of H_2O (Kucha, 1985; Kucha & Pawlikowski, 1986). Such fluids can be responsible for replacement of K-feldspars by calcium sulphate, and displacement of the Cu-horizon down to the underlying sandstones (ibidem). They can also cause an extensive cementation of the upper sections of white sandstone by anhydrite and gypsum (Mayer & Piestrzyński, 1982).

3) fluids ascending from the Rotliegendes deposits and mixing up with local reduced fluids. This type of fluid mixing could produce myrmekites of chalcopyrite+hematite+ oxysulphides, bornite+hematite, and chalcocite+hematite (Kucha, 1980, 1995). This type of fluid mixing was probably the most important during the formation of this deposit (Kucha & Pawlikowski, 1986; Wodzicki & Piestrzynski, 1994). Myrmekitic intergrowths of the kind discussed here appear practically at all stages of the mineralization including also framboidal sulphides cemented with oxysulphides (Kucha, 1990). Framboidal sulphides are considered to be the earliest metal precipitates (Sawłowicz, 1990).

A detailed analysis of microtextures containing $CuFeS_2$, Cu_5FeS_4, PbO_2, $PbSO_4$, $PbCO_3$, Fe_2O_3 and Cu-Fe thiosulphates and sulphites (Fig. 1–3) may suggest yet another possibility of their formation. The mineral assemblage discussed is always encompassed by banded chalcopyrite, suggesting oscillatory zoning with the respect to both metals

A detailed analysis of microtextures containing $CuFeS_2$, Cu_5FeS_4, PbO_2, $PbSO_4$, $PbCO_3$, Fe_2O_3 and Cu-Fe thiosulphates and sulphites (Fig. 1–3) may suggest yet another possibility of their formation. The mineral assemblage discussed is always encompassed by banded chalcopyrite, suggesting oscillatory zoning with the respect to both metals and sulphur valencies. Assuming precipitation of the assemblage at the sulphide-sulphate fence, Cu-Fe-Pb oxysulphides may be precipitated as banded overgrowths on the surfaces of fractures within dolomite (Fig. 1–3). Such a mixture of oxysulphides (and sulphides as well?) may be decomposed into the observed mineral myrmekitic textures by separate reactions changing valencies of the involved metals and sulphur. The starting precipitate may be based on the sulphoxylic (H_2SO_2, Valensi *et al.*, 1963) and sulphitic (H_2SO_3) anions. Reactions of transformation of such a mixture of metal sulphoxylanes and sulphites probably involves oxidation of some metals as well as oxidation and reduction of some part of sulphur, depending on the initial valencies, to achieve the observed mixture of banded chalcopyrite $CuFeS_2$, hematite Fe_2O_3, thiosulphates $(Cu,Fe,Pb)S_2O_3$, sulphites $(Cu,Fe,Pb)SO_3$, sulphates $PbSO_4$, and plattnerite PbO_2. The reaction is balanced assuming sulphur valencies of −1 and +5 in thiosulphate (Vairavamurthy *et al.*, 1993):

$$\begin{gathered} Cu^{1+}SO_2 + 3Fe^{2+}SO_2 + 2Pb^{2+}S_2O_3 + Cu^{2+}SO_3 \Rightarrow \\ Cu^{2+}Fe^{2+}S_2{}^{2-} + Fe^{3+}{}_2O_3 + Pb^{4+}O_2 + Pb^{2+}SO_4 + \\ 2Cu^{2+}S_2{}^{1-,5+}O_3 \end{gathered}$$

Further complexity of this reaction may be increased by adding organic matter, which by oxidation can produce also $PbCO_3$ and will act in favour of increasing amount of newly formed chalcopyrite or bornite. There is, however, an open question if the proposed reaction can result in oxygen activity high enough to oxidize some part of lead into PbO_2. This problem has a fundamental importance for the origin of Kupferschiefer ores. If a mixture of oxysulphides can by disproportionation and reduction-oxidation produce PbO_2 than an involvement of the surficial fluids during ore formation is not required. However, if PbO_2 can be only precipitated due to the activity of fluids descending from the surface, than the suitable window for mineralising event will be probably reduced only to the Bunter Sandstone period. This may form a strong, time related discrimination factor for the timing of mineralising event and help to outline prospective areas for the Kupferschiefer mineralization.

CONCLUSIONS

1) Plattnerite, PbO_2, is a common mineral in assemblages containing oxysulphides.

2) Sulphides, oxysulphides and PbO_2 form finely banded, recurrent microtextures suggesting precipitation from fluids characterised by oscillating Eh–pH conditions.

3) The formation of plattnerite requires high Eh values, close to these occurring at the surface. This suggests mixing of oxidising descending fluids with reducing fluids within the orezone.

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Streszczenie

PLATTNERYT ZE ZŁÓŻ KUPFERSCHIEFER W POLSCE I JEGO ZNACZENIE DLA OKREŚLENIA WARUNKÓW PROCESU MINERALIZACJI SIARCZKOWEJ

Henryk Kucha

Plattneryt PbO_2 występuje w dolomicie granicznym na kontakcie łupek–piaskowiec, oraz w samym łupku. Minerał ten współwystępuje z pasiastym chalkopirytem, bornitem, oksysiarczkami Cu-Fe-Pb, dolomitem, hematytem, anglezytem i cerussytem.

Plattneryt tworzy spektakularne zrosty myrmekitowe z pasiastym chalkopirytem. Minerał ten jest bezpośrednio zrośnięty z chalkopirytem, anglezytem i rzadziej z cerussytem. Równoczesna precypitacja PbO_2, $PbSO_4$ i $PbCO_3$ może nastąpić tylko w przypadku wysokiej aktywności S i wysokich wartościach Eh, zbliżonych do panujących w warunkach powierzchniowych. Druga możliwość powstania opisanych struktur to utworzenie PbO_2 z prekursora oksysiarczkowego Cu-Pb-Fe, który rozpadł się po strąceniu na mikroskopową mieszaninę hematytu, plattnerytu, anglezytu z mniejszą ilością cerussytu zcementowaną pasiastym chalkopirytem.

Pierwsza z wymienionych możliwości wymaga penetracji strefy złożowej przez roztwory powierzchniowe i ich mieszania się z lokalnymi redukującymi roztworami. Druga możliwość mogła mieć miejsce w warunkach mieszania się dwu roztworów: jednego, będącego w równowadze z solankami porowymi Czerwonego Spągowca i drugiego, będącego lokalnym roztworem redukującym.

Opisane struktury myrmekitowe są pospolite w strefie złożowej, zatem ich obecność wskazuje, że warunki w jakich się one tworzyły odpowiadają tym, w których powstała mineralizacja typu Kupferschiefer. Powstanie takich struktur wymaga obecności dwu roztworów: lokalnego będącego w równowadze z czarnym łupkiem oraz drugiego utlenionego, pochodzącego z zewnątrz.