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GEOCHEMISTRY AND MINERALOGY OF GOLD AND PGE'S IN MESOTHERMAL AND EPITHERMAL DEPOSITS AND THEIR BEARING ON THE METAL RECOVERY

In mesothermal-epithermal (below 250 °C) noble metal deposits mineralogy and geochemistry of Au, Pd and Pt are complex. The metals form substitutions in arsenides, antimonides, sulphides, organic matter, arsenates and oxysulphides. In some deposits the metals form their own oxysulphides, organometallic compounds, silicates, tellurides, selenides, sulphides, arsenides and arsenates. Such complex mineralogy and geochemistry of noble metals involving direct chemical bonding to the host lattice causes difficulties in the metal recovery. A treatment of such ores requires prior geochemical and mineralogical study to design optimal technology of the ore treatment.

INTRODUCTION

Ores of metallic gold are still the main type of Au ores treated today. They contain gold in concentration ranging from about 1 to a few dozen ppm. The main mineralogical type of gold in these deposits is metallic gold, and therefore the gold can be easily recovered either by gravity separation or by cyanization.

During past two decades industry started to turn an increasing attention to mesothermal and epithermal deposits, where gold mineralogy and geochemistry are very complex. They include such minerals like Au-tellurides: petzite Ag_3AuTe_2 , calaverite AuTe_2 , krennerite AuTe_2 , montbrayite $(\text{Au}, \text{Sb})_2\text{Te}_3$; sulphides: uytenbogaardite Ag_3AuS_2 ; selenides; fischesserite Ag_3AuSe_2 ; bismuthides: maldonite Au_2Bi ; and thiosulphates $(\text{Au}, \text{Cu})\text{S}_2\text{O}_3$. Extraction of gold from the above discussed minerals by cyanization is not possible. The minerals have to be first converted by oxidation (roasting, chemical oxidation, bacterial oxidation) into oxide forms, which involves breaking of the Au-Te, Au-S, Au-Se chemical bonding (Yvonne et al., 1991). Only after breaking the chemical bond gold becomes susceptible to cyanide leaching. However, an identification of gold chemical bonding must be done prior to the

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oxidation, otherwise wrong method of oxidation may produce a new, unleachable complex (Wagner et al., 1988). Mössbauer spectroscopy indicates that in gold silver chalcogenides Ag_3AuX_2 , where $\text{X} = \text{S}, \text{Se}, \text{Te}$, gold valency is +1 (Wagner et al., 1988, 1989).

In the recent times there is also an increasing treatment of ores with an “invisible” gold. In such ores gold occurs in the structure of the common minerals as discrete inclusions smaller than about 100nm, and therefore not detectable by optical and scanning electron microscopy. Minerals acting as hosts are most frequently arsenopyrite and pyrite, although invisible gold occurs also in pyrrhotite, chalcopyrite, bornite, galena and tetrahedrite. Mössbauer study shows gold to be chemically bound to the lattice of arsenopyrite or pyrite (Wagner et al., 1988, 1989). A High Resolution Transmission Electron Microscopy (HRTM) indicates that visible particles of gold are absent in host grains containing even up to 2000 ppm of Au (Cabri et al., 1989). However, many ores contain both the chemically bound gold and discrete particles of gold with size less than 100nm as well (Marion et al., 1991). The content of chemically bound gold in pyrite may reach 4000–5000 ppm (Marion et al., 1991) in Au rich zones. Discrete particles of native gold show valency 0, typical for metallic gold, and chemically bound Au shows valency +1.

The aim of this paper is to present mineralogy and geochemistry of gold associated with organic matter (Kupferschiefer, Maldon), oxysulphides (Mitterberg, Veitsch, Comet Mine, Barberton), sulphides (Kupferschiefer, Barberton, Mitterberg) and silicates (Maldon, Barramiya, Barberton), as well as platinum group element minerals related to the organic matter and redox interface in Kupferschiefer.

DEPOSITS STUDIED

The Barberton Mine is located in Transvaal, South Africa, in the Archean rocks comprising the Zwartkopie and Sheba Formations of the Onverwacht and Fig Tree Groups, respectively (Schouwstra, de Villiers, 1988). The locus for gold mineralization of the Main Reef Complex at Barberton is a major anticlinal structure (Birthday No. 2 Anticline), which consists of green quartz-carbonate schists and banded cherts (Zwartkopie Formation) with overlying shales and graywackes (Sheba Formation). The highest-grade gold mineralization occurs in fractures in sheared and brecciated rocks of the Sheba Formation and is associated with quartz-carbonate veins and disseminated sulphides. Gold occurs in association with sulphides – mainly as inclusions in pyrite and arsenopyrite. Pyrite is ubiquitous whereas arsenopyrite occurs in restricted areas of the fracture zones (Schouwstra, de Villiers, 1988). High gold grades correlate better with quantity of arsenopyrite than with quantity of pyrite. Associated minerals are gersdorffite, pyrrhotite, sphalerite, chalcopyrite, tetrahedrite, rutile, Fe-oxysulphides, anhydrite, chlorite, and graphite (Kucha et al., 1994). Arsenopyrite-pyrite-pyrrhotite geothermometry indicates a temperature range of 350–400 °C (Schouwstra, de Villiers, 1988).

The Barramiya gold prospect is located in the southern part of the Eastern Desert, Egypt. The oldest rocks of the late Proterozoic age comprise graphite, actinolite, tremolite and chlorite schists. They are intruded by ultramafic rocks converted to serpentinite and talc carbonate rocks (El Shazly, 1977). Younger intrusions comprise two sets of granite and tonalite intrusions. Post granitic dykes include felsites, dacites as well as quartz veins with sulphides, gold and chlorites. The gold content in quartz veins varies between traces and 18, most often between 5 and 18ppm. Gold is accompanied by: pyrite, gersdorffite, ankerite, siderite and As-bearing chlorite.

The Comet Mine, New South Wales, Australia, is one of slate belt-type gold deposits in the Armidale area of the New England Fold Belt hosted by Paleozoic carbonaceous metasediments (Plimer, 1982). The mine is located on the largest of the three parallel quartz pyritic veins that are hosted by the Permo-carboniferous Rockvale Adamellite, an S-type adamellite that forms a part of the Hillgrove suite of granitic rocks in the New England Fold Belt (Shaw & Flood, 1981). The veins which are enclosed by a narrow quartz-sericite-pyrite-chlorite alteration assemblage, comprise quartz, pyrite, arsenopyrite, chalcopyrite, pyrrhotite, magnetite, haematite, Bi tellurides, gold and thiosulphates. Fluid inclusions temperatures reveal two thermal maxima at 290 and 400 °C and the ^{34}S values of sulphides group around 0 (Kucha et al., 1994).

The Kupferschiefer Cu–Ag deposits are located in the South-Western Poland. Mining operations at four mines „Lubin”, „Polkowice”, „Rudna” and „Sieroszowice” produce per annum about 400,000 t Cu, 12,000 t Pb, 1,000 t Ag, 300 t Ni, 600 kg Au and 150 kg of Pt + Pd. Quantities of V, Mo and Co in the ore are similar to those of silver but none of these metals is recovered. 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. The lateral zoning patterns are oriented radially outwards from Rote Föule in the following order: hematite – chalcocite – bornite – chalcopyrite – galena – sphalerite – pyrite (Rydzewski, 1976). The vertical zonation from the bottom upwards is: 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 clear units independent from changes in lithology (Kucha, 1990). The mineralization is discordant to time lines. The distribution of noble metals is controlled by the redox interface (Kucha, 1981, 1990; Kucha et al., 1993). The highest noble metals contents are observed at the redox interface, especially when the interface runs between black shale resting directly on the red sandstone, and/or when the interface is crossing stratigraphic boundaries of the black shale (Piestrzynski, Wodzicki, 1996). The first type of occurrence is observed in the Lubin West Mine, Polkowice East Mine and less in the Polkowice Central Mine, the second type of occurrence is seen mainly in the Polkowice West Mine (Piestrzynski, Wodzicki, 1996) as well as in the Sieroszowice Mine (Kucha et al., 1993). On the reduced side of the redox boundary, 3 to 300 mm thick, there are:

electrum (Ag-rich gold), Pd arsenides, Ni–Co arsenides, Bi sulphides, native Bi, uraninite, brannerite, thucholite, Au–Pd–Pt-bearing thucholite, and covellite but the Cu content does not exceed 0.2–0.8 wt. % (Kucha 1982). The redox interface may be marked by two phase gold, where silver rich gold containing about 60 wt. % of Au is embedded in gold of high fineness containing 92–97 wt. % of Au (Kucha, Pocheć, 1983). On the oxidized side of the redox boundary which may be up to 50–60 cm thick the main mineral is haematite accompanied by gold of high fineness, platinian gold contains up to 1.60 wt. % of Pt, PdBi sobolevskite, $\text{Ag}_6\text{Au}_4\text{Pb}_2$, native Pb, PbSe clausenthalite, metallic palladium, relicts of metal-bearing organic matter replaced by black calcite (Kucha, 1981), and palladium arsenates. Characteristically only traces of Cu are observed on the reduced side of the redox interface. Larger quantities of copper appear 1.0–1.5 m. above the redox interface (Kucha, 1981, 1982). The temperature of the deposit formation was around 100 °C, as indicated by thermal stability of sulphide assemblages (Kucha, 1990).

Maldon, Victoria, Australia, hosts a number of auriferous quartz reefs which occur in argillaceous and arenaceous hornfelses, a variety of schists, and nodular schists (Moon, 1897) of early Ordovician age adjacent to the late Devonian Harcourt Granodiorite (Morgan & Woodland, 1990). Contact metamorphism converted the original sediments, which consisted mainly of greywackes and less frequently shales, predominantly into hornfelses composed of varying proportions of quartz, biotite, cordierite and andalusite. The sediments have been tightly folded along parallel axes approximately 230 m apart with extension at 345° (Ramsay & Willman, 1988; Morgan & Woodland, 1990). Mineralized faults are often sub-parallel to bedding. The quartz reefs are generally concordant with surrounding sediments, but in places they cross fold axes and sediment bedding and then they attain an increased thickness. The reefs predate at least the final stage of the granodiorite emplacement (Ramsay & Willman, 1988). The reefs and veins are composed of massive, milky quartz with a sulphide content of about 1% (Morgan & Woodland, 1990). Clean quartz contains little gold but dark patches in quartz are rich in gold (Moon, 1897). The sulphide assemblage includes (in decreasing abundance): pyrite, arsenopyrite, sphalerite, löllingite (FeAs_2), chalcopyrite, galena, pyrrhotite, marcasite, gold, maldonite, native Bi and Sb, stibnite, oxysulphides of Fe, Cu and Pb, ullmanite and Pb (Sb, Bi) S_4 . Gold is also accompanied by organic matter, As–chlorite and siderite. The oxide assemblage includes: rutile, ilmenite and magnetite.

The Mitterberg deposit is located in the Greywacke Zone close to the Calcareous Alps, Austria. It is composed of five major veins cross-cutting the Paleozoic strata of the Northern Greywacke Zone. The largest orebody is represented by the main vein (Hauptgang) extending W–E over a total distance of 11 km with thickness from 0.2 to 4 m, and 460 to 520 m of mineable vertical extent. The Hauptgang cuts through the Grey Formation (Silurian, Devonian) and the Violet Formation (Rotliegendes). The three veins of the Southern Orefield cut through the phyllites of the Grey Series. The main ore mineral at Mitterberg is chalcopyrite. Sb-fahlore (tetrahedrite) occurred

mainly at the upper sections of the veins. In some sectors of the veins larger amounts of arsenopyrite, gersdorffite, safflorite–löllingite–rammelsbergite, pyrite, and cubanite occur. The gangue minerals are carbonates, quartz and minor muscovite. Gold occurs as both visible and invisible mainly in tetrahedrite and less often in pyrite, gersdorffite, cubanite and chalcopyrite (Bernhard, 1966). Mineral separates show gold contents (ppm): tetrahedrite 18.7–52.5 (Kucha et al., 1997), and chalcopyrite from traces up to 1.5 (Bernhard, 1966). Mining at Mitterberg ceased in 1976. Ore reserves left underground amount up to 10.5 mio t with an average Cu grade of 1.5 wt. %.

MATERIALS AND METHODS

Samples were cut and polished in a careful way to avoid destruction of fragile micro-inclusions in gold (Kucha et al., 1994). Samples were ground dry on abrasive paper using progressively decreasing grain size until final grinding on paper with abrasive grains of 1 µm. Final polishing was completed with 1 µm diamond polishing spray. The chemical composition of minerals and the valencies of S, Fe, As and Au were determined with a Cameca SX50 microprobe with a stabilized electron beam at the School of Earth Sciences, University of Melbourne, Australia, at the Institute of Mineralogy and Petrology, Mining University Leoben, Austria with an ARL SEMQ microprobe, and with Camebax microprobe at the Institute of Material Sciences, University of Mining and Metallurgy, Krakow, Poland. All used microprobes possessed stabilized electron beam. The beam stabilization permitted a much higher resolution and accuracy of valency determination than is possible using probes without such a facility (Kucha et al., 1989; Kucha et al., 1994). The technique of valency determination relied on general principles developed previously for iron and sulphur (Kucha et al., 1989).

Mineral compositions were determined at 20 kV using the following spectral lines and synthetic standards: F K α (CaF₂), Cl K α (NaCl), Na K α , Al K α , Si K α (NaAlSi₃O₈), Mg K α (Mg₂SiO₄), K K α (KAlSi₃O₈), Ca K α (CaCO₃), Ti K α , Mn K α , Fe K α and S K α (FeS₂), Co K α , Fe K α and As L α , K α (FeAsS), Zn K α , Ni K α and Sb L α (NiSbS), Ag L α and Au M α (Au–Ag alloy), Pb M α (PbS), Hg M α (HgS), and Bi M α . Oxygen and carbon were calculated by difference, but their content has also been checked at 10 kV using haematite and graphite as standards. The carbon content was measured on uncoated sample where a conductivity path was provided by a thin, self adhesive copper foil attached to the sample surface.

Sulphur valencies were measured with a PET crystal by determination of S K α and S K β shifts and S K β /S K α intensity ratios (Kucha et al., 1989), iron valencies were measured with a LiF crystal by determination of the Fe K β shift, arsenic valency was determined by measurement of As K β shift with a LiF crystal and As L β /As L α ratios with a PET crystal. Gold valency was determined by measurement of the Au

M β /Au M α intensity ratios using the following standards: pure Au (valency 0) and AuTe₂ (valency +1), gold cyanide AuCN adsorbed on activated carbon (valency +1), and gold bromide (AuBr₃) adsorbed on activated carbon (valency about +3).

Infrared absorption spectra were performed in reflected light mode using a microscope supplied with a Fourier infrared system with spot size varying from 7 to 10 μ m at the Institute of Forensic Research, Krakow, Poland.

PAY METALS ASSOCIATED WITH ORGANIC MATTER

The first occurrence of noble metals associated with organic matter was found in Kupferschiefer, Poland (Kucha, 1973, 1974, 1975, 1993). Pay metals occur also within reduction haloes in the Permian Sandstones of the Northern Switzerland (Hofmann, 1986). They were also found later in black shales in Canada, USA, and in metal-rich black shales of China (Parnell, 1988). An association of gold with organic matter in Witwatersrand gold and uranium deposits is known for a long time (Schidlowski, 1968). Recent studies indicate their presence also in uranium deposits related to organic matter. It appears that connection of pay metals with organic matter is frequent enough to be interested in this phenomenon also from a practical point of view. The problem will be demonstrated on examples from the Kupferschiefer, Poland, and Maldon, Australia.

Noble metals associated with clay-organic matrix of the Kupferschiefer

Extractable bitumens usually constitute no more than 1–2% of the total organic matter of the shale. Most of the organic matter is insoluble kerogen tightly intermixed with clay minerals forming a clay-organic matrix of the shale. Such a matrix may contain significant amounts of metals (Table 1).

Kerogen obtained after extraction of soluble bitumens and removal of carbonates by HCl, and of clay minerals by HF was studied by infrared spectroscopy. It is composed mainly of hydrocarbons with conjugated benzene rings. Some CO, OH, CH₂ and CH₃ groups are also present. They form short additives to aromatic rings and/or may be incorporated in insoluble resins.

Titanium is a common minor element in Kupferschiefer, and occurs in concentrations from 0.04 to 1.00 wt. %. The Ti budget is controlled by detrital TiO₂, and substitutions in the illite lattice. In the matrix of noble metal-bearing shale (Table 1) the Ti content varies from 0.008 to 4.61 wt. %, and usually is substituted in clay minerals but sometimes it is connected with brannerite (U, Ca, TR) (Ti, Fe)₂O₆ as indicated by an increased content of U.

The Fe content in black shale varies between 0.22 and 3.29 wt. % (Table 1). The distribution of Fe in the clay-organic matrix is controlled by minute inclusions of

sulphides, substitutions in clay minerals (Kucha, 1985), and by haematite on the oxidized side of the redox interface. An average Fe content in the matrix of noble metal-bearing shale determined by MPIXE is 0.71 wt. %, and by EPMA 0.91 wt. % (Table 1). These amounts of Fe may be entirely accommodated by clay minerals.

Table 1. Concentration of selected elements
in the clay-organic matrix of the noble metal-bearing shale free of microscopically visible ore minerals (ppm)

Method	Beam size, μm	<i>n</i>	Ti	V	Fe	Ni	Cu	As	Mo	Pd	Ag	Pt	Au	Pb	U	
PIXE	3000	10	4400	2450	2200	90	2000	50	38	≤ 20	90		≤ 40	≤ 80	20	min
			29300	5700	32900	1400	51300	4900	1080	70	2500		700	6700	3000	max
			13800	4000	10900	600	19400	1400	340	20	560		140	1300	800	mean
MPIXE	3	18	422	307	5270	130	415	490	63	≤ 15.3	≤ 20.1	≤ 6.0	≤ 12.5	≤ 85	170	min
			4896	1038	10777	3045	7650	7062	1572	88.0	196.6	28.0	238.3	109	2600	max
			3294	854	5270	689	1560	1945	261	43.7	91.7	11.0	108.7	94	788	mean
EPMA	1	56	≤ 80	≤ 200	2700	≤ 200	≤ 60	≤ 200	≤ 100	≤ 200	≤ 300	≤ 360	≤ 100		≤ 400	min
			46100	4000	13900	1600	8800	3500	880	1900	1000	600	1900		11300	max
			3375	1100	9100	400	1950	1500	211	55	300	62	70		846	mean

n – number of analyses, PIXE – Proton Induced X-ray Analysis, MPIXE – micro PIXE, EPMA – Electron Probe Microanalysis.

An average Ni content in the black shale is about 200 ppm, but in the very bottom part of the shale Ni abruptly increases up to 500 ppm (Kucha, 1976b). The matrix of noble metal-bearing shale contains 459 ppm Ni measured by MPIXE and 400 ppm measured by EPMA (Table 1). A part of Ni correlates with As and may be present as minute inclusions of sulphoarsenides in the matrix of noble metal-bearing shale. The remaining Ni not balanced by As may be, however, present in porphyrins.

The Cu content in the matrix of noble metal-bearing shale determined by MPIXE is 1587 ppm, and by EPMA is 1950 ppm (Table 1). A part of Cu occurs as microinclusions of sulphides, but a part is also bound to solid bitumens and clay minerals (Kucha, 1985).

The average As content in black shale is 250–300 ppm, with a rapid increase towards the bottom of the black shale (Kucha, 1993). Arsenic partly correlates with Cu, Ni and Co present as microinclusions of sulpho-arsenides in the black shale matrix (Kucha, 1976a, b). Arsenic which does not correlate with the above mentioned metals is bound to solid bitumens (Kucha, 1982).

The Pd content in the matrix of noble metal-bearing shale varies from ≤ 20 to 88 ppm (Table 1), but in the studied profile may reach 1900 ppm. Here Pd does not correlate with any of the other elements. It may suggest the presence of organometallic compounds specific for Pd. Apart from being present in the matrix of the shale as “invisible” palladium Pd forms numerous arsenides with size up to 100 μm (Kucha, 1984). They are intergrown with native gold.

The Pt content measured by MPIXE in the matrix of noble metal-bearing shale reaches occasionally 28 ppm (Table 1), but in more numerous EPMA analyses values as high as 600 ppm were found. Pt does not correlate significantly with any of the other elements. Platinum so far has been detected only in the clay-organic matrix of the shale, in thucholite, and as 1.6 wt. % admixture in platinian gold.

Gold is present in four points out of 28. Only at the point no 6 gold correlates with silver. This suggests the presence of microinclusion of Ag-rich gold. Such an interpretation is suggested by the chemical composition of electrum from Kupferschiefer which contains 55–63 wt. % of Au and 37–45 wt. % of Ag. In the remaining three points no silver was found. This may suggest that these Au peaks are connected with Ag-free solid bitumens containing organically-bound gold. Au $M\beta/AuM\alpha$ emission efficiency ratio suggests that gold at point % 5A has valency +1. Apart of organometallic compounds gold forms numerous native inclusions with size reaching up to 300 μm (Kucha, 1982, 1984).

The average U content in the mineralised area of Lubin is 61.5 ppm (Piestrzynski, 1990). The average U content in the matrix of noble metal-bearing shale determined by MPIXE is 495 ppm, and by EPMA is 846 ppm (Table 1). The main uranium carrier is thucholite, forming grains up to 4 mm in size in the shale. Minor uranium carriers are phosphates, and brannerite.

The above described relationships are characteristic for the matrix of noble metal-bearing shale on the reduced side of the redox interface. The presented results indicate that a significant part of Au, Pt, and Pd present in the matrix of noble metal-bearing shale may be chemically bound to organic matter.

Noble metals associated with organic matter (kerogen–thucholite) in Kupferschiefer

The organic matter constituting clay-organic matrix of Kupferschiefer is soluble in chloroform only in amounts of 1–2%, but may reach 19% in samples rich in alginite. The soluble organic matter is enriched in several metals: V, Fe, Co, Ni, Cu, As and Mo (Kucha, 1993). Vanadium and nickel are present as vanadyl ethioporphyrins (Kucha et al., 1983), and Ni porphyrins (Sawlowicz, 1985). Also some Fe and Mg are connected with pyrrole rings. Despite a high Cu content in some organic extracts no specific copper organic compounds have been found yet.

Thucholite is defined as a bitumen polymerized by radiolytic action of uranium and thorium (Schidlowski, 1968). In the Zechstein copper deposits thucholite is present in areas of γ -anomalies (Kucha et al., 1993) in black shale as rounded nodules, boundary dolomite, and in the top few cm of white sandstones as fillings, veinlets and cements of detrital grains. Within γ -anomalies, the thickness of the black shale is reduced, the Cu content is usually below 1 wt. % and the shale rests directly on the red sandstone free of copper mineralization (Piestrzynski, 1988). The last feature, i.e. a direct contact of red sandstone and black shale is the most important single factor

controlling a lateral distribution of γ -anomalies and an increased content of the pay metals as well (Kucha et al., 1993). This is connected with redox interface which may cross stratigraphic boundaries and shift also above the shale bringing with itself a few cm to 50 cm thick pay metal horizon.

Thucholite grains in black shale are up to 4 mm in size. The shale around thucholite exhibits disturbed lamination, providing evidence for the epigenetic growth of the thucholite with the matrix of the shale. Thucholite is composed of two optically distinct components: isotropic (A) and strongly anisotropic (B). Component A has reflectance in oil from 1.75 to 2.50%, with most measured values grouped around lower figure. The reflectance values are roughly parallel to the uranium content, i.e. the higher the U content the higher reflectance observed. The component A is richer in heavy metals than anisotropic component B. TEM study shows that thucholite A is not crystalline.

Component B is strongly anisotropic in reflected light and has reflectance close to graphite. Electron diffraction reveals three types of small scale ordering (domains) in anisotropic thucholite B: i) with typical graphite cell parameters $a_0 = 0.246$, and $c_0 = 0.672\text{nm}$, ii) with Van der Waals thickness of the benzene ring $a_0 = 0.246$, and $c_0 = 0.740\text{nm}$, and iii) with a greater thickness of the ring where CH_3 , CO , or OH groups are attached to conjugated benzene rings (Kucha, 1982, Kucha and Wieczorek, 1988). The discussed domains in thucholite are usually smaller than 100nm and therefore they are not detectable by standard X-ray diffraction techniques.

Thucholite contains ubiquitous inclusions of Cu–Bi sulphides, PdAs_2 , and native gold present at the boundary between isotropic component A and B. It seems that graphitization of thucholite A caused destruction of organometallic complexes and subsequent exsolution of noble metal minerals at the boundary of thucholite A and B. Similar mineral assemblage appears at the edge of thucholite. The contact of thucholite and replacive calcite may be regarded as micro-redox interface demonstrating that on such boundary there is an efficient accumulation of pay metals minerals.

Geochemistry of thucholite was studied with EPMA, PIXE, MPIXE, SXRFA, and TEM (Table 2). Several grains were studied including one with a profile traversing across the whole grain.

Uranium

Thucholite free of microscopically visible UO_2 grains have U contents ranging from ≤ 35 to 162400 ppm (Table 2). Optical and Transmission Electron Microscopy (TEM) shows that budget of uranium in thucholite is controlled by three major phases:

- Uraninite. Hipidiomorphic uraninite has size up to 25 μm . TEM diffraction gives unit cell size $a_0 = 0.542$ (0.004nm close to Th-free uraninite. Uraninite forms also submicroscopic inclusions in the thucholite matrix. Such inclusions have sharp contacts to the enclosing organic matrix and sizes ranging from 0.04 to 0.02 μm .

• Brannerite (U, Ca, TR) (Ti, Fe)₂O₆. Brannerite grains with size up to 30 µm. are dispersed through the organic matrix of thucholite. The mineral contains also Y, Ce and La. On TEM brannerite produces ring diffraction patterns due to radioactive decay.

Table 2. Concentration of selected elements in the thucholite (organic matrix) free of microscopically visible ore minerals (ppm)

Method	<i>n</i>	Ti	V	Fe	Ni	Cu	As	Pd	Ag	Pt	Au	Pb	U	
PIXE	25	120	120	2200	≤7	300	11	≤12	≤10	≤13	≤13	≤18	≤35	min
		5900	460	28700	900	93700	600	100	100	≤13	800	6400	38000	max
		1084	172	10620	220	23780	292	26	28	≤13	35	1400	19600	mean
MPIXE	33	182	≤18	140	≤3.5	33	≤10	≤78.6	≤58.0	15.2	≤9.8	50.2	12000	min
		521	82	5800	273.3	5560	3439	4578.5	1065.7	464.9	2527.8	3700.0	55114	max
		262	41	876	72.2	412	781	787.4	332.5	123.0	862.0	861.3	36330	mean
SXRF A	21			73	≤5	1300	5			≤2	≤1	≤3		min
				1300	650	5000	5100			1770	1900	490		max
				396	67	2207	1432			162	175	215		mean
EPMA	27	≤130	≤300	≤200	≤150	≤200	≤100	≤300	≤300	≤200	≤300	≤600	≤400	min
		1420	2200	2200	500	1800	5000	5000	3900	2100	800	1400	162400	max
		620	504	390	109	510	270	390	504	480	291	410	28600	mean

n – number of analyses, PIXE – Proton Induced X-ray Analysis, SXRF A – Synchrotron X-ray Fluorescence.

• Uranium-organic compounds. The organic matrix of thucholite contains numerous finely dispersed inclusions with sizes from 4 to 20 nm. These inclusions are not crystalline as shown by a selected area diffraction. Energy dispersive analysis indicate the presence of U and often also Ti. As a rule these inclusions, unlike uraninite, have diffuse boundaries with the enclosing organic matrix. The identity of the inclusions is not certain, but they may be uranium organometallic compounds. The uranium distribution in the organic matrix of thucholite is unhomogeneous, and varies from ≤400 up to 162400 ppm (Table 2). U does not correlate with other studied elements except of Ti and TR.

Palladium

The palladium content in the organic matrix (thucholite A) varies between ≤11 and 5000 ppm (Table 2), but occasionally may reach even 2 wt. % (Kucha, 1975). In the studied profile it changes from 260 up to 1117 ppm. Pd does not correlate with other elements, also in the former studies some correlations with As has been found (Kucha, 1982).

Platinum

The Pt content in the matrix of thucholite varies from ≤ 2 to 2100 ppm (Table 2). In the studied profile set across thucholite grain Pt reaches 800 ppm. Occasionally the Pt content in the organic matrix at the edge of thucholite grains replaced by calcite may reach 1.06 wt. % (Kucha, 1975, 1981, 1982). Pt is antipathetic to U, but in general is sympathetic with Ni. This suggests that Pt, like Ni, is partly connected with the pyrrole ring. This idea is further supported by the presence of inclusions in the organic matrix of thucholite containing some Pt and Ni. Such inclusions have size about 20 nm, and diffuse boundaries to the enclosing organic matrix. During replacement of thucholite by calcite (oxidation) platinum is depleted in the rim of thucholite down to 0.54 wt. % from 1.06 wt. % in the center (Kucha, 1982).

Gold

The Au content in the organic matrix varies from ≤ 1 to 1900 ppm (Table 2), but occasionally may reach 6800 ppm (Kucha, 1982). Au is antipathetic to U. Gold forms both visible and submicroscopic inclusions in the organic matrix of thucholite. The size of invisible gold inclusions is about 40 nm. The energy dispersive analysis indicates that such inclusions in the organic matrix contain Au but are Ag-free. A lack of silver and non-crystalline nature of such inclusions may indicate that these are in fact organometallic compounds of gold. This may be further supported by observation that metallic gold occurring in Kupferschiefer contains 36–45 wt. % of Ag. The Au M β /Au M α emission efficiency ratio suggests that gold at point 18 shows valency +1, which speaks in favour of organically bound gold. Apart of organometallic compounds in the organic matrix gold forms numerous native inclusions with size reaching up to 50 μ m (Kucha, 1982, 1984).

Other elements

Thucholite contains also (ppm): Pb ≤ 3 –6400 which is probably entirely radiogenic, Y 50–560, Ce 35–380, La 25–120, as well as some K, Rb, Cl, Br, Sn, P, Ca, Bi, Sr, W, Ir and I.

Redox interface as a control of a distribution of pay metals in Kupferschiefer

By definition a redox interface is a plane (or a thin horizon) developed between: 1) reduced and oxidized rocks, or between 2) reduced and oxidized fluids. The redox horizon has thickness from a few cm up to 1–1.5 m. The reduced part of the horizon has different pay metal mineralogy, thickness, and pay metal contents than the oxidized portion.

1. The first case occurs when black shale rests directly on the red sandstone. It occurs in the Lubin West and Polkowice East Mines, and partly also in the Central part of the Polkowice Mine (Kucha et al., 1993). Due to a direct contact between the most reducing rock (black shale) and the most oxidized rock (red sandstone with haematite) redox gradient is so strong that involved reduction-oxidation reactions catalysed by

α -, β -, γ -radiation of uranium, noble metal catalysts of Pt, Pd, Au and other transition metals (Waters, 1960; Kucha, 1981, 1982; Kucha et al., 1993) produce the highest observed concentrations of pay metals (ppm): Au 1–3000, Pt 2–340, Pd 2–1000 (Table 3). The copper horizon is located 1–1.5 m above the redox interface. This means that pay metal horizon is located well below economic copper ore.

Table 3. The content of noble metals in selected areas of black shale and in some mineral processing products. Upper figure – range, lower figure – average. Ag to Pd in ppm, Rh in ppb (modified after Kucha et al., 1993)

Area	<i>n</i>	Side of redox interface	Thickness m	Ag	Au	Pt	Pd	Rh
Lubin West, Polkowice East	31	reduced	0.1–0.4	310–5780 1222	1–3000 40	2–340 18	2–1000 37	
	6	oxidized	0.3–1.0	1–25 5	0.05–9 1.8	0.01–4.1 0.19	0.01–0.8 0.1	
Polkowice Central	5	reduced	0.1–0.25	265–3080 856	1–115 24	0.01–3 0.3	1–15 3.5	1–52.0 9.1
	4	oxidized	0.4–0.5	1–19 6	0.05–10 3.95	0.01–1.5 0.19	0.01–0.6 0.07	≤5
Sieroszowice	8	reduced	0.34–0.50	117–3991 518	0.01–13 5	0.01–1 0.2	0.10–2.0 0.42	2.0–45.2 12.3
	5				0.74–2.10 1.42	0.05–0.16 0.09	0.07–0.14 0.12	2.5–53.0 22.0
Flotation concentrate Polkowice	5							
Gravity concentrate Polkowice	5				4.0–56.2 17.3	0.10–0.81	0.10–25.0 4.91	5.0–84.7 32.2

n – number of analyses.

2. The second case occurs when the redox interface is crossing stratigraphic boundaries. The oxidized side of redox boundary is spotted with red stains of haematite, which makes the interface well visible on faces of mine workings. Such development occurs in Sieroszowice Mine (Kucha et al., 1993), locally in the Lubin West or Polkowice East (Kucha, Pocheć, 1983). The largest occurrence of such development is located in the Polkowice West (Piestrzynski et al., 1996). The total thickness of the discussed redox interface horizon reaches 1.5 m., although in the Sieroszowice Mine it may locally attain greater thickness which results in very strong

dilution of pay metals content. The interface is usually marked by an increased uranium content on the reduced side.

Mineralogical, geochemical and textural signature of the oxidized and reduced sides of the redox boundary is different:

- Reduced side of redox horizon – has much smaller thickness than oxidized counterpart which varies from 0.03 to 0.4m. (Table 3). The pay metal content is distinctly higher (Table 3), but known horizontal extension is much smaller than in the case of oxidized portion. The copper content varies between 0.2–0.8 wt. % (Kucha, 1982). Main minerals observed are: covellite, Ni-Co arsenides, castaingite, Cu-Bi sulphides, native Bi, graphite, continuous series of native silver-gold (electrum), pay metal bearing thucholite which locally may be a main mineral, Pd arsenides PdAs₂, Pd₃As₅, Pd₂As₃, Pd₅As₂, Pd₈As₂S, Pd₃As vincentite, (Ni, Pd)₃As₄, PdCu (As, S)₆, and Pd₈As₆S₃ (Kucha, 1975, 1984), and up to 5.50 wt. % of Pd in nickel diarsenides. Characteristic non opaque minerals are: white phosphate, β-boracite (Kucha, 1983), and fine euhedral quartz.

Table 4. Chemical composition of plumbian gold from the Lubin Mine (wt. %)

No.	Cu	Ag	Au	Hg	Pb	Total
96/E5	≤0.08	33.81	43.54	1.39	22.00	100.74
96/F1	≤0.09	32.93	42.89	1.12	22.83	99.77
96/F2	≤0.09	33.92	43.28	0.41	22.53	100.64

Table 5. Chemical composition of palladian gold from the Lubin Mine (wt. %)

No.	Cu	Pd	Ag	Pt	Au	Hg	Total
96/C1	1.53	0.15	83.11	0.21	0.50	14.82	100.32
96/D1	0.42	4.16	15.94	0.46	78.91	0.99	100.88
96/D2	0.37	0.19	14.20	0.49	85.56	≤0.10	100.81
96/D3	0.55	4.99	11.49	0.79	81.05	0.83	99.70
96/E1	≤0.09	3.73	30.45	0.55	38.62	3.78	100.11
96/E4	0.34	3.00	12.47	1.33	78.69	6.04	101.87
96/E7	0.30	6.89	17.90	1.27	73.60	≤0.10	99.96

- Oxidized side of redox horizon – has much greater thickness than reduced counterpart varying from 0.3 to 1.5 m. (Table 3). The pay metal content is distinctly lower (Table 3), but known horizontal extension is much larger than in the case of oxidized portion (Piestrzynski et al., 1996). The copper content is well below 0.5 wt. %. Main minerals observed are: gold of high fineness (92–98wt. % of Au), palladian gold (Table 4), plumbian gold (Table 5), native Pb, clausthalite, PdBi sobolevskite (Kucha, 1981), two-phase gold (Kucha, Pocheć, 1983), Pd arsenates PdAsO₄ and Pd₂AsO₄ (Table 6), relicts of kerogen, and most of all haematite.

Locally trace amounts of covellite and chalcopyrite are observed. One of characteristic minerals are also gypsum with red internal reflections and strontianite SrSO_4 .

- Within oxidized side of the redox horizon microscopic redox interfaces are developed. They occur around relicts of thucholite. At first during replacement of pay metal rich thucholite noble metal minerals are precipitated at the boundary between organic matter and replacive calcite. If progress of replacement (oxidation) continues than in the massive calcite with fine haematite only minute relicts of thucholite and dispersed native gold, clausstahlite, Pd arsenides and arsenates are visible. This indicates that the redox interface was advancing on pre-existing reduced sediments and ore minerals (Kucha, 1981).

Table 6. Chemical composition of palladium arsenates (wt. %/mol), Lubin Mine

	S	Co	Ni	Cu	As	Pd	Ag	Pt	Au	Bi	Σ
81/B4a	≤0.06	0.30	0.47	0.73	30.11	37.50	2.10	0.73	0.43	0.80	73.17
		0.0127	0.0199	0.0285	1.0000	0.8767	0.0484	0.0093	0.0054	0.0095	
33/6c	0.90	0.25	1.80	3.50	19.60	57.10	2.80	≤0.08	0.88	≤0.09	86.83
	0.0969	0.0146	0.1057	0.1901	0.9031	1.8520	0.0895		0.0154		
42/A2	1.20	0.40	4.20	0.55	19.60	51.20	7.70	≤0.08	≤0.08	≤0.08	84.85
	0.1251	0.0227	0.2393	0.0289	0.8749	1.6087	0.2386				
42/B1	1.10	0.37	0.54	1.00	19.70	47.10	10.40	0.50	0.72	≤0.08	81.43
	0.1154	0.0211	0.0309	0.0529	0.8846	1.4887	0.3243	0.0086	0.0123		
55/A4a	0.13	0.35	0.90	≤0.05	21.50	53.10	5.10	0.50	2.90	≤0.08	84.48
	0.0139	0.0204	0.0527		0.9861	1.7143	0.1624	0.0088	0.0505		
55/A7	≤0.06	≤0.05	3.00	≤0.05	22.65	51.30	3.40	0.55	1.40	0.70	83.00
			0.1690		1.0000	1.5943	0.10542	0.0093	0.0235	0.0111	

Inclusions of solid hydrocarbons in gold and inclusions of gold in solid hydrocarbons, Maldon, Australia

The entire range in ratios of native gold to solid organic matter may be observed in intergrowths of these two substances in the different deposits under study.

“Brown gold” with reflectivity of 30–40% in air occurs in fractures and voids in FeAs_2 at Maldon. It contains 81–83 wt. % Au (Table 7). The balance consists of C, 1–2 wt. % of Fe, S and traces of Cl, Sb and Bi. Another type of gold found here is “dark gold” with reflectivity of about 25% in air. It contains 90 wt. % Au and much finer inclusions of solid hydrocarbons than “brown gold”. Characteristically both of these types of gold are silver-free (Table 7). The true nature of brown gold and dark gold can not be revealed in reflected light, but under the higher magnification of SEM it becomes obvious that they consist of fine intergrowths of two phases: bright gold and dark solid organic matter. Infrared spectra collected with an infrared microscope from “brown gold” indicate that the solid organic matter in gold is composed mainly

of conjugated benzene rings with short aliphatic additives, and some carbonyl groups as well. The proportion of metallic gold to solid organic matter varies from 50 to 80 vol. %. The two substances are so tightly intergrown as to suggest simultaneous precipitation of both from the same fluid. “Brown” and “dark” gold has been observed in fractures and voids in löllingite. The FeAs₂ host is separated from quartz by a siderite rim several tens to several hundredths µm wide which contains small inclusions of metallic gold. Siderite matrix free of visible gold may still contain Au at a level of 0.09 wt. %. It is possible that gold intergrown with solid hydrocarbons and siderite with minute inclusions of native gold may be genetically linked. Mechanism would be similar to this operating in Kupferschiefer at the redox interface – oxidation of gold tightly intergrown with solid hydrocarbons after oxidation (replacement) may be converted into siderite full of small gold inclusions.

Table 7. Chemical composition of “brown gold” (reflectivity in air 36%) No. 7A3 – 7A5a, and “dark gold” (reflectivity in air about 25%) No. 7A5b – 7A5d, Maldon, Vic., Australia (wt. %)

	Al ₂ O ₃	SiO ₂	K ₂ O	Cl	S	Fe	Ag	Sb	Au	Bi	C _{diff}	C _{meas.}
7A3	0.08	0.18	≤0.01	0.14	1.18	1.67	≤0.01	0.16	81.52	0.15	14.92	15.0
7A4	0.10	0.20	0.04	0.12	1.22	1.60	≤0.01	0.12	80.40	0.15	16.05	15.0
7A5	0.12	0.20	0.05	0.09	1.16	2.08	≤0.01	0.08	79.22	0.31	16.69	14.5
7A5a	0.09	0.22	0.05	0.11	1.20	1.93	≤0.01	0.10	80.27	0.27	15.76	15.5
7A5b	0.10	0.20	≤0.01	0.12	0.50	0.81	≤0.01	0.05	89.50	0.30	8.42	9.0
7A5c	0.10	0.20	≤0.01	0.20	1.00	1.01	≤0.01	≤0.01	90.03	0.10	7.36	9.0
7A5d	0.15	0.22	≤0.01	0.16	1.12	1.50	≤0.01	0.10	89.88	0.18	6.69	6.0

PAY METALS ASSOCIATED WITH SILICATES

In gold deposits of greenstone belt type native gold is often associated with chlorites. Even gold residing in quartz veins cutting through greenstones contain chlorites well visible under microscope as veinlets and/or nests. Usually chlorite content in quartz positively correlates with gold grade. In some deposits native gold occurs as inclusions in chlorites. Also larger gold grains may contain chlorite inclusions. Such phenomena were observed in Maldon, Vic., Australia, in Barramiya, Eastern Desert, Egypt and in Barberton, Transvaal, South Africa.

Inclusions of As-chlorites in gold and inclusions of gold in chlorites, Maldon, Australia

Clean quartz veins at Maldon contain little gold (Moon, 1987). Most gold occurs in dark patches, nests, veins and veinlets composed mainly of chlorites, with smaller amounts of biotite and muscovite, which cut through quartz veins. Under the microscope chlorites are also visible as nests and veinlets cutting through earlier ore minerals. Chlorites are finely intergrown with gold, and form myrmekitic intergrowths with metallic gold. On the other hand, chlorite nests and veins in quartz contain fine inclusions of native gold and larger grains of FeAs₂. Secondary, later chlorite veins are free of visible gold.

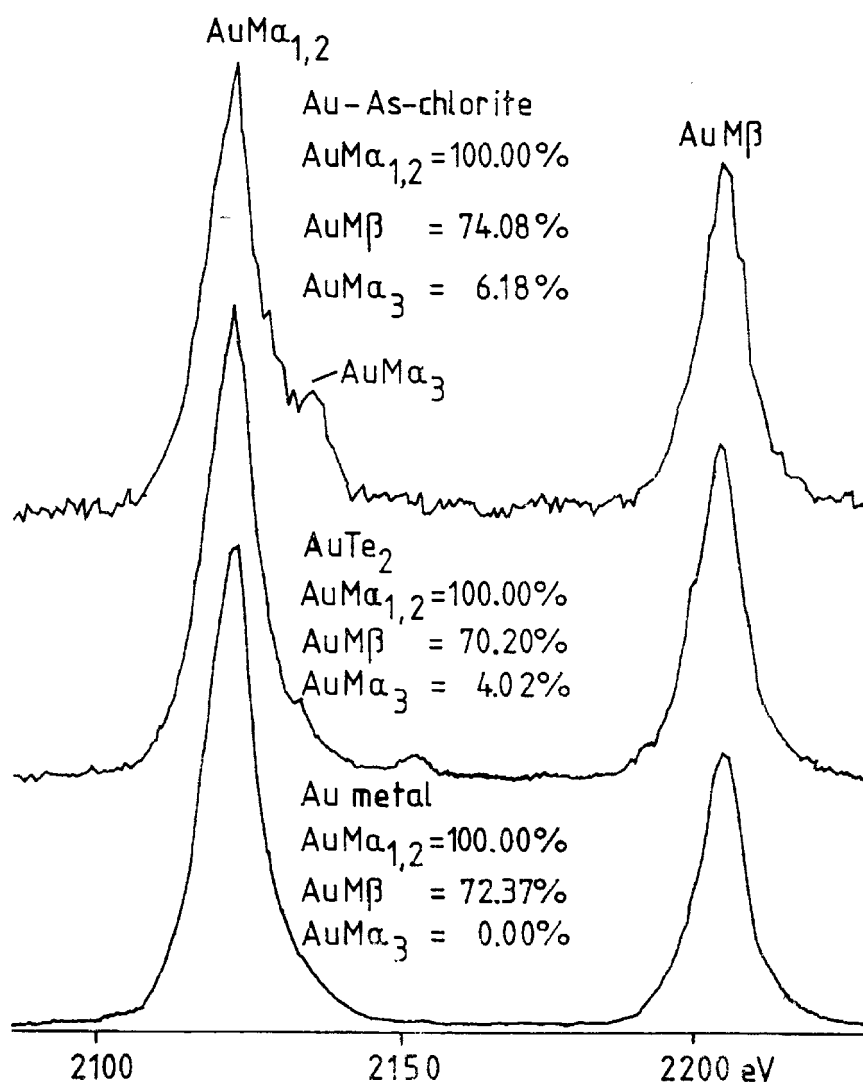
Table 8. Microprobe composition of As-chlorites tightly intergrown with gold, Maldon, Vic (wt. %/mol)

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	MnO	FeO	SO ₃	Au ₂ O	As ₂ O ₃	Cl	H ₂ O
7B18e	2.38	5.55	5.98	28.95	0.64	0.38	≤0.02	≤0.02	12.04	0.20	3.66	28.91	0.50	10.81
light	0.5418	1.9429	0.8268	6.7982	0.0959	0.0959			2.3648	0.0353	0.1256	2.0615	0.1990	8.9680
7B18e2	2.31	5.25	5.25	28.14	0.84	0.70	≤0.02	≤0.02	11.42	1.20	8.31	24.95	0.68	10.95
light	0.8488	1.8823	0.7445	6.7701	0.1287	0.1807			2.2972	0.2168	0.2920	1.8230	0.2776	9.3074
7B18e1	1.76	6.78	6.45	33.31	0.80	0.23	≤0.02	0.18	11.81	0.85	3.52	23.79	≤0.02	10.52
light	0.6280	2.2768	0.8569	7.5032	0.1150	0.0555		0.0338	2.2254	0.1435	0.1164	1.6271		8.3726
7B18d	0.59	4.57	6.42	32.14	0.62	0.39	0.17	0.19	15.32	0.79	2.10	21.04	≤0.02	15.66
dark	0.2031	1.4383	0.7991	6.7845	0.0837	0.0888	0.0266	0.0342	2.7042	0.1256	0.0647	1.3483		11.6784
7B18 1	0.65	6.86	6.53	34.62	0.68	0.36	0.08	≤0.02	17.44	≤0.05	≤0.05	22.23	0.19	10.36
dark	0.2332	2.2733	0.8548	6.3966	0.0948	0.0855	0.0134		3.2416			1.5013	0.0721	8.1358
7B18	1.41	7.21	5.41	31.21	0.78	0.26	≤0.02	0.15	15.30	≤0.05	0.73	17.77	0.71	19.06
dark	0.2764	2.1782	0.6465	6.3239	0.1010	0.0560		0.0256	2.5921		0.0219	1.0933	0.2438	13.6443

Formula has been calculated based on 36 (O, OH).

Chlorites have characteristic chemical signatures which depends on their paragenesis. Young chlorite veinlets cutting older minerals contain less than 0.49 wt. % of As₂O₃ and are free of gold. Older chlorite veinlets contain inclusions of native gold. Away from gold inclusions these older chlorites contain from 0.45 to 1.19 wt. % As₂O₃ and from ≤0.02 to 0.46 wt. % Au. Close to gold grains they contain from 1.56 to 2.21 wt. % As₂O₃ and from 0.30 to 0.54 wt. % Au. The most striking composition is shown by chlorites tightly intergrown with gold. They are As chlorites containing from 17.77 to 28.91 wt. % As₂O₃ and from 0.20 to 8.31 wt. % Au₂O and 0.20 to 1.20 wt. % SO₃ (Table 8). As always in research on geochemistry of *invisible* gold there is a question on chemical status of gold in the investigated chlorites. The gold content is very high yet no metallic gold inclusions are seen under SEM. Gold bearing chlorites in reflected electrons of SEM show two varieties: one darker with gold content (2 wt. % of Au, and another brighter with gold content between 2 and 8 wt. %. X-ray emission spectra of AuMβ and AuMα, AuMβ/AuMα ratios, and fine structure

of gold standards of metallic gold with valency 0, and AuTe_2 with gold valency +1 suggests that As chlorite (Table 8, 7B18e2) containing 7.99 wt. % of gold is chemically bound to chlorite structure. It shows characteristic split of the $\text{AuM}\alpha$ line interpreted as a resolved $\text{AuM}\alpha_3$ line (see Fig) which is similar in position and intensity to AuI_3 standard adsorbed on activated carbon. This component was observed in Au-As-chlorite at both 23 and 16 kV. These differences are large enough to argue a different chemical status of gold in Au-As-chlorite as opposed to AuTe_2 and metallic gold (see figure).



Normalized X-ray emission spectra of $\text{AuM}\alpha$ and $\text{AuM}\beta$ region in standards metallic gold Au 100%, AuTe_2 (synthetic), and in Au-As-chlorite containing 7.99 wt. % Au. Emission efficiency is

normalized to AuM (1,2 taken as 100%. Au-As-chlorite shows a distinct AuM (3 component barely visible in AuTe₂ (Au valency +1), and absent in metallic gold (Au valency 0)

Arsenic valency, as determined in the above chlorites by microprobe, is about +3.5 and gold valency varies around +3. Although these measurements should be regarded as preliminary, they suggest that gold present in chlorites is bound chemically to their structure. This may open a new chapter in gold mobility research. As-chlorites which contain above 2 wt. % Au appear distinctly brighter under SEM than As-chlorites containing less than 2 wt. % Au. The two types of As-chlorites sometimes form intergrowths with clearly visible boundaries marking the contact between the two minerals. Gold intergrown with As-chlorites is of high fineness and contains only 0.09–0.28 wt. % Ag and 0.10–0.16 wt. % Fe. The gold forms so tight myrmekitic intergrowths with As-chlorites that rapid, simultaneous precipitation from the same parent fluid is indicated.

Chlorite veinlets in gold bearing quartz veins at Barramiya contain small inclusions of metallic gold. They are As-bearing chlorites with As₂O₃ varying between 2.00 and 3.39 wt. % and gold content changing between ≤0.05 and 1.21 wt. %. Under reflected light microscope these chlorites are texturally similar to those observed at Maldon, and may be of similar origin. Chlorite inclusions intergrown with native gold in pyrite from Barberton, South Africa contain up to 2.89 wt. % of As₂O₃ and up to 0.41 wt. % of Au.

Gold associated with oxysulphides and occurrence of Au-oxysulphides

Oxysulphides were reported from the Lubin deposit, Poland (Kucha, 1990). Some of them contain detectable gold content. Oxysulphides associated with gold are present at Barberton and Pilgrim's Rest, South Africa, Comet Mine, NSW, Australia (Kucha et al., 1994) as well as in Maldon, Vic., Australia. They were reported from Veitsch, Austria, where they contain 0.12–0.21 wt % of Au (Kucha et al., 1995). So far significance of these compounds in gold metallogeny escaped attention of students of gold mineralogy and mineral processing.

Au–Cu oxysulphides from Mitterberg, Austria

Sb-fahlore in Mitterberg is a major gold carrier. This has been overlooked in the past, and subsequently fahlore has never been considered as the most attractive target during mining and mineral dressing procedures.

Five types of gold can be distinguished in the Sb-fahlore:

1. Gold (primary?) present in massive, unfractured fahlore. This gold usually forms grains only a few μm in size, rarely up to 20 μm . It is composed of (average, wt. %): Ag 25.18, Au 67.39 and Hg 7.05.

2. Native gold and electrum present in microfractures in fahlore together with pyrite, gersdorffite, chalcopyrite, cubanite and quartz. The chemical composition of gold depends on the paragenesis. Gold of the highest fineness appears together with Cu–As-bearing fractured pyrite replacing tetrahedrite. Gold associated with quartz is rich in silver.

3. $\text{Ag}_2\text{Au}_3\text{Hg}$ present in microfractured fahlore with or without chalcopyrite II and/or gersdorffite.

4. Gold with oxysulphide inclusions and intergrowths. This type of gold has distinct pink hue in reflected light and is spotted with irregular dark inclusions often of under 1 μm in size. Gold with oxysulphide inclusions has a very distinct chemical composition. It is rich in (wt. %): Cu (3.73–4.94) and Sb (3.17–4.44) but it has very low contents of Ag $\leq$ (0.03–0.14) and Hg $\leq$ (0.03–0.21), similar to such gold from Veitsch (Kucha et al. 1995).

5. Refractory gold occurs in the fahlore matrix at a distance of up to 100 μm away from gold inclusions. The content of refractory gold in such microareas may reach of 1.81 wt. % of Au with an average value equal to 0.71 wt. %. Such microareas of tetrahedrite are enriched in As, Hg, Fe but depleted in Zn and Ag.

Table 9. Microprobe composition of thiosulphate intergrown with pink gold, Mitterberg, Brander Gang, sample PR1B-3 (C) and PR1B4 (A) (wt. %/mol)

No.	S	Cl	Fe	Ni	Cu	Zn	As	Ag	Sb	Au	Hg	Pb	Total	O _{diff.}
C11a	2.47 0.0770	$\leq$ 0.10	2.21 0.0380	0.15 0.0026	4.54 0.0715	$\leq$ 0.01	0.63 0.0084	0.16 0.0015	2.68 0.0220	45.06 0.2285	$\leq$ 0.02	0.50 0.0024	58.31	41.69
C11	2.05 0.0639	$\leq$ 0.10	2.12 0.0380	0.15 0.0026	4.50 0.0708	$\leq$ 0.01	0.29 0.0039	0.08 0.0007	2.72 0.0223	65.63 0.3328	0.07 0.0004	0.50 0.0024	78.11	21.89
C12	18.31 2.0000	$\leq$ 0.10	4.48 0.2809	0.18 0.0109	14.07 0.7755	0.34 0.0182	0.35 0.0165	0.14 0.0045	3.11 0.0893	44.20 0.7849	$\leq$ 0.02	0.43 0.0074	85.61	14.39
C13	15.40 0.4803	$\leq$ 0.10	3.96 0.0709	0.52 0.0089	24.06 0.3786	0.72 0.0110	0.92 0.0123	0.06 0.0005	3.59 0.0295	40.11 0.2034	$\leq$ 0.02	0.49 0.0024	89.83	10.17
C16	9.27 0.2891	$\leq$ 0.10	4.80 0.0859	0.16 0.0027	10.84 0.1706	$\leq$ 0.01	0.53 0.0071	0.06 0.0005	3.20 0.0263	33.27 0.1687	$\leq$ 0.02	10.34 0.0499	72.47	27.53
C10	15.17 1.6588	$\leq$ 0.10	1.98 0.1241	0.200 0.119	16.94 0.9347	$\leq$ 0.01	0.46 0.0214	4.31 0.1403	11.11 0.2146	29.76 0.5291	3.75 0.0655	0.78 0.0133	84.16	15.54
A11	7.62 0.2376	11.92	1.07 0.0192	$\leq$ 0.05	23.57 0.3709	$\leq$ 0.01	0.36 0.0048	1.15 0.0107	3.77 0.0310	28.77 0.1459	$\leq$ 0.03	11.26 0.0543	89.49	10.51
A12	8.90 0.2776	7.93	1.53 0.0274	0.11 0.0019	15.69 0.2469	$\leq$ 0.01	0.33 0.0044	0.21 0.0019	7.14 0.0586	47.39 0.2403	$\leq$ 0.03	0.19 0.0009	89.42	10.58
														0.6613

Pink gold contains numerous dark inclusions with reflectivity in air of about 20%; their size varies from sub-micron up to 20 μm . Some of the oxysulphides studied surround gold grains and form dark twisted wavy veinlets cutting through the tetrahedrite. The oxysulphides discussed have gold content ranging between 33.27 and 44.20 wt. % (Table 9). Analysis C12 (Table 9) is close to the thiosulphate composition – $(\text{Au}, \text{Cu}, \text{Fe})\text{S}_2\text{O}_3$. The SK (peak shift in this compound is 0.70 (0.08

eV close to the peak position in the standard thiosulphate. Another inclusion (Table 9, C13) shows composition close to $(\text{Cu}, \text{Au})\text{S}_2\text{O}_3$ and the $\text{SK}\beta$ peak shift equal to 0.61 (0.09 eV). The Au valency measured by microprobe in the thiosulphates discussed is close to +1. Both compounds studied show a double $\text{SK}\beta$ peak and S^{6+} satellites similar to those seen in the thiosulphate standard. Therefore taking into account the chemical composition of the oxysulphides considered (Table 9) and results of the X-ray spectroscopic studies these compounds may be tentatively identified as Au–Cu- and Cu–Au-thiosulphates. Not all inclusions in gold (Table 9) show such clear stoichiometry. Because of their small size and exsolutions of nanoinclusions of metallic gold many of them represent a physical mixture of oxysulphides and metallic gold (Table 9, C11, C11a). Non-stoichiometric analyses with significant oxygen content may suggest that the process of decomposition of Au–Cu–Fe oxysulphides continued after precipitation producing a complex nano-mixture of solid native metals, sulphides, oxysulphides and oxides. The tetrahedrite matrix directly surrounding the gold with oxysulphide inclusions is enriched in As, Fe, Hg and distinctly depleted in Zn, Ag and Sb. This may suggest that the first three elements moved from the fluid phase to the solid by ion exchange, and simultaneously the second three elements moved from the solid to a liquid phase.

Oxysulphides of iron and gold from the Comet Mine, NSW, Australia

Native gold at the mine occurs in two distinct parageneses:

- gold with quartz and Bi-tellurides. Gold forms inclusions in the quartz matrix with or without Bi tellurides.
- gold with pyrite, thiosulphates, sulphates and haematite. Gold occurs as intergrowths with sulphates, haematite and pyrite with thiosulphate relics. Often gold is present at grain boundaries between haematite and sulphate and as inclusions in Fe thiosulphates, suggesting the involvement of thiosulphate in the transport and/or redistribution of Au within the orebody. Sulphates have an increased content of Pb, Cu, Zn, Al and Si (Kucha et al., 1994).

Thiosulphates are ubiquitously associated with gold at the Comet Mine, forming irregular aggregates up to 1 mm in size, being partly replaced by sulphates and haematite and also forming relics in pyrite. Two different types of pyrite are recognized. The first is euhedral and takes a clean polish, whereas the second contains numerous dark, cloudy inclusions of thiosulphates and was probably formed by the replacement of an Fe thiosulphate precursor. Microprobe analyses reveal that S, Fe and O are main components of oxysulphides studied. Main trace elements are Cu, As, Ag and Pb ranging from ≤ 0.05 to 0.85 wt. % (Kucha et al., 1994). Sometimes gold is present above detection limit as well. The $\text{SK}\beta$ emission spectra show S^{6+} and S^{4+} satellites and a double $\text{SK}\beta$ peak top indicating the presence of thiosulphates and sulphites (Kucha et al., 1994). Gold is so tightly and finely intergrown with oxysulphides that this texture will affect gold recovery.

GOLD IN SULPHIDES

Gold is present as an admixture in sulphide minerals from Lubin (Kucha, 1975, 1984). It also occurs as an admixture together with Pd and Pt in arsenides at this location (Kucha, 1984). Gold in sulphides is also found at Maldon, Bendigo, Australia, at Veitsch (Kucha et al., 1995, 1997 a, b) as well as at Mitterberg, Austria. Preliminary microprobe measurements of gold valencies in sulphides suggests that below certain concentration characteristic for each mineral gold occurs as Au +1, and above saturation limit in a given lattice it occurs as metallic submicroscopic inclusions as Au 0. In deposits of gold bearing arsenopyrite, and/or pyrite invisible gold of both types i.e. chemically bound to the lattice and minute inclusions of metallic particles may control most of gold budget. This has strong influence on choice of metal recovery technology.

DISCUSSION

Chemical status of gold in deposits discussed differs from case to case. This indicates that each of them has to be treated as an individual case to choose a proper gold and/or PGM recovery. In recent times mesothermal and epithermal deposits are becoming more and more important gold producers. Therefore advanced mineralogical and geochemical studies are getting increasingly important. They include gold valences measurements, identification of chemical status of „invisible” gold, as well as textures and microtextures of gold and gold-bearing minerals.

One of principal associations discussed in this note are associations of pay metals with organic matter. It seems to be important in the Kupferschiefer. Most of gold and PGE's associated with hydrocarbons occurs on the reduced side of the redox interface where they form thin but higher grade accumulations, but with limited lateral extension. On the oxidized side of the interface pay metals occur mainly as native metals and palladium arsenates where they form thicker but lower grade accumulations and are laterally extensive. A rough estimation of reserves on both sides of the redox interface suggests that on reduced side it may about 20–25% of reserves, and on the oxidized side remaining 75–80%. In case of mining both types will be mined together and extracted ore will have a mixed nature. Therefore, the ore processing will have to cope simultaneously with organically fixed pay metals, with pay metal minerals such as native metals, arsenides and arsenates, as well as pay metals substituted in arsenide and sulphide carriers.

Close intergrowths of native Au and Au–As-chlorites at Maldon, Australia, Barramiya, Egypt, and Barberton, Transvaal, South Africa present a new challenge for mineral processing. Properties of gold silicates are virtually unknown, also quantitative partition of gold between native gold and various mineral carriers present a challenge for mineralogical and geochemical study.

Gold thiosulphates occurring at Mitterberg, Austria open a new field of study on gold mineralogy and geochemistry. These compounds are leachable by acidic water and could be recovered by heap or bacterial leaching. This would have an extra bonus because this treatment will also recover gold substituted in sulphides, which contain up to 1.8 wt. % of Au (Kucha et al., 1977a, b).

Well conducted research on mineralogy and geochemistry of pay metals in mesothermal-epithermal deposits shall be conducted with care starting from sample preparation to avoid destruction of fragile oxysulphide minerals. Main methods of research should include high quality reflected light microscopy, EPMA, SEM, HRTM as well as microbeam techniques with very high detection limits such as SXRFA and MPIXE.

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Kucha H., Plimer I. R., Stumpfl E. F., Geochemia i mineralogia złota i metali szlachetnych w złożach mezotermalnych i epitermalnych i ich znaczenie w procesie odzysku metalu. *Fizykochemiczne Problemy Mineralurgii*, 32, 7–30 (w jęz. angielskim)

W mezotermalnych i epitermalnych złożach metali szlachetnych mineralogia i geochemia Au, Pd i Pt jest złożona. Wymienione metale tworzą domieszki izomorficzne w arsenkach Ni–Co (Lubin, Maldon), antymonkach (Maldon), siarczках (Veitsch, Mitterberg, Lubin, Maldon, Barberton), materii organicznej (Lubin, Maldon). W niektórych złożach wymienione metale tworzą własne oksysiaczki $\text{Au}_2\text{S}_2\text{O}_3$ (Veitsch, Mitterberg), związki organometaliczne (Lubin, Maldon), krzemiany (Maldon, Barramiya, Barberton), tellurki, selenki, siarczki, arsenki (Lubin) i arseniany Pd_2AsO_4 (Lubin). Obecność złota chemicznie związanego z siecią minerałów goszczących potwierdzona została obecnością Au +1 i Au +3. Tak złożona mineralogia i geochemia metali szlachetnych tworzących bezpośrednie wiązania chemiczne z siecią goszczącą powoduje trudności z odzyskiwaniem metali szlachetnych z rudy. Przeróbka takich rud wymaga najbardziej nowoczesnych badań geochemicznych i mineralogicznych w celu dobrania właściwych metod przeróbki. W przeciwnym razie straty w odzyskiwaniu metali szlachetnych mogą sięgać nawet do 50%.