Exploration for Au and PGE in the Polish Zechstein copper deposits (Kupferschiefer)

A. Piestrzyński a, Z. Sawlowicz b,*

a Department of Ore Deposits, University of Mining and Metallurgy, Mickiewicza av. 30, 30-059 Krakow, Poland
b Institute of Geological Sciences, Jagiellonian University, Oleandry Str. 2A, 30-063 Krakow, Poland

Accepted 25 February 1999

Abstract

Results of preliminary exploration for possible economic accumulations of gold and PGE in the working Cu–Ag mines of southwest Poland are presented. High contents of Au (avg. 0.5 ppm), Pt (avg. 0.2 ppm) and Pd (avg. 0.1 ppm) occur in oxidized shales and in places in the underlying sandstones. Maximum contents of Ru, Rh and Ir are 22, 12 and 2 ppb, respectively. These shales are characterized by low contents of TOC and sulphides, degraded organic matter, and lower Re-contents in comparison with typical Cu-rich shales (Au 20 ppb, Pt <5 ppb, Pd 4 ppb). Samples with high contents of Pt and Pd are typically rich in Au. Gold is present as native gold, electrum, in native silver, possibly as organometallic compounds, and in some Cu and Ag sulphides. Some of the Pt and Pd occur as diarsenides or Pt-alloys, but most occur in unknown carriers. The most promising areas in the Lubin–Sieroszowice mining district seem to be the transition zones between sulphide-rich facies and the oxidized Rote Fäule facies developed both laterally and vertically in the lower part of the shales and/or the upper part of the sandstones. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Au; PGE; Kupferschiefer; Cu-deposits; exploration

1. Introduction

Possible economically significant accumulations of Au and PGE in anoxic sediments have been reported in the past few years, including the Mo–Ni–PGE deposits in Cambrian black shales of China and Devonian black shales of the Yukon, Canada (Coveney et al., 1992), and Zechstein Cu deposits of Poland (Kucha, 1982; Sawlowicz, 1993b; Piestrzyński et al., 1996) (see also Pasava, 1993, for a review). A growing interest in the exploration for precious metals in black shales and reports on very local but high enrichments in these elements in the mining area of the Polish Kupferschiefer stimulated a detailed study. Occurrences of Au and PGE in the Permian Kupferschiefer from Germany were already reported in 1948 by Goldschmidt et al. (in Schüller, 1959). New studies from these areas reveal various concentrations in different lithological types, ranging from 43 ppb PGE in the Kupferschiefer to about 1250 ppb PGE in underlying conglomerate and overlying limestone (Pfeifer et al., 1997). In the mining area of the Polish part of the Kupferschiefer, high concentrations of noble metals (maximum values: Au 3000 ppm, Pt 340 ppm, Pd 1000 ppm and Ru 53 ppm) were described from a very local and thin layer...
(few mm to cm) at the base of the Kupferschiefer by Kucha (1981, 1982). In ores, Banas and Kijewski (1987) found maximum values of 0.21 ppm Pt, 0.63 ppm Au and 0.08 ppm Pd. A significant enrichment of Au and PGE (10 to 100 times) in bulk samples from the oxidized facies (Rote Fäule = RF), present within the mining area (Sawłowicz, 1993b), stimulated an exploration program for economically important accumulations of these metals. Data and recommendations presented in this paper are the results of a preliminary stage of research and are based on underground field observations, fire assay–ICP chemical data for bulk samples and on ore and SEM–EDS microscopy.

Three underground (700–1200 m deep) Cu–Ag mines (Lubin, Rudna, Polkowice–Sieroszowice) are in operation in the Fore-Sudetic Monocline (southwest Poland, Fig. 1). Gold and PGM’s are recovered from copper concentrates as by-products during metallurgical processes. According to the annual report of the KGHM–Polska Miedz Company, 474 kg of gold and 95 kg of Pt + Pd sludge were recovered in 1995.

2. General geology

The geology of the Lubin–Sieroszowice district was described by Oberc and Serkies (1968). The basement is composed of Proterozoic gneisses, schists, phyllites and granitoids, overlain by deformed Carboniferous conglomerates, sandstones and mudstones and by clastic Permian rocks (mainly sandstones and conglomerates). The Lower Permian red beds have been divided into lower and upper units (Klapcinski et al., 1984). The lower red beds (up to 1000 m thick) are composed of conglomerate, sandstone and mudstone and contain in some places bimodal volcanics (rhyolites, trachybasalts and rhyolitic tuffs) (Ryka, 1981; Pokorski, 1981). The upper
unit (up to 500 m thick) contains mostly fine-grained sandstone with local conglomerates. In the upper part of this unit, the Weissliegende sandstone (up to 45 m thick), the Kupferschiefer and evaporitic cyclothems (limestones, dolomites, anhydrites, rock salts and clays) (up to 200 m thick).

A metal-bearing lower Zechstein black shale formation (Kupferschiefer — T1) covers about 54.5% (170,000 km²) of Poland, while the Lubin–Sieroszowice polymetallic ore deposits on the Fore-Sudetic Monocline embrace only 0.4% of the total Kupferschiefer area. Economic Cu–Ag mineralization occurs at the border between Lower and Upper Permian sediments in the southwestern part of the Polish Permian basin (Fig. 1).

The Kupferschiefer is characterized by highly variable thickness, with an average of ∼0.27 m in the ore district (Mayer and Piestrzyński, 1985). It is composed of clay (illite), dolomite and calcite, organic matter and terrigenous quartz and feldspars. The shale was deposited in deep and shallow shelf environments (Oszczepalski and Rydzewski, 1987). The ore zone is 0.4–26 m thick and contains three types of ore: the black shale (Kupferschiefer), the underlying white sandstones (Weissliegendes), and the overlying Werra carbonates. It transgresses the underlying rocks at low angles (avg. 6°). Within the Kupferschiefer, oxidized facies (Rote Fäule) are known from several places, one of the largest occurrences being in the western part of the deposit (Rydzewski, 1978) where it forms the western border of the Lubin–Sieroszowice area.

To date, 115 ore minerals have been recorded in the mining area, with the main assemblages consisting of chalcocite–covellite group, bornite, chalcopyrite, pyrite and tennantite (Mayer and Piestrzyński, 1985), forming disseminations, veinlets, lenses, veins, spots and massive ores.

The present controversial genetic models of Cu mineralization range from syn-diagenetic to epigenetic, depending mainly on the type of mineralisation considered (Wedepohl, 1964, 1994; Jowett, 1986; Wodzicki and Piestrzyński, 1994). The mineralisation process was probably complicated and long-term, lasting from the deposition of the Kupferschiefer (dispersed mineralisation) (Sawlowicz, 1990, 1992) to the deposition of massive ore-bearing sandstone in the Middle–Late Jurassic (Sawlowicz and Kosacz, 1995). Oxidized chlorine-rich brines formed in the underlying thick molasse rocks and entered the Kupferschiefer sulphide-rich bed probably in the Rote Fäule areas during several pulses (Rentzsch et al., 1976; Jowett, 1986; Oszczepalski, 1989; Wodzicki and Piestrzyński, 1994).

3. Field investigations of the noble metal zone

Exploration is focused on economically barren zones (avg. Cu <1.1%) within Cu-rich areas. The typical lithology of the sections containing noble metal occurrences is shown in Fig. 2. The red-brown and grey shales are characterized by low contents of Cu and organic matter (Sawlowicz, 1991), but native gold was observed on the surface of crushed and cut red shale samples. The transition zone between Cu-rich and Cu-poor zones is observed both laterally and vertically (Oszczepalski, 1989; Speczik et al., 1997). Its most common feature is the presence of red coloured layers or spots in sandstone (Fig. 3), shale or dolomites, or greyish layers in the black shales (Fig. 4). In some areas a red layer of dolomitic sandstone and shale is present. The width of the transition zone varies from several cm to ∼1 m. It continues horizontally or diagonally, crossing all lithologies (Fig. 2) for up to a few hundred metres. Macroscopic sulphides are rare, although some hand specimens of red shale contain 1-cm-long diagonal veinlets with chalcopyrite, bornite and galena, and vertical veinlets of pyrite occur in red sandstone.

Au–PGE-rich sections occur locally within mapped Cu-poor areas although it is not clear if a Cu-rich zone occurs above. They have never been found below massive copper-rich accumulations in sandstones.

The main sampling method for noble metals involves the collection of ∼1 kg samples taken in vertical profiles (every 20 cm or less in the case of changes in lithology), crushing, milling and splitting to 30 g. Au, Pt and Pd were determined by fire assay and ICP. Selected samples of 50 g were are analyzed for Au, Pt, Pd, Rh, Rh, Os and Re by INAA after FA–NiS preconcentration (ACTLABS Canada).
Fig. 2. Cross-section through the contact between Cu-rich and Rote-Fäule zones, Polkowice mine: 1 = white sandstone; 2 = carbonate-rich red sandstone; 3 = carbonate-rich brownish sandstone; 4 = red shale; 5 = black shale; 6 = dolomite; 7 = red spots.

Fig. 3. Weissliegendes sandstone with red spots, underlying dark shale (Kupferschiefer) and dolomites (badge = 3 cm).
4. Geochemistry and mineralogy

High concentrations of Au (max. 100 ppm, avg. 0.5 ppm), Pt (max. 2.5 ppm, avg. 0.15 ppm) and Pd (max. 4 ppm, avg. 0.08 ppm) (Table 1) occur in the oxidized facies (RF) composed of shales, and locally in overlying dolomites and in the uppermost part of the underlying sandstones (Fig. 2). A significant correlation between the noble metal distribution and RF oxidation front has recently been found by Pfeifer et al. (1997). Maximum contents of Ru, Rh and Ir in a few samples studied are 22, 12 and 2 ppb, respectively. These shales are characterized by low contents of TOC (2–5%), sulphides (0.2–0.7% S), degraded organic matter and Re (1 ppm) in comparison with the Cu-rich shales (Table 1). Samples with high contents of Pt and Pd are typically rich in Au, but the reverse relationship is not so obvious. The highest enrichment is observed for platinum, with Pd/Pt ratios of 1.3 for rich samples (above 500 ppb

Table 1
Contents of Au, Pt, Pd and some other elements in the Lubin–Głogów mining district

<table>
<thead>
<tr>
<th>Facies</th>
<th>Au (ppb)</th>
<th>Pt (ppb)</th>
<th>Pd (ppb)</th>
<th>TOC (%)</th>
<th>S (%)</th>
<th>Cu (%)</th>
<th>Re (ppm)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-rich</td>
<td>48</td>
<td>8</td>
<td>7</td>
<td>6.5</td>
<td>2.2</td>
<td>8.3</td>
<td>5.3</td>
<td>25</td>
</tr>
<tr>
<td>Secondary oxidized Roß Faule</td>
<td>460</td>
<td>145</td>
<td>74</td>
<td>1.8</td>
<td>0.2</td>
<td>0.8</td>
<td>1.5</td>
<td>56</td>
</tr>
<tr>
<td>Lithological types:*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zechstein limestones (dolomites)</td>
<td>50</td>
<td>2</td>
<td>1.5</td>
<td>0.5</td>
<td>nd</td>
<td>2.5</td>
<td>nd</td>
<td>27</td>
</tr>
<tr>
<td>Kupferschiefer (shale)</td>
<td>2500</td>
<td>186</td>
<td>88</td>
<td>6.5</td>
<td>nd</td>
<td>7.1</td>
<td>nd</td>
<td>23</td>
</tr>
<tr>
<td>Weissliegendes (sandstones)</td>
<td>500</td>
<td>54</td>
<td>30</td>
<td>0.2</td>
<td>nd</td>
<td>0.2</td>
<td>nd</td>
<td>19</td>
</tr>
</tbody>
</table>

n = number of analyses; nd = not determined.
* From Pfeifer et al. (1997).
Fig. 5. Comparison between gold analyses by FA–ICP (30 g sample) and INAA (~5 g sample).


Au, Pt and Pd) and 2.2 for those low in Au, etc. (<500 ppb). There is no correlation between noble metals and other elements, except rhenium. The Ag-content in these samples is low. In sections rich in noble metals, the maximum concentrations of Au are typically present in the uppermost part of the profile and those for Pd are in the lowermost part. However, it must be stressed that exceptions to this are locally common. A typical cross-section through a transition zone is shown in Fig. 2.

A few samples with red spots were split into red spotted material and grey host rock. Contents of Pt and Pd were higher and contents of Au lower in the red spots, suggesting a close relationship between haematite and Pt and Pd.

Areas with high concentrations of Au, Pt and Pd are present mainly in the southwestern part of the mining district, proximal to the extensive Rote Fäule area (Fig. 1). Individual samples with abnormal concentrations of Au and PGE were also found in other small secondary oxidized areas within other parts of the mining district.

A comparison between different methods of gold determination was carried out to find a reliable, reasonably priced, method of analysis. About 70 samples were determined by ICP with FA preconcentration (30 g sample) and INAA without preconcentration (5–10 g) (Fig. 5). Significant differences of up to 1000% were found for individual samples, although with a statistically large population, the difference is less marked. The average Au-content for 70 samples was 2.2 ppm with INAA and 3.2 ppm with FA–ICP. Thus, for preliminary geochemical mapping, the less-costly INAA analyses are sufficient. Reproducibility of FA–ICP using only three samples of shale and sandstone splits was poor, with differences up to 2000% for a sample with low Au-contents (Table 2).

Gold is present as native gold, electrum, as isomorphic substitutions in native silver, and in some Cu and Ag sulphides (Kucha, 1974, 1976; Salamon, 1976; Kucha and Piestrzyński, 1991; Piestrzyński et al., 1996; Speczik et al., 1997). Some Pt and Pd occur as Pd arsenides or Pt-alloys, but most are within

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au (ppb)</th>
<th>Pt (ppb)</th>
<th>Pd (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEB1</td>
<td>1722</td>
<td>1496</td>
<td>127</td>
</tr>
<tr>
<td>SPEB1</td>
<td>3747</td>
<td>1583</td>
<td>288</td>
</tr>
<tr>
<td>SPEE3</td>
<td>99</td>
<td>17</td>
<td>8</td>
</tr>
<tr>
<td>SPEE3</td>
<td>5</td>
<td>&lt;5</td>
<td>&lt;3</td>
</tr>
<tr>
<td>SPI2</td>
<td>17</td>
<td>31</td>
<td>6</td>
</tr>
<tr>
<td>SPI2</td>
<td>15</td>
<td>&lt;5</td>
<td>&lt;3</td>
</tr>
</tbody>
</table>
unknown carriers (Kucha, 1976, 1982). Mineralogical studies of noble-metal-rich ores indicate two paragenetic groups. The first is composed of native gold, haematite and covellite. This gold is of very high fineness (Piestrzyński et al., 1996). The second group consists of gold, electrum, digenite, half-borne, and covellite, occurring in the uppermost part of the Weisliegende sandstone and in the transition zone of the Kupferschiefer. Electrum is the more common gold mineral; and the native gold has a lower fineness (~87%). In addition to Pd-arsenides, traces of Pt and Pd were found in some gold-bearing minerals such as haematite and bornite, and in native gold (Piestrzyński and Pieczonka, 1997).

Based on ore microscopy, there is a correlation between the number of gold grains and the chemical analyses for Au, and this method should be applied as a rough back-up to the analyses as well as for recognizing the character of its occurrences.

5. Genesis of precious metal enrichments

Au and PGE enrichments are relatively common in shaly and organic-rich sediments associated with thick complexes of sandstones and conglomerates (often with volcanics) or carbonates (Kupferschiefer; Zambian Copper Belt — Unrug, 1985; Jedwab, 1988; Cu–Ag mineralization in the Proterozoic of Namibia — Borg et al., 1988). Organic-rich, often pyritic-rich, sediments serve as a low-permeability redox barrier. The transport of Au and PGE in solution is now generally accepted especially in view of increasing experimental data. These noble metals can be transported as chloride, cyanide or thiosulphate ions (Mountain and Wood, 1987, 1988; Wood et al., 1989; Jaireth, 1992) and a significant role in transport can also be played by organic acids (Wood, 1990; Bowles et al., 1994a,b). The precipitation of Au and PGE from oxidizing solutions could result from higher pH and Eh potential at the redox barrier of the Kupferschiefer black shale. One of the main reducing factors was probably the organic matter (Kucha, 1982; Sawlowicz, 1993b). The reduction of PGE by sedimentary matter has been described by Baranger et al. (1991) and Bowles et al. (1994a). Van der Flier-Keller (1991) suggested precipitation of PGE from groundwaters from an ultramafic complex at the contact with a reducing environment of coal. There is a general agreement that the metals in the Kupferschiefer were carried in oxidizing, chloride-rich solutions which leached underlying red beds and volcanics (Rentzsch et al., 1976; Wodzicki and Piestrzyński, 1994). The Rote Fäule facies were probably the areas where such solutions entered the Kupferschiefer (Rentzsch et al., 1976), and expanded during the diagenesis (Oszczepalski, 1989), similar to oxidation rolling fronts in the uranium deposits of Wyoming. Subsequent processes including dissolution of Cu and Cu–Fe sulphides, degradation of organic matter coupled with its sulphidation (Sawlowicz, 1993a), dissolution and reprecipitation of carbonates (Sawlowicz and Halas, 1990), formation of sulphates and thiosulphates (Kucha and Piestrzyński, 1991), created specific physico-chemical conditions in such areas. The transition zone between the Rote Fäule zone (oxidation) and Cu-rich zone (reduction) was the place where very complex reactions leading to Au and PGE concentration could proceed.

Two mechanisms of enrichment can be envisaged: (1) release of Au and PGE from earlier deposited Cu–Fe sulphides during an enlargement of Rote Fäule areas and their deposition at the oxidation/redox front; (2) late stage introduction of Au–PGE-rich solutions and deposition in the transition zone.

6. Exploration model

Documented areas of low Cu-contents bordering or within Cu-rich areas should be the first choice in the search for noble metals. The most promising target seems to be the transition zone between the sulphide-rich facies and the typical oxidized Rote Fäule facies which developed both laterally and vertically (5–50 cm), in the lower part of the shales and/or the upper part of the sandstones. Primary oxidized facies which were never mineralized do not seem to be promising for exploration.

Features significant for precious metal exploration in the Kupferschiefer are as follows:

(1) Low content of Cu and lower contents of TOC, S and Re in shales (usually clay–carbonate shales).

(2) Dark-red or brownish colour of shales and/or
sandstone, typically below Cu-rich black shales (occasionally shales are macroscopically black, but numerous red internal reflections from finely dispersed haematite are visible under the ore microscope).

3. Presence of sulphide relics, mainly chalcopyrite and covellite.

4. Presence of coarse grains of haematite of hydrothermal origin in red coloured strata.

5. Red spots and poor Cu mineralization in the upper part of sandstones.


7. Vertical separation of Au and Pt, Pd, with Au enrichment overlapping Cu-mineralization.

We suggest that before carrying out a costly stage involving Au, Pt and Pd analyses, samples should be examined by ore microscopy, Cu analyses and simple organic geochemical analyses (solvent extraction and IR analysis of aliphatic versus aromatic bands, Sawlowicz, 1989). This procedure should help in delineating a transition zone.

In addition, very local (on mm–cm scale) occurrences with high concentrations of precious metals may be found in samples with high radioactivity, and enrichments in Hg, Ag, Bi, As, P, and organic matter, and with low Cu contents. A radiometric survey could be useful in such cases.

It is worth to stress that a possible future exploration program must be carried out selectively since the Au–PGE-rich zones are Cu-poor. Separate processing may also be necessary due to different enrichment overlapping Cu-mineralization.

Acknowledgements

The assistance of the mining geologists during field studies is gratefully acknowledged. The study was supported by KBN grant to ZS (0112/P2/07/94).

References


