Gold mineralization within contact-metamorphic and shear zones in the “Zloty Jar” quarry — the Zloty Stok As-Au deposit area (Sudetes)

Mineral paragenesis of gold mineralization in the “Zloty Jar” quarry has been formed during three separated stages. The stage I of skarn-like mineralization was due to metasomatic processes developed in the exocontact zone of the Variscan Klodzko – Zloty Stok granodiorite massif. Preliminary results of primary fluid inclusion studies demonstrate that the earliest stage with pyroxene, garnet and scheelite have low salinity fluids (4.9–5.2 wt. % NaCl equiv.) at temperatures between 464–480°C and pressure below 1.4 kbar. During later phases of this stage widespread gold-bearing ore mineralizations (loellingite, arsenopyrite) were formed. Definitely most gold occurs as fine-dispersed submicroscopic particles within ore minerals in calc-silicate and black serpentinite rocks (up to 10 and 29 g/t, respectively). Younger gold-bearing stages (II and III) revealed a succession of cycles of brittle deformation and hydrothermal infill of mineralizing fluids connected with development of shear zones. Th of primary inclusions of quartz veins containing ores with native gold were determined at 220–280°C and salinity 4–10 wt. % NaCl equiv. “Visible” gold was found as inclusions from 5 to 50 μm in size among Ni-Fe-Co sulphoarsenides, sulphides and as individual micro-grains in quartz ± calcite veinlets. In the youngest described gold-bearing stage (III), inclusions of electrum and gold-bismuth myrmekites in sulphoarsenides were commonly observed. Processes of redistribution of primary gold on a local scale from loellingite-arsenopyrite mineralization, and on regional scale from metavolcanic rocks, were widely developed. Precipitation of “visible” gold within sulphoarsenides and sulphides was carried out by sulphur-bearing solutions at 350–250°C and near neutral — to alkaline environments, with dominant role of hydrosulphide complex Au(HS)₃⁻. Main sources of metals were probably the metal preconcentrations in volcano-sedimentary rocks with mantle contribution (Pt, Pd) (7) which later underwent mobilization due to formation of granitoid intrusions and development of shear zones.

INTRODUCTION

The “Zloty Jar” (Golden Creek) quarry is located in northern part of the Góry Złote Mts. (Sudetes, SW Poland) between old mining fields of the Zloty Stok As-Au deposit (Fig. 1). The big gold rush took place between 1545 and 1549 when over 190 mining workings were
Fig. 1. Geological sketch of the study area (according to S. Cwojdzinski, 1974, 1975; L. Finckh, G. Fischer, 1938; L. Sawicki, 1956) with location plan of principal workings of the Zloty Stok As-Au mine (according to the mines report, L. Baldys, 1954) marked by the author

1 - blastomylonitic schists and biotite gneisses; 2 - streaky quartz-feldspar gneisses; 3 - amphibolites; 4 - marbles and calc-silicate rocks; 5 - Haniak gneisses; 6 - Jawornik granodiorites; 7 - Klodzko - Zloty Stok granitoids; 8 - Quaternary sediments (undivided); 9 - faults; 10 - mine workings; 11 - the "Zloty Jar" quarry; A - Emanuela drain adit; B - Barbara gallery; C - Gertruda conveyor road; D - Krzyżowa gallery; E - Książęca gallery; F - Czama gallery; G - Nowa gallery; SMF - Sudetic Marginal Fault

Szkic geologiczny badanego obszaru (według S. Cwojdzinskiego, 1974, 1975; L. Finckha, G. Fischera, 1938; L. Sawickiego, 1956) z planem sytuacyjnym głównych wyrobisk górniczych kopalni As-Au w Zlotym Stoku (według dokumentacji kopalnianej L. Baldysa, 1954) zaznaczonym przez autora

1 - blastomylnotyczne łępy i gneisy biotytowe; 2 - kwarcowo-skalenio we gneisy smugowane; 3 - amfibolity; 4 - marnyce i skały wapieno-krzemianowe; 5 - gneisy haniackie; 6 - granodiority jawomickie; 7 - granitoidy klodzko-zlotostockie; 8 - osady czwartorzędnego (nierozdzielone); 9 - uskoki; 10 - wyrobiska kopalnicze; 11 - kamieniołom "Zloty Jar"; A - szyb odwadniający Emanuela; B - sztolnia Barbara; C - droga transportowa Gertruda; D - sztolnia Krzyżowa; E - sztolnia Książęca; F - sztolnia Czama; G - sztolnia Nowa; SMF - sudecki uskot brzęczy
Gold mineralization in the Zloty Stok As-Au deposit operating from which about 140 kg of gold was obtained annually (L. Baldys, 1954). Since the beginning of XVIII c., gold production gave place to production of arsenic. As an example, rocks exploited in XVI c. were so highly mineralized with arsenic compounds that approximately contained 40 g/t of Au (L. Baldys, 1954). In 1514, arsenic ores with 11.4 g/t of Au and in 1744 with 17 g/t of Au were exploited (T. Dziekoński, 1972). During the Inter- the World Wars period, content of gold in 1% arsenic ores was at the level of 0.5 g/t of Au (L. Baldys, 1954). As economic 7% arsenic ore with content of gold from 3 to 5 g/t was considered (L. Baldys, 1954). It follows from the known documents that since 1481 to 1944 about 3 800 000 t of arsenic ores and 9–13 t of gold were exploited in the region (L. Baldys, 1954). After the Second World War economic arsenic ores had an average arsenic content up to 6% and yielded 3.2–3.5 g/t of Au (L. Baldys, 1954). Gold was chemically identified in loellingite up to 30 g/t of Au and in arsenopyrite from 5.2 up to 34.8 g/t Au (O. Wiencke, 1907; H. Quiring, 1914). H. Budzyńska (1971) as the result of spectrographic investigations determined that main gold concentration occurs in loellingite and glaucopyrite and traces were found in arsenopyrite, glaucodot, pyrite and galenite. On the base of analysis done by I.C.P.-E.A.S., colloidal-size gold in pyrrhotite (up to 52 g/t), pyrite (up to 55 g/t) and in magnetite (26 g/t) was detected (A. Muszer, 1992). Additionally invisible gold (0.4 wt. %) in (Ni, Fe, Co) sulphoarsenides and in bismuthinite (up to 2.3 wt. %) was also described (S. Z. Mikulski, 1995b). Investigation made with microprobe observations on samples taken from old waste dumps (A. Muszer, 1992; K. Niczyporuk, S. Speczik, 1993) and from natural outcrops in the near vicinities and from the “Zloty Jar” quarry (S. Z. Mikulski, 1994) proved presence of submicroscopic and microscopic-size particles of native gold. The Zloty Stok As-Au deposit is of the contact metasomatic type and its genesis and metal source are linked with the Klodzko – Zloty Stok intrusion (A. Neuhaus, 1933; H. Schneiderhöhn, 1955; W. M. Kowalski, 1969; J. Kanasiewicz, 1992; S. Speczik, 1994) or, according to others, ore-formation process begun before intrusion was formed (M. Banaś, 1973; A. Muszer, 1995).

MATERIALS AND METHODS

Over 100 rock samples were collected from the “Zloty Jar” quarry and outcrops nearby in the years 1992–1995. Petrography studies were based on 18 thin sections and over 70 polished sections. The above materials have been partly illustrated on plates. Detailed microscopic studies in reflected light using LEITZ microscope of ORTHOPLAN-PL type were carried out in order to recognize the composition and succession of ore paragenesis. “Visible” gold was found during studies under the ore microscope in reflected light and than proved by detailed microprobe investigations with use of EDX Link ISIS System coupled with electron microscope of JEOL JSM-35 in PGI. Additional studies were carried out in Polish Academy of Sciences with use of microprobe Link System connected with JEOL JSM-840A under following conditions: accelerating voltage — 20 kV, sample current — 6x10^-9 and counting time — 20 μs. Study of dispersed gold were carried out with use of equipment and under the same conditions described above.

Preliminary geobarometric measurements on samples supplied by the author were made by A. Kozłowski (1995). Homogenization temperatures were measured with use of micro-
scopic thermocamera made by Fluid Co. This allowed for very high accuracy of determined temperature of ±1°C. The carbon dioxide inclusions used for P determination were made with accuracy of ±0.1°C.

Rock samples for chemical analyses presented in this paper were collected from the I and II exploitation level of the “Zloty Jar” quarry. Especially calc-silicate rocks and rocks containing ore mineralization in form of impregnation and veins were chosen. Chemical gold determination was made in the PGI Central Chemical Laboratory with precision of 1 ppb. Rock samples, after burning at temperatures 450 and 640°C, were digested by HCl concentrate and then dissolved with use of aqua regia. The obtained gold-bearing chloride complex was extracted into organic form. All results were obtained using Flameless Atomic Absorption method (GFAAS) by spectrophotometer PERKIN ELMER model 4100 ZL.

Tungsten was determined with use of Fluorescence Roentgen Spectrophotometer made by Rigaku Co. (Japan) under following condition: 200 mA and 50 kV.

GEOLOGICAL SETTING OF THE “ZŁOTY JAR” QUARRY AREA

The “Zloty Jar” quarry of blastomylonitic schist is located in the northern part of the Orlowiec Synclinorium (J. Don, 1964) which is a part of the Zloty Stok – Skrzynka Dislocation Zone (J. Don, 1964; S. Cwojdzinski, 1975). Just recently, it was defined as Zloty Stok – Trzebieszowice (ZSTSZ) regional shear zone up to 4 km wide which has NE–SW trend and was developed at the time of the Variscan deformations (Z. Cymerman, 1996). Its northern part is cut by the Sudetic Marginal Fault (SMF) of NW–SE direction (Fig. 1). In the southern part of the ZSTSZ, close to its contact with the Śnieżnik metamorphic complex, occur the Jawornik granitoid (335 Ma; J. Borucki, 1966). From the west, this metamorphic complex is bordered by the Kłodzko – Zloty Stok plutonic massif. These granitoid rocks are cropping out on the surface about 1.5 km to the west from the quarry. The late-tectonic Kłodzko – Zloty Stok massif is an intrusion of mixed granitoids of syntectonic-contamination type (K. Smulikowski, 1979) origin developed along dislocation planes with NW–SE trend, during late phases of the Variscan orogeny (298–262 Ma; T. Depciuch, 1972). Just recently, it was classified as I type granitoid (M. W. Lorenc, 1995).

Intruding magma had a high temperature what is marked by reomorphic liquidation of so-called Haniak gneisses, by intensive microclinization, appearance of cordierite, especially in biotite rich rocks, formation of migmatites within biotite schist (M. Kozłowska-Koch, 1973; S. Cwojdzinski, 1975; I. Wojciechowska, 1975; B. Wierzchołowski, 1976; K. Smulikowski, 1979), and was responsible for ore forming metasomatic processes on the Zloty Stok As-Au deposit (H. Schneiderhöhn, 1955; W. M. Kowalski, 1963; S. Speczyl, 1994).

Excavation works in the “Zloty Jar” quarry begun in 1961 at the same time when decision about closing mining activity in the Zloty Stok As-Au deposit was made. The quarry was open to produce crushed stone from blastomylonitic schist and surrounding rocks for road construction purpose. Actually, in the quarry exploitation is not carrying out. This quarry is over 200 m long and 70 m high and has a moon like shape open to east. Accessible to the observations are three lower levels (380–410 m a.s.l.). Rocks in the quarry belong to the eastern part of the ZSTSZ. The five strongly different rock blocks were
Gold mineralization in the Zloty Stok As-Au deposit

distinguished there (I. Wojciechowska, 1976; J. Žaba, Z. Będkowski, 1995). Each of them is separated by normal faults which are usually dipping (70–80°) to SW. The rock blocks in the central and northeastern part of the quarry are built of blastomylonitic biotite-oligoclase schist, biotite gneiss with number enclosures of amphibolite schist and chlorite-amphibole schist, locally associated with silicate-calcite rocks, amphibolites, and black serpentinites (Fig. 1). In SSW part of the quarry rock blocks are consist mainly of leptynite leuckogneisses with inserts of biotite schist and chlorite-amphibole schist. The rock block located most to SSW is built of biotite-quartz schist and leptynite gneisses. The quarry is located on eastern slopes of the Krzyżowa Mt. between the old Krzyżowa Mt. (Eastern) Ore Field (II) and the Soltysia Mt. Ore Field (IV) of the “Zloty Stok” mine. In the Eastern Ore Field arsenic ore occurred in several nest-like concentrations. The predominating ores were those occurring in calc-silica rocks, the black and green serpentinites. Contrary to Western Ore Field arsenopyrite and Cu-sulphide dominate here over the loellingite. The ore aggregations have a N–S strike and general dip of 30–40°SW (L. Baldys, 1954). The arsenic content in ores with disseminated mineralization went up to 7% (L. Baldys, 1954). The Soltysia Mt. Ore Field characterized by poorer disseminated sulphide mineralization in diopside-tremolite rocks with arsenic content from 4 to 8%. The ore zone has a NNE–SSW strike and dips towards ENE at the angle of 60–70°E (L. Baldys, 1954). Influence of the Kłodzko – Zloty Stok granodiorite intrusion in the area of II and IV Ore Fields are much weaker than in the Western Ore Field (W. M. Kowalski, 1961, 1963).

DESCRIPTION AND TEXTURAL STUDY OF GOLD MINERALIZATION

In the “Złoty Jar” quarry ore mineralization was found on the lowest extraction level, within three narrow separate zones, in the band of calc-silicate rocks and pyroxene skarn and in surrounding (S. Z. Mikulski, 1994, in press). Three types of mineralization can be distinguished: disseminated, stringer and on the minor scale massive. Often the two first types occur in the same sample. The former as a wall-rock impregnation and the later as a fracture-fill. These types are superimposed on pre-existing ore mineralization (ilmenite, magnetite, pyrrhotite, pyrite). Epigenetic mineralization of gangue or/and ore veins and veinlets with thickness from a few millimetres up to 2–3 cm in size are hosted mainly by calc-silicate rocks and leptynites. Mineralization textures indicate a succession of cycles of ductile-brittle and brittle deformation and hydrothermal infill. Most interesting are rocks appearing in the central part of the quarry. These rocks are represented by diopside skarn and diopside ± tremolite ± calcite ± talc rocks of light green colour. They occur in form of lens about 1 m thick and are enveloped by amphibole-chlorite schist and leptynite gneiss (85°/60–65°SW). Within these rocks nest-like zone of intensive silification and carbonatization about 1.5 m thick was observed. Locally, the massive ore mineralization also occur within zone up to a few tens of centimetres, as dense disseminated impregnation, thick spots, and nests as well. The main ore minerals are: arsenopyrite, loellingite and pyrite. Less frequently occur scheelite and sulphoarsenides, pyrrhotite, chalcopyrite, sphalerite, and magnetite. In black-serpentinite rocks predominate magnetite mineralization.
Arsenopyrite is the principal component of the ore and shows the most characteristic textures. Textural relationships between arsenopyrite and gangue or host correspond to the types: disseminated, stringer or fine-banded and massive ores. Disseminated type (a) is characterized by finely disseminated arsenopyrite grains usually idiomorphic from a few micrometres up to millimetres in size and aggregates (up to 5 X cm) which may form lenticular shapes (Pl. II, Fig. 14a). Bigger arsenopyrite grains are usually crushed down to microclasts. Often related to hydrothermal infilling structures which are usually not parallel to rock texture. In the “Zloty Jar” quarry it is a big importance. Different forms have irregular arsenopyrite concentration within loellingite and its marginal parts (Pl. I, Fig. 13a–d). Loellingite-arsenopyrite coarse-grain aggregates occur commonly in calc-silicate rocks and their relation is changeable. In the central part of some younger arsenopyrite grains the remnants of loellingite were observed (Fig. 2). SEM studies of arsenopyrites, disseminated in calc-silicate rocks, allow to detect among them compositional differences (Fig. 3a). Chemical composition of arsenopyrite crystals is shown on the ternary Fe-As-S phase diagram on Figure 3b. Content of arsenic is 46.40–51.62 wt. %, sulphur 15.89–18.64 wt. % and iron 32.59–34.64 wt. %. Traces of Au, Sb (up to 0.19 wt. %), Co and Ni were detected (Fig. 3c). Chemical formula of arsenopyrite (I): Fe$_{0.99-1.14}$As$_{1.05-1.10}$S$_{0.88-0.96}$.

Single idiomorphic crystals of the younger arsenopyrite generation also occur as impregnation in calc-silicate rocks but exhibit lower arsenic content and enrichment in
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Fig. 3a–c. Arsenopyrite composition: a — electron microprobe analyses of arsenopyrite; b — Fe-As-S graph of individual microprobe analyses (at. %); c — quantitative microanalysis of arsenopyrite with increased content of Au (EDS)

Skład chemiczny arsenopyrytu: a — tabela wyników badań w mikroobszarze; b — skład arsenopyrytu w % atom. w trójkacie Fe-As-S; c — wyniki mikroanalizy ilościowej arsenopyrytu z podwyższoną zawartością Au (EDS)
sulphur. The content of As is from 42.92 up to 44.4 wt. %, S — 19.37–20.18 wt. %, and Fe — 33.80–34.48 wt. %. Chemical formula of arsenopyrite younger generation: Fe$_{1.00-1.01}$As$_{0.95-0.99}$S$_{1.01-1.04}$.

The following younger generation of arsenopyrite revealed textures which contribute to a typological classification scheme of shear-zone gold ores (R. Castroviejo, 1990). The stringer or fine-banded type (b): arsenopyrite or scheelite (II) grains occur as an infill in microfissures and veinlets with widths from micrometres up to 3 mm (Fig. 4c; Pl. II, Fig. 14b, c). It was also found arsenopyrite intergrowths with loellingite as fillings of fissures and voids in cracked earlier crystallized grains of FeAs$_2$. Within this generation of arsenopyrite, “visible” native gold inclusions were sporadically observed. Massive ores type (c): arsenopyrite occur in thick spots or nests of millimetres/centimetres thickness. These forms are built of coarse-grained aggregates, intergrowths with other ores and with gangue (Pl. II, Fig. 14d).

**Loellingite** is subordinate with respect to arsenopyrite although being in places the principal component. Loellingite occurs in grains of columnar and acicular habits, which are loose disseminated in rocks in the form of impregnation or nest-like concentration of radial-concentric shaped (up to several centimetres in size) (Pl. II, Fig. 14a–d). Columnar crystals of loellingite rich up to 3 cm of length and up to 0.5 cm of thickness. Lower sizes (0.0X–2.X mm) have loellingite grains of needle shape. Coarse grains are cataclasized and cemented by a younger generation of gangue (quartz, calcite) or arsenopyrite. Under the are microscope some of loellingite crystals revealed heterogeneous composition what is shown by different optical features. Microprobe analyse proved these observations. Darker irregular parts of loellingite grain are richer in sulphur and relatively poorer in arsenic content (iron content is at the same level). These concentrations are formed by arsenopyrite. Determination of chemical composition of loellingite revealed arsenic, iron and sulphur contents around 70.48–72.96, 27.68–28.21, and 1.07–1.45 wt. %, respectively (Fig. 1b, d). Formula of loellingite: Fe$_{0.99-1.0}$As$_{1.9-1.93}$S$_{0.07-0.09}$1.99-2.01.

**Scheelite** is the next ore mineral and for the first time was described from the Zloty Stok deposit area by S. Z. Mikulski (1994). Scheelite occurs most commonly in forms of individual impregnation, thick spots and nest-like crystalline grains and veinlets (Fig. 4c). Two generations of scheelite were observed. The first one appears as less or more idiomorphic single grains from 0.0X up to a few millimetres in size. Bigger ones are solid crystalline aggregates up to 2–3 cm. Scheelite intergrowths with pyrite were sporadically observed, despite its common intercalations with quartz or calcite. These mineral aggregates are often tectonically fractured, exhibit signs of fissure fills by younger generation of calcite (Pl. III, Fig. 15a). Scheelite II generation appears close in association with quartz or quartz and calcite in form of incrustation in central part of epigenetic veinlets and as irregular fillings of voids in calc-silicate rocks (Fig. 6b; Pl. III, Fig. 15b). These veinlets are usually from 0.X up to 2.X mm thick. The results of microprobe analysis of scheelite I revealed its inhomogeneous chemical structure with admixture of Mo up to 4.5 wt. % and traces of Cu, Sr, Y (S. Z. Mikulski, 1995a) (Fig. 4a, b). Scheelite I crystals contain WO$_3$ from 80.97 up to 83.08 wt. % and CaO from 17.30 up to 18.91 wt. %.

**(Ni, Fe, Co) sulphoarsenides** appear in the light green calc-silicate rocks in the form of filling of microfissures in association with pyrite, calcite and as single or thin aggregate concentration (Pl. IV, Fig. 16c). Sulphoarsenide grains have sizes from 0.0X up to 2.X mm,
Gold mineralization in the Zlóty Stok As-Au deposit

Fig. 4a–c. Scheelite from the "Zlóty Jar" quarry: a — composition of scheelite as revealed by microprobe studies (EDS spectrum); b — quantitative microanalysis of scheelite with increased content of Mo (EDS); c — scheelite occurrences in the forms of spot, nest or veinlet which infill voids and microfissures in calc-silicate rocks.

Scheelit z kamieniołomu „Zlóty Jar”: a — skład scheelitu na podstawie badań w mikroobszarze (widmo EDS); b — wyniki mikroanalizy ilościowej scheelitu z podwyższoną zawartością Mo (EDS); c — plamiste, gniazdowe i żyłkowe formy wystąpienia scheelitu wypełniające mikrosęknięcia i pustki międzyziarnowe w skałach węglanowo-kronionowych.
Fig. 5a, b. Composition: a — of Co-gersdorffite as revealed by microprobe studies; in upper corner — NiAsS-FeAsS-CoAsS diagram with projection points of Co-gersdorffite and Ni-cobaltite; b — of Ni-cobaltite as revealed by microprobe studies.

Skład: a — Co-gersdorffitu na podstawie badań w mikroobszarze; w górnym rogu — diagram trójkątny w układzie NiAsS-FeAsS-CoAsS z zaznaczonymi punktami Co-gersdorffitu i Ni-kobaltynu; b — Ni-kobaltynu na podstawie badań mikro sondą.
Gold mineralization in the Zloty Stok As~Au deposit and usually normal habit with inhomogeneous chemical structure (Fig. 5a, b; Pl. IV, Fig. 16a, b). Under the ore microscope each of this zone shows a slightly different reflectivity, colour, isotropy or weak anisotropy. The most characteristic optical feature in the reflected light is their white colour with rose or rose-creamy tint intensified in immersion. Sulphoarsenides are represented mainly by a series of different Ni, Co and Fe compounds. These minerals may be placed among the minerals of the cobaltite-gersdorffite series (D. Klemm, 1965). Most often Ni-cobaltite and Co-gersdorffite were observed. Internal part of such sulphoarsenide grains is built by Co-gersdorffite with higher content of As (51–63 wt. %), Ni (19–28 wt. %) and lower of Co (3–8 wt. %) and Fe (2–8 wt. %) (Pl. IV, Fig. 16a, b). Chemical formula of Co-gersdorffite: \( (\text{Ni}_{0.66-0.83}\text{Fe}_{0.08-0.26}\text{Co}_{0.09-0.23})O_{0.86-1.1}(\text{As}_{1.18-1.61}\text{Bi}_{0.00-0.01})_{1.18-1.62}\text{S}_{0.52-0.79} \).

Such core is covered by Ni-cobaltite rim with content of As 47–49 wt. %, Co 17–21 wt. %, Ni 9–14 wt. %, Fe 5–6 wt. %, and S 15–16 wt. % (Pl. IV, Fig. 16a, b). Chemical formula of Ni-cobaltite: \( (\text{Ni}_{0.28-0.40}\text{Fe}_{0.17-0.19}\text{Co}_{0.5-0.6})_{1.04-1.08}\text{As}_{1.08-1.11}\text{S}_{0.81-0.86} \).

Outer part is characterized by an increase in Co and decrease of Ni component. Au, Ag, Bi, Cu, and W admixtures were also determined (S. Z. Mikulski, 1995b). Some of analyzed grains have more homogeneous structure and content of Ni 11.95–14.85 wt. %, Co 14.04–16.47 wt. %, Fe 6.7–7.2 wt. %, As 47.8–50.1 wt. %, S about 15 wt. %. Chemical formula of this mineral: \( (\text{Ni}_{0.35-0.44}\text{Fe}_{0.21-0.22}\text{Co}_{0.41-0.49})_{1.05-1.07}\text{As}_{1.11-1.15}\text{S}_{0.81-0.85} \).

Microscopic observation proved by chemical analysis allowed to notice that chemical hydrothermal remobilization of Ni, Co, Fe, As, and S from primary ore minerals are responsible for crystallization of these minerals in lower temperatures.

Bismuthinite and native bismuth formed fine irregular, denticulate or spongy shaped inclusion in (Ni, Fe, Co) sulphoarsenides. Pyrite commonly was found in association with arsenic and sulphoarsenide minerals. Beside, its idiomorphic grains up to a few millimetres in size occurs also as solid coarse-aggregates up to 5 cm big and in form of veinlets as well. Pyrites of different generation appear in intergrowths with arsenopyrite, chalcopyrite or pyrrhotite. Chalcopyrite, pyrrhotite, sphalerite and magnetite occur less frequently and as disseminated impregnation in form of individual grains or intergrowths (up to 1.1 mm in size) in calc-silicate and skarn rocks. Some of these minerals appear in a few generations (Fig. 7).

Titanite occurs in silicificated and carbonated zones in form of single idiomorphic crystals up to 1.1 mm in size with very characteristic rhombic sections.

"VISIBLE" GOLD

Native gold grains and inclusions were observed as infill of microfractures, within disseminated or veinlet ore mineralization in pyroxene-garnet skarn and diopside ± tremolite ± calcite ± talc rocks from the central part of the quarry lowest exploration level. Most often, Au inclusions appear in aggregates of (Ni, Fe, Co) sulphoarsenides between zones of Co-gersdorffite and Ni-cobaltite (Pl. V, Fig. 17a–c). Individual gold grains are larger and were noticed in epigenetic quartz ± calcite veins (Fig. 6a; Pl. V, Fig. 17d). Under the ore microscope the colour of native gold polished surface is a luminous golden yellow much
Fig. 6a, b. EDS spectrum: a — of native gold in diopside; in upper corner — distribution maps of characteristic SiKα and AuMα1 radiation; x 1600; b — of electrum in Ni-Fe-Co sulphoarsenides

Widmo EDS: a — złota rodzimego w diopsydzie; w górnym rogu — mapy rozkładu promieniowania charakterystycznego SiKα i AuMα1; 1600 x; b — elektrum w siarkoarsenkach Ni-Fe-Co
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variable with the silver content, the reflectivity is enormously high (P. Ramdohr, 1969). Usually, two or more native gold inclusions were observed in individual grains of (Ni, Fe, Co) sulphoarsenides. Some of them have a strong white tint what indicate higher silver admixture and was proved by microprobe analyse (up to 31.6 wt.% of Ag and from 3.8 up to 4.5 wt.% of Bi) (Fig. 6b). It is worthy to notice the constant admixtures of As up to 1.93 wt.%, Ni — 1.57 wt.%, and W — 1.34 wt.%. According to P. Ramdohr (1969) such high Ag-content in native gold indicates presence of electrum (30–45 wt.% of Ag). Electrum inclusions have from 0.5 up to 20 μm in sizes and curvilinear elongated forms (Pl. IV, Fig. 16c). Beside, inclusions of native gold with admixture of Ag and Bi also gold-bismuth myrmekites within sulphoarsenides were observed. These intergrowths reach up to 5 μm in size. In natural occurrences such structures form as a result of solid solution decomposition of maldonite (Au3Bi) (P. Ramdohr, 1969). Usually it is found that maldonite is decomposed into a predominantly coarse myrmekite of Au and Bi with ~1:1 surface proportion. Smaller and larger intact remnants occur only in wedges. The formation of maldonite is apparently limited to a narrow margin within the high temperature range (P. Ramdohr, 1969). In the pole part content of bismuth in native gold reaches up to 30.5 wt.% or up to 33.8 wt.% of gold admixture in bismuth. Non numerous grains of native gold observed in quartz ± calcite veinlets were bigger (5–50 μm in size) and characterized by more intensive yellow colour, lower admixture of other elements up to 15 wt.%. Native gold grains have most often oval shape with more or less regular edges (Pl. V, Fig. 17d). One gold grain found in diopside has much lower size — 2 μm in regard to this tests of microprobe analysis came to grief (Au < 60 wt.%). The visible gold contained within loellingite is interpreted to have been released during replacement by arsenopyrite. During progressive sulphidation of the loellingite the arsenopyrite grain boundary against the loellingite migrated towards the core of the loellingite.

SEQUENCE OF CRYSTALLIZATION

Paragenetic sequence of the main minerals in calc-silicate and skarn rocks from the “Zloty Jar” quarry is shown in Figure 7. The sequence of crystallization of the gold-bearing minerals described above may be divide into three main stages. Stage I was developed in result of different metasomatic type of the fluid fronts (at about 500°C and low salinity, see below) connected with granodiorite intrusion which replace primary calcareous rocks into calc-silicate and pyroxene-garnet skarn rocks. This stage may be divide into:

a — calc-silicate sub-stage A (pyroxene — diopside, garnet, quartz, and calcite);

b — oxide sub-stage B (magnetite, “invisible” gold(?), scheelite, titanite, powellite, quartz, and calcite);

c — sulphide sub-stage C (pyrrhotite, loellingite, arsenopyrite, glaukodote(?), gersdorffite, “invisible” gold, pyrite, chalcopyrite, sphalerite, native gold, and quartz).

A core of corroded loellingite can be found in calc-silicate rocks, indicating that the reaction loellingite plus pyrrhotite to form arsenopyrite took place. The minerals of Fe-As-S system are followed by chalcopyrite, pyrite. The regional metamorphism and the subsequent dynamic metamorphism (strong mylonitization) related to the emplacement of granodiorite intrusion and development of the ZSTSZ in the Variscan time constitute a frame of reference.
for the late-stage cataclasis ores (II, III), according to the brittle deformational effects produced in them. Stage II is represented by quartz, quartz-calcite or green serpentine veinlets also containing ore minerals such as: arsenopyrite, pyrite, native gold, chalcopyrite or scheelite and on the minor scale pyrrhotite and sphalerite. There is no big difference between the ore minerals content of different zones. Stage III was marked by an increase in the content of barren calcite or calcite enriched in Ni-Fe-Co sulphoarsenides and inclusions of native gold. Among ore minerals the main role are played by pyrite, Co-gersdorffite, Ni-cobaltite, native gold, native bismuth, electrum, maldonite, bismuthinite, and galenite. The overall ore-mineralization of stage I, II and III permits to include such mineralization to tectonic and hydrothermal evolution within transition from ductile-brittle to brittle condition by hydrothermal circulation and accumulation of ores.
ARSENOPYRITE GEOTHERMOMETER

The As/S ratio of the arsenopyrite coexisting with other phases in the system Fe-As-S has been experimentally calibrated as a geothermometer by U. Kretschmar and S. D. Scott (1976). However, application is often rather problematic. Among the main problems is the widespread presence of significant amounts of other elements within arsenopyrite. Furthermore, arsenopyrite is very often zoned with respect to As content and true buffered assemblages are often hard to find. Within the studied samples, only a few arsenopyrite grains disseminated in calc-silicate rocks seems to be suitable for geothermometry; the majority being excluded because of high Co contents or unclear paragenetic relationships with neighbouring minerals. Arsenopyrites from veinlets were not investigated here. Conditions close to loellingite + pyrrhotite + arsenopyrite (lō+ po + asp) equilibrium have been assumed for the arsenopyrite which also contains relics of loellingite. Arsenopyrite I shows compositional variation with a mean of 35.53 at. % As (2σ = ±1.52) (Fig. 3a). According to the scheme (Fig. 8a) arsenopyrite I could have originated at temperatures of about 420 to 530°C and was calculated using lō+ po + asp buffering curve. However, the logfS2 values indicated their crystallization in lower temperatures ranging from 400–440°C. U. Kretschmar and S. D. Scott (1976) notes that such arsenopyrite contain more As than arsenopyrite formed together with pyrite. This conclusion is supported by the data in Figure 3a. Arsenopyrite II (x = 32.20 at. % As; 2σ = ±0.64) temperatures calculated using the po + asp + py buffering curve are lower compared to arsenopyrite I (from 415 up to 455°C). As arsenopyrite was considered pure FeAsS2 in the experimental calibration, it is not possible to confirm the S content of this mineral, that this assemblage was actually in equilibrium. The temperatures received on diagram of isopleths of atomic As in arsenopyrite in a sulphur fugacity versus temperature (U. Kretschmar, S. D. Scott, 1976) are outside the stability field of arsenopyrite (315–325°C). In the Figure 8b arsenopyrite compositions in atomic percentage in the ternary system Fe-As-S from the "Zloty Jar" quarry are presented to compare with other deposits according to Z. D. Sharp et al. (1985). Two groups of arsenopyrites with different contents of As and S from the "Zloty Jar" quarry are visible.

PRELIMINARY RESULTS OF GEOBAROMETRIC STUDIES

The majority of the fluid inclusion studies have been made on quartz from veinlets but scheelite, pyroxene, and garnet from calc-silicate rocks were also included, although lack of clarity of these minerals made measurement of homogenization and particularly melting temperatures difficult. Micrometry data reported here refers only to inclusions classified as primary (syngenetic with its host-mineral — A. Kozłowski, 1995). Th data are shown for quartz, pyroxene, scheelite and garnet in Figure 9a. Fluid inclusions in quartz from veinlet have a Th value from 330–296°C, corresponding to a salinity 4.8–8.6 wt. % NaCl equiv. The limited Th data obtained for garnet show range of 352–316°C (2.4–5.7 wt. % NaCl equiv.). Fluid inclusions in scheelite have Th from 346–328°C (5–5.4 wt. % NaCl equiv.). Th measurements for pyroxene have a range 365–329°C (4.9–6.3 wt. % NaCl equiv.). Lower temperatures have fluid inclusions in quartz containing arsenopyrite mineralization from
Fig. 8a, b. Arsenopyrite geothermometer: a — phase diagram of dependence of As (at. %) in arsenopyrite composition on temperature (°C) (U. Kretschmar, S. D. Scott, 1976); b — arsenopyrite compositions (at. %) in the ternary system Fe-As-S; coexisting phases shown in parentheses (according to Z. D. Sharp et al., 1985); arsenopyrites from the “Złoty Jar” marked by the author.

Veinlets representing younger generation. Th temperatures ranges from 288–254°C (3.8–6.6 wt. % NaCl equiv.). To the same range Th temperatures but of higher salinity (7.0–9.5 wt. % NaCl equiv.) corresponds fluid inclusions in quartz containing arsenopyrite mineralization from the Western Ore Field. Lowest Th temperatures show quartz from younger generation of veinlets 234–206°C (3.1–5.6 wt. % NaCl equiv.).

Fluid inclusions data in pyroxene, scheelite and garnet are hosted by quartz-silicate and skarn rocks indicating deposition at Th temperatures of about 364–316°C from fluids contain 2.4–8.1 wt. % NaCl equiv. The Th-salinity diagrams for the skarn mineral assemblages (pyroxene, scheelite, garnet) show increasing salt concentrations in the aqueous phase of inclusions with decreasing temperature. Using the method of intersecting isochores of aqueous and carbonic fluid inclusions temperatures of pyroxene, scheelite, garnet, quartz and pressures of their crystallization have been established (Fig. 9b). Scheelite is the principal tungsten mineral and fluid inclusion data indicating deposition at temperatures of about 473°C from a fluid contain about 5.2 wt. % NaCl equiv. in pressure of 1.24 kbar.
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Fig. 9a, b. Fluid inclusion results: a — microthermometry data for pyroxene (wheels, crosses), garnet (triangles), scheelite (squares) and quartz (circles, asterisks) stages; homogenization temperature versus salinity plot; b — estimation of pressure and temperature using the method of intersecting isochores (symbol explanations the same as for a)

ZS/22, ZSL-D-2, Zst9-11, and Sel — samples number's

Wykres badań inkluzji fluidalnych: a — dane mikrotermiczne dla piroksenu (kółka kierownicy, krzyżyki), granatu (trójkąty), scheelitu (kwadraty) i kwarcu (kółka, gwiazdki); wykres temperatur homogenizacji inkluzji i ich zasolenia; b — określenie ciśnien i temperatur krystalizacji mineralów na podstawie przecięcia odpowiednich isochoir (objaśnienia symboli jak przy a)

ZS/22, ZSL-D-2, Zst9-11 i Sel — numery próbek

Pyroxene was formed during the similar conditions at 480°C and 1.22 kbar from fluid containing 4.9 wt. % NaCl equiv. Garnet was formed in a lower temperature at 464°C and pressure of 1.32 kbar from fluid containing 5 wt. % NaCl equiv.

These values of temperatures are close to crystallization conditions of loellingite + pyrrhotite + arsenopyrite (I) association.

"INVISIBLE" GOLD IN ORE MINERALS

The term "invisible" gold is applied to that which occurs either as submicroscopic inclusions within the host mineral or as a solid solution or chemically bound gold, thus rendering the gold refractory to conventional cyanidation (Z. Johan et al., 1989). "Invisible" gold was found in loellingite, arsenopyrite, bismuthinite, and (Ni, Fe, Co) sulphoarsenides in calc-silicate and skarn rocks from the quarry. Highest gold content was determined in bismuthinite and arsenopyrite (Fig. 10a). But some results of the gold determination had a very low precision even ±0.84 wt. %. Bismuthinite grains contained from 0.94 up to 2.22
Fig. 10a, b. Histograms of the "invisible" gold concentration in the "Zloty Jar" quarry: a — gold content in ore minerals (wt. %); b — gold content in rocks (ppb)

Histogramy koncentracji złota „niewidzialnego" w kamieniołomie „Zloty Jar”: a — zawartość złota w mineralach kruszcowych (% wag.); b — zawartość złota w skałach (ppb)
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wt. % of Au ($x_{n=3} = 1.65$ wt. %) and high admixture of Ag up to 2.93 wt. %. Gold content in arsenopyrites from the “Zloty Jar” quarry was from 0.82 up to 1.4 wt. % ($x_{n=5} = 0.83$ wt. %). Detectable amounts of gold were found mainly in the fine-grained arsenopyrites of prismatic habits. Coarse-grained aggregates of arsenopyrite rarely contained measurable gold. First generation of arsenopyrite contain more chemically bound gold than the second one. Probably, it was due to higher arsenic content 46.40–51.62 wt. % in arsenopyrite (I). By comparison arsenopyrite II contains from 42.92–44.24 wt. % of As. In grains of arsenopyrite (I) Co and Sb admixtures were also determined. The relation was noticed that zone of crystals with the relative highest content admixtures usually has the lowest content of Au. Point analyses of a few loellingite grains confirmed also Au admixture up to 0.72 wt. % ($x_{n=12} = 0.224$ wt. %). Traces of chemically bound gold in (Ni, Fe, Co) sulphoarsenides were also determined (0.16–0.4 wt. %). A visual examination allows to consider gold-bearing arsenides and sulphoarsenides mineralization, as contact metasomatic and hydrothermal types and include into a group of syn- and post-mylonite related to the late cataclasis.

CHEMICAL DETERMINATION OF GOLD IN ROCK SAMPLES

Highest gold concentrations in calc-silicate and skarn from the “Zloty Jar” quarry rocks were determined in samples contained massive ore mineralization (loellingite-arsenopyrite aggregates). In three samples shown on Figure 10b the gold concentration was more than 8 g/t in each. Arithmetic mean of gold content for calc-silicate and skarn rocks from the quarry is $x_{n=6} = 4573.78$ ppb (86.7–9210 ppb). In these rocks Au occurs as chemically bound gold in ore minerals, “visible” gold in form of microscopic inclusions in ore minerals, very fine grains in quartz ± calcite veinlets, or in tiny fissures in rock minerals. Calc-silicate rocks have a different composition of rock-forming minerals and are represented by pyroxene-garnet skarn or diopside ± tremolite ± calcite ± talc rocks, quartz-calcite rocks, and calc-serpentinite rocks.

Lower contents of gold were determined in leptynite gneisses and other rocks. Arithmetic mean of gold content in leptynite gneisses is $x_{n=5} = 430.42$ ppb (3.9–1111 ppb). Highest Au content was detected in strongly silicificated leptynite sample cut by ore veinlets of arsenide and sulphide minerals from 1 up to 3 cm thick.

Arithmetic mean of gold content for all studied samples from the “Zloty Jar” quarry was almost 2 g/t for $n = 18$ (1.3–9210 ppb).

However, highest gold concentration (29 000 ppb) was determined in black serpentinites from old waste dumps of the Western Ore Field. This value and some other results of Au concentration in different rocks from the Western Ore Field are not marked on Figure 10b. Arithmetic mean of gold content for these samples was almost 3 g/t ($x_{n=23} = 2.8$ ppm).

Slightly lower Au concentrations from 1.4 up to 4.4 g/t were determined in samples of arsenic ore in calc-silicate rocks from old waste dumps of the Krzyżowa Mt. Ore Field.
Fig. 11a, b. Histograms of element concentrations in rock samples: a — Au, Ag, As, Fe, Be, Pt and Pd content in rocks from old waste dump of the Western Ore Field; b — Au and W content in rocks from the "Zloty Jar" quarry.

Histogramy zawartości pierwiastków w próbkach skał: a — Au, Ag, As, Fe, Be, Pt i Pd w skałach ze starych hald kopalnianych Zachodniego Pola Rudnego; b — Au i W w skałach z kamieniołomu "Zloty Jar"
CHEMICAL RESULTS OF OTHER ELEMENT DETERMINATIONS

It is worth to present here, other results of element determination in calc-silicate rocks from the “Zloty Jar” quarry and in rocks from old waste dumps of the Western Ore Field (Fig. 11a, b). In black serpentinite sample, contained massive ores, the highest determined concentration of As was almost 4%, Au — 29 g/t, and over 35 ppm of Be. In the one sample of blastomylonitic amphibolite schist contained dense ore mineralization Pt (2 ppm) and Pd (3 ppm) were also determined.

Chemical results of W and Au presented here refers to calc-silicate rocks, skarn and leptynite gneisses from the “Zloty Jar” quarry. Samples were selected by use of U. V. lamp for the highest W content. Within them places with the highest visible scheelite mineralization (blue luminescence colour) have usually lower content of sulphides. Tungsten concentrations were from below 10 ppm (leptynites) up to 340 ppm (calc-silicate rocks). In Figure 11b are shown relations between W and Au in the same samples (max. 91 ppm and 56 ppb, respectively). Relatively high concentration of tungsten occurs in light green calc-silicate rocks which contains disseminated scheelite mineralization. Individual scheelite grains have sizes from 0.0X up to 1. X cm and in some places they formed spot-like concentration up to a few centimetres in size.

CONCLUSIONS

The exploitation of blastomylonitic schist for road construction use carried out in the “Zloty Jar” quarry, exposed narrow lenses of calc-silicate rocks, contained gold-bearing ore mineralization. These lenses are separated from old mining fields of the Zloty Stok As-Au mine by several faults. Origin of gold-bearing mineralization in the “Zloty Jar” quarry was a result of hydrothermal metasomatic processes developed in contact zone of the Klodzko – Zloty Stok granitoid massif and within the regional shear-zone of post-Variscan time (Fig. 12). Although, in the “Zloty Jar” quarry a thicker zone of typical skarns (direct contact with granite is about 1.5 km apart) has not been developed. Nevertheless different metasomatic fronts carried various silicates along fractures allowed to form, at a smaller scale to compare to Western or Krzyżowa Mt. Ore Fields (W. M. Kowalski, 1963), gold-bearing calc-silicate rocks which in some narrow parts represent even poorly developed pyroxene and garnet skarns with gold-bearing ore minerals (stage I). The arsenides or sulphides are irregularly distributed in the calc-silicate rocks, and only in some local places formed small massive bodies. Especially enriched in gold-bearing ore minerals are zones developed in the primary contact of carbonate rocks with metavolcanites, which underwent strong alteration and supplied additional elements into metasomatic fluids. The dominant types of alteration are: silicification, carbonatization, serpentinization, sericitization, sulphidation, talcization, and prehnitization. All calc-silicate rocks in the quarry containing impregnated ore mineralization are cut by veinlets of a later paragenesis (quartz, calcite, adularia, amphiboles, green serpentine, prehnite, and others). Some of them contain ore mineralization and were developed as late stage cataclasis ores (stage II and III) according to the ductile-brittle and brittle deformational effects during development processes of the Zloty Stok – Trzebieszo-
wice regional shear zone (ZSTSZ). Native gold and the rest of sulphides and ore minerals were found with these paragenesis.

Gold in the "Zloty Jar" quarry occur in two different forms:

a — in own phases as native gold, electrum;

b — as fine-dispersed isomorphic admixture in ore minerals.

The first form was documented during detailed microscopic studies in the forms of sub- and microscopic inclusion (“visible” gold) in (Ni, Fe, Co) sulphoarsenides, arsenopyrites, pyrites, as individual fine-grains in quartz ±calcite veinlets or in microfissures within rock forming minerals (e.g. diopside) in calc-silicate rocks. On the base of microprobe analyses three types of native gold are distinguished: electrum with content of Ag up to 31.6 wt. %, bismuth gold with Bi admixture up to 35 wt. % and “pure” native gold which sometimes contains up to 15 wt. % of Ag, Cu, As, and W. Most often the electrum in form of micro-inclusions (0.5-20 μm) in (Ni, Fe, Co) sulphoarsenides was observed. Within them an inclusion of bismuth gold was also found. Most purest native gold occurs in the form of individual fine grains in quartz veins which cutting calc-silicate rocks.

The second form of gold was determined with use microprobe analyse, as fine-dispersed admixture (so-called “invisible” gold) in: bismuthinite (up to 2.22 wt. % of Au), arsenopyrite (up to 1.4 wt. %), loellingite (up to 0.72 wt. %), (Ni, Fe, Co) sulphoarsenides (up to 0.4 wt. %).

Fine-dispersed gold occurring in ore minerals was syngenetic to associated high temperature mineralization in arsenopyrite and loellingite (stage I). Preliminary results of thermo-barometric studies of garnet, pyroxene, and scheelite from skarn and calc-silicate rocks, containing gold-bearing arsenopyrite and loellingite, indicated 464-480°C for real temperature of their crystallization and of pressure about 1.4 kbar from fluids with low salinity (4.9-5.2 wt. % NaCl equiv.). As a geological thermometer was used arsenopyrite of the I generation associated with loellingite in calc-silicate rocks. The arsenopyrites contain from 35.12 up to 36.72 at. % As, what may indicate for their crystallization in the temperature range from 420 up to 530°C.
Appearance of “visible” gold should be linked with younger stages (II, III) of hydrothermal fluids migration preceded by the following tectonic movements connected with development of the Zloty Stok – Trzebieszowice regional shear zone. In the considering area, fissures and voids within calc-silicate rocks were infilled by younger generations of ore minerals with “visible” gold inclusions or grains and numerous veins and veinlets of quartz ± scheelite ± calcite composition as well as adularia or phrenite ones. Preliminary results of thermo-barometric studies indicate for homogenization temperature of inclusion in quartz veinlets containing younger arsenopyrite-pyrite mineralization below 350°C (S. Z. Mikulski, 1995b). Presence of numerous inclusions of visible gold was connected with hydrothermal middle-, low-temperature mineral assemblages, represented mainly by (Ni, Fe, Co) sulphoarsenides associated with calcite and with As and Fe sulphides (stage III). Similar electrum-Fe-Co-Ni-As-S paragenesis was described in the mica schists from Przeczynica region in the Kamienica Range (A. Piestrzyński et al., 1992). Characteristic features this gold-bearing mineral association are: inhomogeneous chemical composition, locally zone structure of some sulphoarsenides crystals, and native gold (± native Bi) inclusions with different share of Ag (electrum, silver gold), Bi (bismuth gold) admixtures. Despite to observation presented by other geologists (A. Muszer, 1992; K. Niczyporuk, S. Speczik, 1993) described materials allow to propose an idea that native gold mineralization of this type in the earlier stages of crystallization are much pure and become progressively enriched in admixtures (silver > 30% Ag) with later remobilization.

Observed gold-bismuth myrmekites within sulphoarsenides in natural occurrences form as a result of solid solution decomposition of maldonite (Au₂Bi) in narrow margin within the high temperature range (P. Ramdohr, 1969). Common presence of Co-gersdorffite and Ni-cobaltite in carbonatized zones indicates Co, Ni and Fe remobilization processes from primary sulphoarsenides (arsenopyrite, cobaltite, gersdorffite) and their replacement and recrystallization in lower temperatures (stage III). Presumably, processes of Au, Ag, As, Ni, Co, Fe and other metals redistribution are more widespread in the Variscan hydrothermal systems of the Sudetes. Especially among mineralization associated with arsenic-polymetallic formation in Sudetes (S. Z. Mikulski, 1995c).

Other problems are native gold micrograins within fissures of ore minerals such as arsenopyrite, pyrite and loellingite. Gold remobilization process was occurring in a few stages. After primary deposition of invisible Au in solid-solution with oxide (?), sulphide and arsenide minerals began process of redistribution and concentration of solid-solution gold to form colloidal and microscopic particles in fractures and voids within the host minerals. Redistribution process of gold from arsenopyrite and loellingite started immediately after they formed (J. Heinhorst, B. Lehmann, 1994; P. Möller, G. Kersten, 1994; A. Mumin et al., 1994). Further migration of Au, out of the host mineral and interstitial, to gangue minerals where the gold appears to have a long distance residence time (A. Mumin et al., 1994). In the case of primary gold from the quarry redistribution of solid-solution Au and its concentration were observed in various stages. Gold-bearing rocks underwent a few tectonic stages during geological development. Arsenopyrite-loellingite association with pyrrhotite or magnetite evidence for reducing but moderately sulphide conditions of the ore formation. Gold has high solubility and mobility in the solutions from which crystallizations of sulphide-arsenic paragenesis are possible. The chloride complexes AuCl₂ and HS⁻ dominate in acid solutions at a temperature above 300°C. The hydrosulphide complex
Au(HS)$_2$ is a dominant species in the near-neutral to alkaline solutions (G. A. Pal’Yanowa, G. R. Kolonin, 1991; K. Hayashi, H. Ohmoto, 1991). The “visible” gold from the “Zloty Jar” quarry formed during several stages and processes of redistribution of primary gold from loellingite-arsenopyrite, magnetite(?) or pyrrhotite mineralization were wide developed and carried out by sulphur-bearing solutions at 350–250°C and near neutral — to alkaline environments with dominant role of hydrosulphide complex Au(HS)$_2$ in shear zones of brittle character.

REFERENCES


DZIEKOŃSKI T. (1972) — Wydobywanie i metalurgia kruszców na Dolnym Śląsku od XIII do XX w. Ossolineum, PAN.


Gold mineralization in the Złoty Stok As-Au deposit


MINERALIZACJA ZŁOTONOŚNA W STREFIE METAMORFIZMU KONTAKTOWEGO I W STREFACH SCINAN W KAMIONIOLOMIE „ZŁOTY JAR”
— ZŁOŻE As-Au ZŁOTY STOK

Streszczenie

Złotonośne asocjacje mineralne w kamieniołomie „Złoty Jar” utworzyły się podczas trzech oddzielnych etapów. W etapie I — skamienopodobnego okruszczowania — miały miejsce procesy metamorficzne kontaktowe zachodzące w strefie cegokontaktowej kłodzko-złotostockiego masywu granodiorytowego. Wstępne wyniki badań pierwotnych inkluzy oraz fluidalnych wykazują, że najwcześniej etap krystalizacji piroksenu, granatu i scheulitu zachodził z roztworów o niskim zasoleniu (4,9–5,2% wag., (NaCl) w temperaturach 464–480 °C i przy ciśnieniu poniżej 1.4 kbar. Z najmłodszymi fazami tego etapu związane jest najstarsza generacja kruchych mineralizacji löllingitowo-arsenopyrowej. Zdecydowana większość złota drobno-dispersyjnego występuje w postaci submicroskopowej wielkości drobiny w mineralizacjach, głównie w skałach węglano-kreozonianych i w czarnych serpentynitach (odpowiednio w stwierdzonych ilociach maksymalnych do 10 i 29 g/t). Młodsze złotonośne generacje kruchych minerałów (etapy II i III) występują w postaci ochkostrzępujących, które pozwalają zaliczyć je do typowych mineralizacji rozwiniętych w strefach cśnain. Wystąpiły one głównie wskutek wypełnienia hydrotermalnych związanych z migracją roztworów mineralotworczych w następstwie rozwoju kruchych stref cśnain. Temperaturna homogenizacja pierwotnych inkluzy naświetla, zawierającego okruszczowanie i złoto „widzialne”, wynosi 220–280°C, przy zasoleniu 4–10% równowagi NaCl. Złoto „widzialne” stwierdzono w formie wrostków o rozmiarach od 5 do 50 μm w siarkoarsenakach i w postaci jednoznakowych mikroziarenek w żyłkach kwarcowych lub kwarcowo-kaliowatych. W najmłodszej opisanej złotonośnej asocjacji mineralnej w obrębie Ni-Fe-Co siarkoarsenaków powszechnie obserwowano wrostki elektrytów i mniej eklatowe przerosty złota i bizmutu. Proces redystrybcji złota pierwotnego z mineralów arsenowo-löllingitowych na skalę lokalną i na skalę regionalną był szeroko rozprzestrzeniony. Wytwórczość złota „widzialnego” w obrębie młodszych asocjacji siarkoarsenaków i siarkowców zachodziło najprawdopodobniej przy udziale roztworów zawierających strefę w warunkach oobjętych do zasadowych, w temperaturach poniżej 350°C i pod wpływem siarczku. Głównym źródłem metali były prawdopodobnie pre-warszawskie koncentracje metali w skałach wulkaniczno-osadowych (zawierających również elementy z górnego płaszcza — Pt, Pd), które uległy mobilizacji podczas formowania się intruzji granitowej. W arsenowo-złotonośnych nagromadzeniach widoczne są z kolei młodsze procesy redystrybcji metali spowodowane rozwojem stref cśnain.

Stanisław Z. MIKULSKI

WIERZCHOWSKI B. (1976) — Graniteoids of the Kłodzko - Złoty Stok massif and their contact influence on the country rocks (petrographic characteristics) (in Polish with English summary). Geol. Sudetica, 11, no. 2
Fig. 13

Stanislaw Z. MIKULSKI — Gold mineralization within contact-metamorphic, and shear zones in the “Złoty Jur” quarry — the Złoty Stok As-Au deposit area (Sudetes)
Fig. 13a–d. Loellingite-arsenopyrite grain aggregates in calc-silicate rocks from the “Zloty Jar” quarry: a, c — backscatter electron images showing relationship between loellingite and arsenopyrite (lo — loellingite, as — arsenopyrite); b, d — distribution maps of characteristic SKα radiation; a, b — × 130, c, d — × 270

Agregaty ziarniste löllingitowo-arsenopirytyowe w skałach węglanowo-krzemianowych z kamieniołomu „Zloty Jar”: a, c — obraz BEI; widoczna relacja między löllingitem a arsenopirytem (lo — löllingit, as — arsenopirtyt); b, d — mapy rozkładu promieniowania charakterystycznego SKα; a, b — 130 x, c, d — 270 x
Stanisław Z. MIKULSKI — Gold mineralization within contact-metamorphic, and shear zones in the "Zloty Jar" quarry — the Zloty Stok As-Au deposit area (Sudetes)
Fig. 14a–d. Textural relationships between arsenopyrite and gangue or host revealed textures which may contribute to a typological classification scheme of shear-zone gold ores: a - disseminated type, scale bar 4.5 cm; b, c - stringer or fine-banded type, scale bar 4.5 cm; d - massive ores type, scale bar 3 cm; white - arsenopyrite, q - quartz, c - calcite, sch - scheelite, au - native gold in Ni, Fe, Co sulphoarsenides; photo by J. Modrzejewska

Wzajemne relacje między formami wystapienia arsenopirytu (minerałów kruszcowych) i minerałów płonnych lub skały wskazują na tekstury, które można odnieść do typowych schematów klasyfikujących okruszczowanie w strefach ścinań: a - typ rozproszony, długość skali 4,5 cm; b, c - typ żyłkowy i wstęgowany drobno, długość skali 4,5 cm; d - typ masywny, długość skali 3 cm; biały - arsenopyryt, q - kwarc, c - kalcyt, sch - scheelit, au - złoto rodzime w Ni, Fe, Co-siarkoarsenikach; fot. J. Modrzejewska
Fig. 15

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PLATE III

Fig. 15a, b. Scheelite mineralization in calc-silicate rocks: a — fractured scheelite coarse grain cuts calcite veinlet with pyrite; b — replacement of fractured scheelite by calcite; sch — scheelite, py — pyrite, c — calcite; scale bar 1 mm

Mineralizacja scheelitowa w skałach węglanowo-krzemianowych: a — spękane ziamo scheelitu przecięte młodszą żyłką kalcytową z pirytem; b — zastępowanie spokanego scheelitu kalcytom; sch — scheelite, py — pyryt, c — kalcyt; długość skali 1 mm
Stanislaw Z. MIKULSKI — Gold mineralization within contact-metamorphic, and shear zones in the “Zloty Jar” quarry — the Zloty Stok As-Au deposit area (Sudetes)
Fig. 16a–d. Microprobe studies: a — distribution map of characteristic CoKα radiation; rims enriched in Co revealed composition of Ni-cobaltite; b — distribution map of characteristic NiKα radiation; cores enriched in Ni revealed composition of Co-gersdorffite; x 1600; c — backscatter electron images of ore mineralization (as — arsenopyrite, sch — scheelite, su — Ni-Fe-Co sulphoarsenides and sulphides, c — calcite), x 75; d — electrum (e) inclusions in Co-Ni sulphoarsenides grain, scale bar 10 μm

Badania w mikroobszarze: a — mapa rozkładu promieniowania charakterystycznego CoKα; strefa zewnętrzna wzbogacona w Co wykazuje skład Ni-kobaltyn; b — mapa rozkładu promieniowania charakterystycznego NiKα; strefa wewnętrzna wzbogacona w Ni wykazuje skład Co-gersdorffit; 1600 x; c — obraz BEI mineralizacji kruszcowej (as — arsenopyryt, sch — scheelit, su — Ni-Fe-Co siarkoarsenidy i siarczki, c — kalcyt), 75 x; d — wrostki elektrum (e) w siarkoarsenikach niklu i kobaltu, długość skali 10 μm
Stanislaw Z. MIKULSKI — Gold mineralization within contact-metamorphic, and shear zones in the "Zloty Jar" quarry — the Zloty Stok As-Au deposit area (Sudetes)
Fig. 17a–d. Native gold from the “Zloty Jar” quarry: a–c — native gold inclusions in Ni-Fe-Co sulphoarsenides (Au — gold, electrum, Bi — native bismuth), scale bar 20 μm; d — grain of native gold (yellow) in quartz-calcite veinlet (q-c) cuts calc-silicate rock, scale bar 100 μm

Złoto rodzime z kamieniolomu „Zloty Jar”: a–c — wrostki złota rodzimego w siarkoarsenkach niklu, kobalu i żelaza (Au — złoto, elektrum, Bi — bizmut rodzimy), długość skali 20 μm; d — ziarenko złota rodzimego (żółte) w żyłce kwarcowo-kalcytowej (q-c) wypełniającej spękanie w skale węglanowo-krzemianowej, długość skali 100 μm