SYMPOSIUM IV: MINERAL RESOURCES AND HUMAN SOCIETY

ORIGIN OF GOLD PLACERS IN THE POLISH CARPATHIAN FLYSCH BELT (PODHALE REGION)

M. CIESZKOWSKI[1], M. KUSIAK[2], M. MICHALIK[1]
and M. PASZKOWSKI[2]

[1]Jagiellonian University, Institute of Geological Sciences, ul. Oleandry 2a, 30-063 Kraków, Poland; mark@ing.uj.edu.pl; michalik@ing.uj.edu.pl
[2]Polish Academy of Sciences, Institute of Geological Sciences, Kraków Research Centre, ul. Senacka 1, 31-002 Kraków, Poland; ndkusiak@cyf-kr.edu.pl; ndpaszko@cyf-kr.edu.pl

Key words: gold, placer deposits, Carpathians, Magura nappe.

Introduction

This paper gives an overview of the gold occurrences in alluvium on the flysch rocks and in flysch conglomerates of the Magura nappe in Nowy Targ area. The gold has been discovered during detail investigations of sandstones and conglomerates as well as examinations of heavy mineral assemblages both from stream alluvia and flysch bedrock. In Slovakia, as a result of extensive prospection, many placer gold occurrences in recent stream alluvia lying on southern part of Magura nappe were recognised (Križáni 1982). Detrital gold from the Dunajec river valley described by Jęczmykowa & Wojciechowski (1994), probably derived from the Magura nappe area. Gold particles discovered in the Wisła river alluvium (new author's finding), near Kraków, additionaly were compared with gold from the Nowy Targ area. All of the mentioned occurrences most probably represent parts of one wider gold-bearing domain.

Geological setting

The gold containing sandstones of the Magura nappe occur in the innermost flysch belt tectono-facies zone called the Krynica Subunit (Fig. 1). Geology of the studied area has been mapped and described in several papers (e.g. Cieszkowski & Olszewska 1986; Cieszkowski et al. 1998). In the Nowy Targ area the sedimentary succesion of the tectonic Krynica Subunit is represented predominantly by thick bedded sandstone turbidites. Three lithostratigraphic units are distinguished in the Magura Formation. The lowest one, Piwniczna Sandstone Member (Lower and Middle Eocene) comprises a sequence of thick- or very thick-bedded sandstones with frequent coarse-grained sandstones and conglomerates in lower part of this unit, and are overlain by the Kowaniec beds (Middle Eocene). The uppermost unit, Poprad Sandstone Member (Upper Eocene–Lower Oligocene) crops out northward from Nowy Targ. Above the Magura Formation there is the Malcov Formation represented by thin- and medium-bedded flysch (Upper Eocene and Lower Oligocene), locally interfingerig with thick-bedded sandstones of Magura Formation. The sandstone composition is dominated by quartz with remarkable admixture of feldspars, muscovite, and biotite. The lithoclasts of granites, felsic eruptive and albitised igneous, as well sedimentary rocks are recognisable in coarser fractions. Within the Magura sandstone lithotype the heavy mineral composition is uniform (Schnabel in: Cieszkowski et al. 1998). The inventory of heavy mineral includes garnet (66–87 %), zircon (2–6 %), apatite (8–22 %), tourmaline (3–7 %), rare staurolite (1 %) and Cr-spinels (0–2 %).

Occurrence of rare gold particles has been recognised by authors also in the Holocene Wisła river alluvium downstream from Kraków town up to Dunajec river mouth.

Methods of sample preparations and investigation

Two forms of gold occurrences were noticed in the Nowy Targ area (Fig. 1). Some clasts of vein quartz marked with native gold have been found within fine conglomerates of the Piwniczna Sandstone Member in Rdzawka. In the Nowy Targ area an occurrence of microscopic particles of gold has been explored from a small creek alluvial material close to the Niwa village, which overlie Malcov Formation.

Morphology and chemistry of gold particles were investigated using scanning electron microscope (JEOL 5410) fitted with the energy dispersive spectrometer (Voyager 3100, Noran). Both, natural surfaces of grains and their sections were studied. An accelerating voltage of 20 kV was employed. The measuring time was 100 sec. The content of different chemical elements was determined using programs included in the software supplied by manufacturer.

Results

Morphology of gold particles. The size of gold particles ranges between 20 μm and 250 μm. In some cases the size reaches 0.5 mm. Most of placer gold occurs as irregular grains and flakes. The surface of grains and flakes is irregular or spongy. Randomly oriented scratches occur on numerous grain surfaces. Some grains exhibit plastic deformations. Small quartz grains (and less commonly other minerals) are incorporated into gold grains and flakes. On the surface of some grains rusty patches can be observed.

Chemical composition of gold grains. SEM-EDS investigations of surfaces of gold grains indicate almost pure gold composition. Locally a higher content of iron is noted. Analyses of cross-section of gold grain indicate important silver contents ranging between 7 and 11 wt. % (Fig. 2). The pattern of distribution of silver is highly irregular. At the rim of a gold grain the content of silver lowers (2–0 wt. %). In some places, however, the contents of silver reach 10 wt. % at the distance of 2–3 μm from the grain border.

Discussion

Sandstones and conglomerates of the Malcov formation are a probable source of gold in creek alluvia near Nowy Targ. Jęczmyk & Wojciechowski (1994) also consider the Malcov Formation as one of possible sources of detrital gold in the Dunajec river valley. Such suggestion is supported by results of gold prospection in Slovakia where gold occurrences are linked to innermost part of the Magura unit (Križáni 1982).

The flattening of gold particles and plastic deformations of gold grains and flakes and incorporation of quartz grains suggest fluvial transport. The degree of deformations compared with published data on other gold placers (Hallbauer & Utter 1977; Vavelidis et al. 1997) is relatively low — it can be interpreted as indices of a relatively short-distance transport. The degree of flattening of gold particles from the Nowy Targ area is much lower in comparison with those from alluvia of the Wisła river near Kraków (author's unpublished materials).
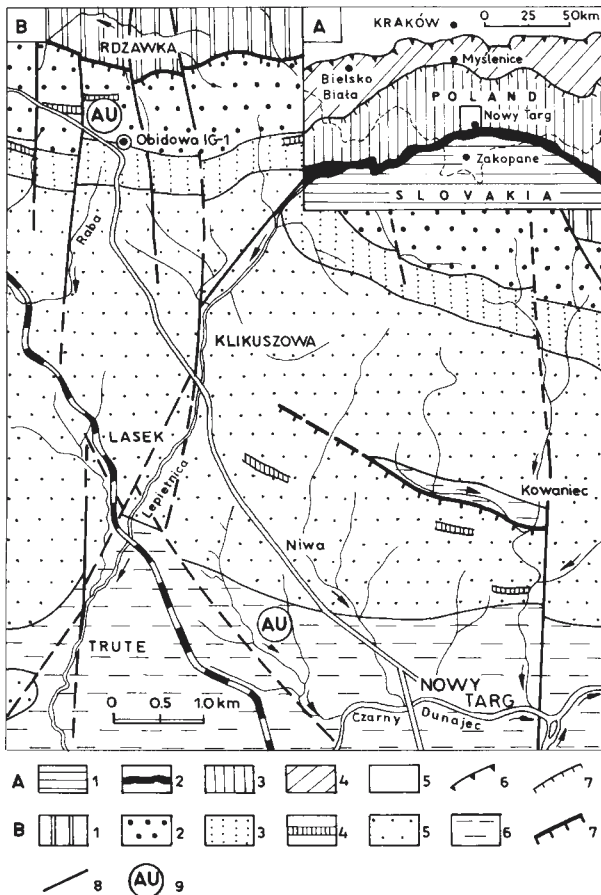
Fig. 1. Geological setting of gold occurrences within the Magura nappe in the Nowy Targ area. **A** — Geological sketch-map of the Western Carpathians of Poland: 1 — Central Carpathians, 2 — Pieniny Klippen Belt, 3 — Magura Nappe, 4 — other Outer Carpathian nappes, 5 — Carpathian Foreland, 6 — Main Carpathian overthrust, 7 — Magura thrust. **B** — Geological map of the Magura Nappe — Krynica Subunit in the Nowy Targ area: 1 — Szczawnica Formation, Magura Formation: 2 — Piwniczna Sandstone Member, 3 — Kowaniec beds, 4 — variegated shales, 5 — Poprad Sandstone Member, 6 — Malcov Formation, 7 — slice thrusts, 8 — faults, 9 — location of gold occurrences.
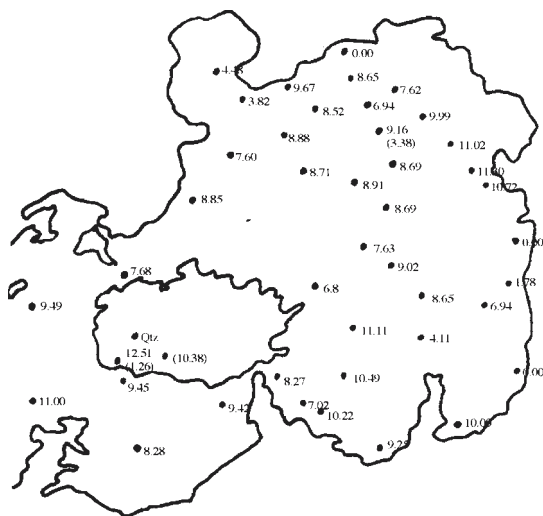

Fig. 2. Section of a gold particle from Niwa — distribution of Ag and Fe (in brackets) contents (in wt. %).

The occurrence of thin and irregular silver-poor rims around gold particles is noted relatively often in gold placers (Desborough 1970; Desborough et al. 1971; Vavelidis 1998). The mechanism of this depletion is the subject of discussions (e.g. Krupp & Weiser 1993; Moller 1993) but it probably may be related to the influence of highly oxidising conditions in alluvial environment. The de-alloying processes, which resulted in the depletion in silver at the rim around gold particles, can be the reason of formation of spongy surfaces.

An alternative explanation of filamentous, spongy surfaces of majority gold particles from the Nowy Targ area is their biological (bacterial or fungal) origin. Such explanation is supported with biogenic interpretation of similar grain surface texture observed both in Alaskan (Watterson 1991) and Australian (Günter & Bischoff 1997) gold placers. At the present state of geochemical investigations it is hardly possible to suggest the type of primary source rocks for of gold particles.

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GENETIC MODEL OF THE EPITHERMAL MINERALIZATION IN THE BANSKÁ ŠTIAVNICA-HODRUŠA ORE DISTRICT (WESTERN CARPATHIANS, SLOVAKIA)

S. JELEŇ[1], M. HÁBER[1], V. KOVALENKER[2],
L. NOSIK[2] and V. NAUMOV[3]

[1]Geological Institute, Slovak Academy of Sciences, Banská Bystrica, Severná 5, Slovak Republic; haber@gu.bb.sanet.sk
[2]Institute of the Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, Staromonetny pereulok 35, 109017 Moscow, Russia; vak@igem.msk.su
[3] Institute of Geochemistry Russian Academy of Sciences, Kosygina 19, 117 334, Moscow, Russia

Key words: Banská Štiavnica stratovolcano, Au-Ag-base metal mineralization, P-T-X conditions, isotopic composition, K/Ar age.

Introduction

The Banská Štiavnica-Hodruša ore district is located in Central Slovakia, in the central part of a polygenic stratovolcano, whose pre-Tertiary basement consists of Paleozoic rocks, Mesozoic sediments and Tertiary sediments. Evolution of the stratovolcano progressed beyond the caldera stage. Final uplifting of the central zone, formed a geologically recent and well defined horst. The volcanic rocks are composed of andesites, quartz diorite and granodiorite porphyry, diorites and granodiorites. Ring-shaped extrusive formations encompassing the horst represent a component of the central zone.

Magmatic activity is dated at 6.8–17.2 Ma by "volumetric" K/Ar and fission track geochronology. However, the most recent K/Ar data obtained from the most important volcanic rocks by isotopic dilution with [39]Ar confine this range to 5.8–12.8 Ma (Chernyshev et al. 1994).

Ore-forming process

The evolution of the stratovolcano was accompanied by polystage mineralization processes (Burian et. al. 1985; Grecula et al. 1997). There are various genetic types of ore mineralization: *intrusion related mineralizations* (magnetite skarn; porphyry/skarn Cu ± Mo,Au; stockwork/disseminated base metal; higher temperature (mesothermal?) Au-carbonate-quartz vein system), *high sulphidation epithermal mineralization* (quartz-pyrophyllite-pyrite system), *low sulphidation epithermal mineralizations* (precious and base metal veins hydrothermally metasomatic base metal mineralization; Au-Ag ± Hg-Sb-As veins). The precious and base metal vein-type mineralization is the most abundant and economically most important mineralization in this region.

The hydrothermal precious- and base-metal mineralization originated in three successive cycles. A new type of mesothermal (?) precious metal mineralization (**I ore-cycle**) was found in the last years in the Hodruša ore field, about 500 m below the surface (Maťo et al. 1996). In the short part of the filling of the vein system there are several types of structures: asymmetrically banded, brecciated and massive; fragments of the earlier precious and base metal mineralization in the light grey quartz with banded structure with anhedral leaves of earlier gold, and also with fragments of rhodochrosite are impregnated by milky quartz and transparent crystalline quartz with later disseminated mineralization. The earliest mineral assemblage consists of mesothermal (?) gold-quartz-carbonate mineralization, accompanied by small amounts of pyrite and sphalerite. It

was formed at relatively high temperatures (395–230 °C) in acid and subneutral solutions at depths from 2.0 to 1.5 km. Temperature decrease was accompanied by gradual pH increase from 3.6 to 4.5. The salinity of the aqueous solutions ranges from 0.4 to 7.7 wt. % NaCl equiv. and sporadic presence of carbon dioxide is also characteristic. The $\delta^{34}S$ values in sulphides of this type precious mineralization characterized variability from 1.0 to 6.7 ‰. These isotopic data with $\delta^{34}S \approx 3$ ‰ indicate a magmatic source of sulphur that has probably been derived from fluids of deeper origin.

The **II ore-forming cycle** (base metal productive only) of the epithermal vein represent the following stages: 1 — hematite-quartz (including rhodonite, rhodochrosite), 2 — sphalerite (incl. galena, chalcopyrite, pyrite, quartz), and 3 — rhodonite-carbonate-quartz (including adularia). It was formed at temperatures from 380 to 200 °C, pH from 4.7 to 6.0, lg a_{S2} from –11 to –14 and lg a_{O2} from –32 to –41 at depths from 0.75 to 1.60 km.

The **III ore-forming cycle** represents the economically most significant ore-forming cycle from the point of view of concentration of precious and base metal ores in the steeply dipping fissures. It is characterized by the two stages of mineralization: 4 — galena-chalcopyrite (incl. sphalerite, tetrahedrite, Ag-Cu-Pb-Bi sulphosalts, gold, hematite, scheelite, ferberite, a o.) and 5 — sulphosalts-precious metal-barite (incl. quartz, sphalerite-cleiophane, chalcopyrite, pyrite, marcasite, electrum, acanthite, and other Ag minerals). These stages originated at temperatures from 310 to 50 °C, pH from 3.5 to 7.6, lg a_{S2} from –8 to –17 a lg a_{O2} from –30 to –46, at depths from 0.4 to 1.1 km.

Isotopic composition of minerals and fluids

The $\delta^{34}S$ values in minerals (pyrite, sphalerite, galena, chalcopyrite, marcasite) from the II and III ore-cycles fluctuate in a relatively broad range from –9.9 to +11.8 ‰ in sulphides and from 17.5 to 22.5 ‰ in barite. The sulphur isotopic data indicate, that $\delta^{34}S$ values of sulphides are generally representative for fluids expelled from the uncontaminated granitic magmas. A portion of the $\delta^{34}S$ values in late sulphides and sulphates might suggest sulphur contamination attributed to leaching the evaporitic sediments.

The calculated oxygen isotope compositions of water ($\delta^{18}O$) in equilibrium with carbonate and barite vary between –3 and –11 ‰, thus yielding further evidence for the presence of meteoric waters in the mineral-forming solutions. On the other hand, equilibrium isotopic composition of CO_2 coexisting with carbonates 2nd stage ($\delta^{13}C$ = –8.4 to –11.8 ‰ PDB) and 4th+5th stage ($\delta^{13}C$ = 0.2 to –13.3 ‰) do not rule out its partially magmatic origin. The oxygen isotope composition ($\delta^{18}O$) of quartz, hematite, scheelite, barite (from –4.0 to 13.6 ‰) and carbonates (from 3.5 to 25.1 ‰), hydrogen isotope composition δD of OH-bearing minerals — kaolinite, chlorite (from –75 to –76 ‰) as well as those of the fluids trapped in quartz, sphalerite, barite (from –52 to –71 ‰), unequivocally indicate progressively increasing proportions of meteoric waters from earlier to later stages of mineral formation with barite and carbonate (from –94 to –113 ‰).

Age of mineralization

Precise low-background K/Ar method permitted the first age determination of $2M_1$ sericite from the deposit (Chernyshev et al. 1994). The obtained values (12.3–13.3 Ma) constrain the duration of the main, 4th stage to approximately 1 Ma. Owing to the uncertainty in the age determinations (from ± 0.4 to ± 1.2 Ma in various samples), the obtained values overlap each other and do not thus permit chronological relationships to be defined between selected ore mineralizations and magmatic complexes.

Conclusions

The ore-forming processes at the deposit were thus accompanied by concomitant decreases of temperature, oxygen and sulphur activity. Temperature decrease accompanied by gradual pH increase from 3.6 to 4.7 possibly caused the ore precipitation in the second and fourth mineralization stages. pH values ranging from 5.5 to 7.6 are characteristic of the fifth stage. Essential portions of the base metal ores were formed at rather high (250–300 ^{o}C) temperatures in acid and subneutral solutions containing comparable concentrations of sulphate and sulphide sulphur. The precious-metal ore mineralization precipitated from lower temperature (150-200 ^{o}C), slightly alkaline solutions characterized by superiority of the sulphate sulphur. Authors suppose that on cooling, at the stage of magmatic distillation, excess water and chlorine were expelled from the melt, extracting and concentrating ore components. With decreasing temperature, salt concentration in the fluid was initially increasing. The opposite trend was established during fracture extension, followed by influx of diluted meteoric waters and by constitution of a convective fluid system. During this stage, thermodynamic parameters approving ore precipitation were attained. Duration of the mineral-forming process of the III ore-forming cycle in the central zone of the Banská Štiavnica stratovolcano was 1–2 Ma.

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BANSKÁ ŠTIAVNICA EPITHERMAL FLUID-MAGMATIC SYSTEM: FLUID/SALT MELT INCLUSIONS STUDIES

V. A. KOVALENKER[1], V. YU. PROKOPHIEV[2], M. HÁBER[3] and S. JELEŇ[3]

[1]Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM), RAS, Staromonetny per. 35, 109017 Moscow, Russia
[2]Vinogradov Institute of Geochemistry, Sibirian Branch of Russian Academy of Sciences, Favorsky str.1a, 664033 Irkutsk, Russia
[3]Geological Institute, SAS, Severná 5, 97401 Banská Bystrica, Slovak Republic

Key words: epithermal, salt melt inclusion, Banská Štiavnica, fluid-magmatic system, gold-silver deposit.

Introduction

We think that the Banská Štiavnica Au-Ag- and base metal deposits were formed by epithermal fluid-magmatic systems (EFMS) of deep origin. Such systems are connected with the formation of the great group of Au, Ag, Cu, Pb, Zn, U, Sn, Hg deposits characterized, as a rule, by high levels of concentration of ore components, mineral pecularities and the signs of ore-forming processes of high dynamic activity (Rusinov & Kovalenker 1991). This EFMS in the region of the crust–mantle boundary have large magmatic centres and in the earth crust subvertical zones of high fluid-magmatic activity. This activity is needed for the formation of epithermal ore mineralization on the upper levels of the EFMS, and is connected with the participation of mighty ascending streams of transmagmatic fluids, processes of granitization, intrusive and volcanic magmatism.

Fluid inclusions trapped in magmatic and hydrothermal minerals, have proved to be useful for constraining aspects of the prevailing physicochemical conditions during crystallization and ore deposition. However, to explore the magmatic to hydrothermal transition, a combination of both melt and fluid inclusion research is required, yet published studies on this remain limited with the majority of work focussing on either melt inclusions in magmatic phenocrysts, or fluid inclusions in vein minerals. Another limitation comes from the exclusive use of primary fluid inclusions with little regard for secondary fluid inclusions, especially those in magmatic phenocrysts. However, secondary fluid inclusions in magmatic minerals from intrusives that possess a clear genetic link with hydrothermal mineralization, may preserve a record of phase compositions, physical conditions and processes transitional to hydrothermal.

This contribution presents the results of a detailed microthermometric study of more than 1900 paragenetically constrained primary and secondary melt/salt/fluid inclusions in magmatic and hydrothermal minerals from the Banská Štiavnica EFMS with Au-Ag- and base metal deposits. These data provide a means of constraining the physicochemical evolution of the metal-bearing fluids from initial high-temperature magmatic-hydrothermal to low temperature epithermal conditions.

Fluid/salt melt inclusion studies

The primary melt inclusions (<< 3 to 35 μm in diameter) in magmatic quartz from granodiorites are composed of strongly birefringent silicate(?) crystals, an interstitial liquid phase and a fluid bubble liquid is likely to be a Mg-Na chloride aqueous solution with eutectic temperatures ranging from –38 to –34 ^{o}C and estimated total salinity of 8.3–9.6 eq. wt. % NaCl. Dissolution of the vapour bubble into liquid occurred at 258–302 ^{o}C, and sillicate crystals commenced melting at ~600 ^{o}C. Complete homogenization (melting of all daughter crystals) was achieved at 680–750 ^{o}C in several small (< 5 μm) inclusions. Pressure at these temperatures was estimated to be as high as 3.7–5.6 kbar using the method outlined by Naumov (1979). High H_2O abundances were also calculated in the silicate melt (4.6–6.3 wt. %) using the technique described by Naumov (1979), as well as taking into account the volume increase due to melting of the host quartz from inclusion walls (Reyf & Bazheyev 1985). The concentration of chlorine in the melt was calculated to be within 0.24–0.39 wt. % (based on the assumption that all chlorides occur as NaCl).

A second population of inclusions (5–30 μm in diameter) containing highly mineralized brine (halite crystals, opaque phases, liquid and a vapour bubble, were observed along linear growth zones in magmatic quartz which also hosted silicate-salt melt inclusions. The brine inclusions typically decrepitate during heating, although in some experiments very small inclusions homogenize (i.e. dissolution of halite crystal) at 640 ^{o}C. A salinity of ~79.7 eq. wt. % NaCl was estimated for the brine-rich inclusions using the method described by Bodnar & Vityk (1994), and pressure estimates of ~4 kbar at the point of homogenization. Secondary fluid inclusions in magmatic quartz from granodiorites vary significant-

ly in terms of their appearance, size and phase composition. The most abundant are multi-phase (liquid + vapour + various daughter minerals), three-phase with a halite crystal, and two-phase liquid-rich inclusions. Two-phase vapour-rich inclusions are relatively rare. From microthermometric work the observed and calculated variations in the physical and chemical parameters of these fluid inclusions were: temperature 225–640 °C, salinity 1.5–75 eq. wt. % NaCl, density 0.85–1.3 g/cm^3 and pressure 0.01–4 kbar. These data indicate a progressive decrease in salinity of the fluid along the NaCl saturation line at high temperatures. A similar trend in pressure is also observed.

At 370–260 °C, the salinity and density of the fluid decreased abruptly. Fluid inclusions in the minerals (quartz, barite, fluorite and sphalerite) from the hydrothermal ore-bearing veins comprise aqueous two-phase (liquid + vapour) types. These primary inclusions are often very large in size (up to 100–150 μm) and are aligned along growth zones in the crystals. The coexistence of liquid-rich and vapour-rich inclusions in the same growth zone demonstrates that the fluid was heterogeneous at the moment of trapping. The results of microthermometric work on more than 1800 individual fluid inclusions in different vein minerals and sphalerite indicate that the hydrothermal fluids were low-salinity (0.5–11.5 eq. wt. % NaCl), Mg-Na chloride solutions, and that ore deposition occurred between 50–380 °C and < 225 bar (Kovalenker et al. 1991). The physical and chemical conditions of the ore-forming process during this stage imply that the metal-bearing fluids were systematically displaced toward lower salinities, temperatures and pressures in comparison to the magmatic hydrothermal stage defined by inclusions in magmatic quartz.

Discussion

It has long been accepted that epithermal systems are formed at shallow levels by circulating hydrothermal solutions, and are genetically related to magmatic rocks. Intrusive magmatic bodies are generally regarded as a means of providing heat to drive convecting water (hydrothermal) cells (Berger & Eimon 1983). However, despite the fact that most epithermal deposits demonstrate close spatial and temporal associations with magmatic rocks, the source of fluids, metals and ligands (HS$^-$, Cl$^-$, etc.) in hydrothermal solutions remain controversial. The results of the present study of primary melt, and primary and secondary fluid inclusions in magmatic and hydrothermal minerals from Banská Štiavnica EFMS provide further evidence for the close genetic association between intrusive magmatic systems and at least some epithermal deposits.

The occurrence of brine inclusions in magmatic rather than hydrothermal quartz, as well as their spatial and temporal association with silicate-salt melt inclusions, suggests that they represent a trapped late magmatic fluid phase. This implies that this phase was possibly transitional between silicate magma and later metal-bearing fluids involved in the formation of epithermal mineralization. The evolution of these precursor ore-forming fluids is recorded in the secondary hypersaline to saline fluid inclusions in magmatic quartz. Salinity, density, temperature and pressure of this fluid systematically decrease towards the values of primary fluid inclusions in epithermal veins that host economic mineralization. The abrupt decrease in salinities of these fluids from the NaCl saturation curve values of 260–370 °C can be interpreted as a result of mixing with meteoric water and subsequent dilution in the top of the cooling pluton or lower levels of the developing epithermal system. Overall, the observations and data indicate that secondary fluid inclusions in the magmatic quartz preserve 'snapshots' of the physical and chemical parameters of the mineralizing system, from magmatic to hydrothermal conditions.

The physicochemical evolution of the fluid recorded in salt and fluid inclusions provides a sequential record of the development of the magmatic-hydrothermal system from the mesothermal (magmatic) environment to the formation of ore-bearing veins in the epithermal environment. Further evidence in support of this magmatic-hydrothermal connection is the temporal association between the Banská Štiavnica hydrothermal system (alteration of country rocks and mineralization), and the emplacement of the granodiorite pluton. In addition, the possible source magmas were enriched with water (3–7 wt. %) and chlorine (up to 0.5 wt. %) based on data from primary melt and fluid inclusions in plagioclase from biotite-amphibole andesite, and in quartz and sanidine from biotite-sanidine rhyolite which comprise the comagmatic volcanic pile above the intrusive body (Naumov et al. 1996).

In summary, evidence for the proposed magmatic-hydrothermal transition at the Banská Štiavnica epithermal ore deposit includes: 1. The granodiorite magma was enriched in volatile elements, namely H$_2$O and Cl; 2. Highly concentrated chloride melts or brines were probably formed as a result of exsolution of H$_2$O-rich fluid during the later stages of silicate magma crystallization; 3. Postmagmatic fluids trapped as secondary inclusions in magmatic quartz possess a range of salinities from hypersaline mesothermal magmatic fluid to relatively low-saline, epithermal near-surface fluid. Other parameters such as fluid pressure and density display similar variations.

Therefore, it is proposed that the granodiorite magma was the source of the epithermal metal-bearing fluids at Banská Štiavnica. Upon cooling, the magma exsolved hypersaline fluids that were capable of transporting ore-forming components. During cooling, the salinity of these magma derived brines decreased gradually along the NaCl aqueous solution saturation curve, and then decreased abruptly attaining values typical of epithermal ore-fluids. It is envisaged that this abrupt change in fluid salinity at low temperature (370–260 °C) and associated decrease in fluid density and pressure resulted from the dilution of the brines via mixing with convecting meteoric waters (low temperature and salinity).

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THE ENVIRONMENTAL IMPACT OF ACIDIFICATION IN THE BANSKÁ ŠTIAVNICA MINING AREA

O. LINTNEROVÁ[1], M. LÍŠKOVÁ[1] and M. KUŠNIEROVÁ[2]

[1]Department of Mineral Deposits Geology, Comenius University, Mlynská dolina G, 842 15 Bratislava, Slovak Republic
[2]Geotechnical Institute of Slovak Academy of Sciences, Wattsonova 4, Košice, Slovak Republic

Key words: acid water, sulphide oxidation, acidophilic bacteria, Banská Štiavnica.

Introduction

The acidification of water and soils in the Banská Štiavnica area is one of the most important environmental problem connected with mining and processing industry (Šucha et al. 1997; Lintnerová et al. 1999; Líšková et al. 1999). The rate of weathering of sulphide minerals is generally accelerated by mining and mineral processing. The increased accessibility of oxygen enhances the rate of sulphide oxidation reactions which produce sulphuric acid and result in highly acidic waters with elevated metal concentrations (Jambor & Blowes 1994). Pyrite is the most abundant sulphide mineral in mine wastes and potentially the main source of acid mine drainage (AMD) generation. Although oxygen is the overall oxidant, kinetic data suggest, that ferric iron is the direct oxidant in acid systems and that temperature, pH, surface area, and the presence of iron and sulphur-oxidizing bacteria (Thiobacilli) can greatly affect the rate of reaction (Nordsrtom 1982; Jambor & Blowes 1994). The oxidation of sulphide minerals and consequent release of sulphuric acid in mines and mine wastes can last for decades to centuries (Jambor & Blowes 1994).

Methods

Field and laboratory investigation of waters, soils and neoformed mineral phases were done in 1996 to 1998. pH measurement of water and soils and chemical analyses of Fe-oxide/hydroxides were performed by standard methods (the details see in Lintnerová et al. 1999; Líšková et al. 1999). Fe-oxyhydroxide minerals were studied by X-ray diffraction and electron microscopic methods (TEM, SEM).

Results

Banská Štiavnica-Šobov Mine

Acid water (Fig. 1) generated in quarry and mine dumps is transmitted through the near-surface weathered zone and directed by permeability and area morphology penetrates into the soils and/or outflows as a stream. Elevated contents of exchangeable and toxic Al occur in polluted acid soils and the most acidic soils are devoid of vegetation in the vicinity of mine dumps (Šucha et al. 1997). H$^+$ released by sulphide oxidation contacts with solids and acid neutralization reactions result in an increase in the water pH. This increase in pH is frequently accompanied by precipitation of sulphates and metal-bearing hydroxides and oxyhydroxysulphates, like gypsum, rozenite, jarosite, ferrihydrite, schwertmannite and goethite. The extremely fine-grained Fe-oxyhydroxides attenuate dissolved elements (mainly Al, Mn, As) from acid drainage or pore waters (Lintnerová et al. 1999). Pyrite oxidation is catalyzed by acidophylic bacteria. *Thiobacillus ferrooxidans, Thiobacillus thiooxidans* and

Leptospirilum ferrooxidans were identified in mud samples from the bottom of a 16 m deep piesometer located just below a mine dump. Not only dump discharged waters but also groundwaters are extremely acid (pH 2) and oxidic (Eh > 500 mV). Lower contents or wider variability of groundwater TDS (4 to 17 g/l) may be a result of seasonal precipitation and/or Fe secondar (oxyhydroxide) mineral phases generation and dissolution.

Sulfide tailing impoundments

The large volumes of sulphide mill tailings have been disposed to the impounds in the Banská Štiavnica mine area. The tailing content of sulphide minerals is relatively low (generally less than 10 %), but acidification of anthropogenic soils (pH 2-4) on the Sedem žien impoundment dam have just appeared (Líšková et al. 1999). Sulphide oxidation and subsequent neutralization reactions occurring in these inactive mill tailings resulted in the depletion of sulphides, carbonates and some aluminosilicate minerals and accumulation of metal-hydroxides and sulphate minerals. Sulphide (pyrite) oxidation occurs in the vadose zone of the impoundment, where oxygen diffusion through the partly water-saturated tailings is rapid (Blowes & Ptacek 1994). Oxidation of the sulphides is practically complete in the vadose zone of the impoundment.

Discussion

The negative environmental impact of acid water with high metal concentrations (Fe, Cu, Zn, Al) generated by oxidation of pyrite in Šobov quarry and dump (pyritized illite-pyrophyllite clay gangue rocks) was recognized by Šucha et al. (1997). Documented bacterial activity in the mine wastes, enhanced pyrite oxidation process and high content of pyrite in the mine and dump are the most important factors which increase the environmental risk of this mining area. It can be simply documented by the extremely low pH values of effluent (drainage) waters and its pH-stability in some years. Seasonal increases in water volume basically do not changes the H$^+$ water concentration, probably because of dissolution of secondary minerals, which represent "stored acidity" (Jambor & Blowes 1994). Šobov AMD are collected and returned to the abandoned mines. Neutralization or dilution of such AMD needs very large volume of fresh water and/or lime, which will generate secondary pollution (Šucha et al.1995, 1997). An increase in pH and removal of metals from acid mine water could potentially be done using microbially activated biomass.

Sulphate mine tailing impoundments in the Banská Štiavnica area can be the potential source of acidification of water and/or soils (Líšková et al. 1999). We suggest that, it is important to understand whether the impound of Sedem žien in the vicinity of the Šobov mine area, badly polluted by AMD (Šucha et al. 1997) will
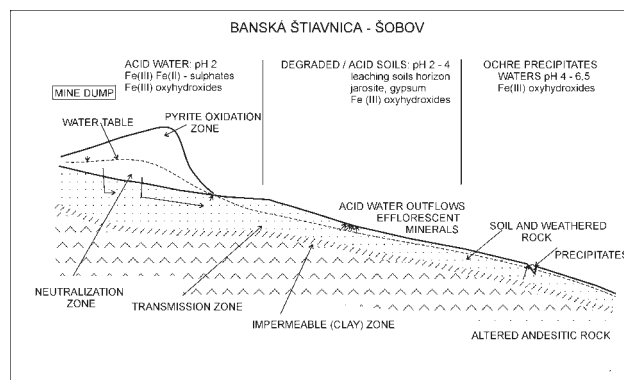

Fig. 1. Schematic profile of the Banská Štiavnica-Šobov Mine area.

be an additional source of acidity and if impoundment recultivation will be successful in the end. The antropogenic soils on the impoundments are more unstable than native soils and can be easily eroded. It can be seen, that not only acidic soils, but also an increased content of neutral salts (commonly gypsum) prevented the growth of grass on the impoundment surface (e.g. impoundment Lintich).

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MANGANESE MINERALIZATION IN THE WESTERN CARPATHIANS, SLOVAKIA

I. ROJKOVIČ

Department of Raw Materials, Faculty of Natural Sciences, Comenius University, 842 15 Bratislava, Slovak Republic; rojkovic@fns.uniba.sk

Key words: manganese deposits, Mn-minerals, origin, Early Paleozoic, Jurassic, Paleogene.

The most important manganese deposits in Slovakia were mined in the Paleogene (Eocene) sediments near Kišovce and Švábovce (Fig. 1). Manganese deposits were formed at the bottom of a shallow sea in a littoral environment as in the case of the well-known Oligocene deposits in Nikopol (Ukraine) and Chiatura (Georgia). Mn carbonates in ore represented by rhodochrosite and kutnahorite reflect more reducing conditions of their origin. Thin oxide-carbonate beds are represented by manganocalcite, pyrolusite and manganite (Konta 1951). A reducing environment is also confirmed by scarcity of fossils, by pyritization of rare foraminifers as well as by increased content of organic carbon (up to 1 wt. %).

Condensed Middle and Late Jurassic limestone and radiolarian chert in the Pieniny Klippen Belt as well as in the Považský Inovec Mts. contain occurrences of manganese ore. They were thought to be of syngenetic or infiltration origin (Andrusov et al. 1955; Ilavský 1955). They correspond partly to recent submarine hardgrounds developed in places of pelagic and hemipelagic oozes. They were also formed on topographic highs in fairly shallow water and they are associated with algal stromatolites and encrusting foraminifers. Stromatolites form columnar shape. Borings of fungi accompany encrusting foraminifers.

Organodetritic micritic limestone in Horné Sŕnie, Hrušové, Lednice, Mikušovce and Vršatec with abundant fossils (columnar stromatolites, foraminifers, lamellibranchiates, sponges and gas-

tropods) as well as radiolarite chert in Šarišské Jastrabie and in Trenčianske Jastrabie contain manganese oxides and hydroxides as pyrolusite, psilomelane, todorokite, cryptomelane and iron hydroxides. Psilomelane secondary veinlets cut iron hydroxides as well as younger carbonate veinlets. These manganese ores show low contents of organic carbon and they were formed in oxidic conditions in a shallow sea. The chemistry of the Jurassic Tethyan manganese nodules is extremely varied and inter-elemental relationships vary from nodule to nodule (Roy 1980). The chemical composition of the studied manganese ores shows a large variability of trace elements especially Ba, Co, Cu, Ni and Pb.

Mn carbonate beds were formed in association with black shale in rifted basins in continental margin during the Toarcian ocean anoxic event in Europe (Jenkyns et al. 1991). Occurrences of manganese mineralization were found in the Lower Jurassic shales (Toarcian) shale in the Malé Karpaty Mts. (Polák 1957), Branisko (Polák & Siráňová 1993) and the Malá Fatra Mts. (Zázrivá). Manganese minerals are represented in the Malé Karpaty Mts. by the dominant carbonates rhodochrosite and kutnahorite and in Zázrivá by manganocalcite. A reducing environment is confirmed by the depletion of fossils and by presence of framboidal pyrite. The content of organic carbon compared to the Middle Jurassic manganese ore is distinctly increased and similar to Paleogene manganese occurrences (up to 1 wt. %). Manganese associated with organic matter in deep parts of the basin was dissolved under reducing condition and the action of microorganisms. $Mn(HCO_3)_2$ was more easily soluble than $Fe(HCO_3)_2$ demanding more acid and reducing conditions. The manganese carbonates were formed after movement of bicarbonates by diffusion to littoral zones and by the effect of Mn-oxidizing bacteria. Pyrolusite and psilomelane were formed later mostly due to oxidation of primary manganese carbonates.

Stratiform manganese deposits are bound to the black phyllite representing the metamorphosed Early Paleozoic black shales accompanied by volcanic rocks in the Slovenské rudohorie Mts. (Čučma and Malá Hekerová near Švedlár). The black shales represent near shore sediments formed in an anoxic environment. Manganese ore forms lenses from 50 to 100 m long and from 1 to 4 m thick. Several kt of oxidic ore was mined from the Čučma deposit (Grecula et al. 1995). The dominant Mn-minerals rhodonite and rhodochrosite are accompanied by spessartite, pyrophanite, pyroxmangite, tephroite, Mn-magnetite, manganocalcite, Mn-tremolite, tremolite, pyrosmalite, bementite, pyrite, chalcopyrite, pyrrhotite, sphalerite, galena, marcasite, hematite, limonite, quartz, calcite, chlorite, muscovite, apatite, barite (Kantor 1954; Faryad 1991; Rojkovič 1998). Mn-silicates and magnetite are cut by veinlets of younger sulphides (pyrite, chalcopyrite, pyrrhotite). The presence of Ni, Co and Cu minerals such as pentlandite, chalcopyrite and cobaltite may reflect the presence of metals adsorbed in the prima-
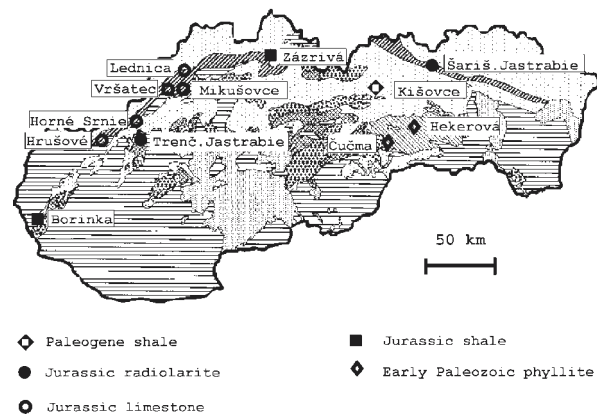

Fig. 1. Manganese deposits in different rocks of the Western Carpathians.

ry manganese ore. Younger manganocalcite and quartz accompany this hydrothermal phase. Manganese mineralization is overprinted by processes of oxidation. The dominant oxide and hydroxide minerals are manganite, psilomelane and pyrolusite.

A high Mn/Fe ratio indicates diagenetic modification due to reducing environment. Reducing conditions were formed in sediments due to abundant organic matter in the sediments and Mn^{+4} and Fe^{+3} was reduced to Mn^{+2} and Fe^{+2} ascending in the pore waters to the sediment-water boundary. Sedimentary diagenetic accumulation of manganese formed due to a reducing environment was overprinted by an association of metamorphic minerals. Sedimentary rocks contained Mn-carbonate, clay minerals and quartz before metamorphism. The recent predominantly silicate character of manganese ore was formed due to metamorphism of silicates and carbonates of manganese. Metamorphosed manganese carbonate-silicate rocks "queltzites" are characterized by the presence of Mn-carbonate, tephroite and absence of low Mn-oxides especially bixbyite. The association of rhodonite, rhodochrosite, spessartite, pyrophanite, pyroxmangite and tephroite suggests the epidote-amphibolite zone of Hercynian metamorphism. The rhodonite-pyroxmangite geothermomer gives $375 \pm 10\ ^{\circ}C$ (Faryad 1991) and our results are close ($390\ ^{\circ}C$) in manganese ores from the Čučma deposit.

Conclusions

Stratiform manganese mineralization in different stratigraphic horizons of the Western Carpathians reflect oxidizing or more reducing environments of marine basins during their formation. Manganese and iron oxides and hydroxides accompanying Jurassic limestone and radiolarite were formed in oxidizing environments. Manganese carbonates in shales and marls with increased content of organic matter were formed in more reducing conditions. They were formed during the Paleogene, Jurassic and Early Palaeozoic. The Early Paleozoic carbonates of manganese underwent the Hercynian metamorphism together with silicate minerals and manganese silicates and titanates were formed.

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A FIRST ATTEMPT TO GEOCHEMOMETRICALLY COMPARE ORE DEPOSITS OF THE WESTERN CARPATHIANS AND THE EASTERN ALPS

E. SCHROLL[1], P. ANDRÁŠ[2] and M. CHOVAN[3]

[1]Institute of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria
[2]Geological Institute, Slovak Academy of Sciences, Severná 5, 974 01 Banská Bystrica, Slovak Republic
[3]Department of Mineralogy, Comenius University, Mlynská dolina G, 842 15 Bratislava, Slovak Republik

Introduction

The comparison of geological bodies, especially of ore deposits, is more objective, if the geostatistical concept of Geochemometry (Schroll 1997) is applied. The combination of chemical and isotopic data including observations and data, such as deviated from fluid inclusions, enables more realistic ideas about the genesis of the ore deposits. The results of the first test concerning the antimony deposits in both metallogenetic provinces have been reported (Andráš et al. 1998). The metallogenetical differences are illucidated with some examples on the basis of the present art of geochemical data.

Pb-isotopes

The comparison of the lead isotope distribution of the two geological units is presented in Fig. 1. The oldest model ages are similar showing high μ_2-values and age values around more than 600 Ma. They are typical of polymetallic massive sulphide mineralizations with exception of the ore district Stubai-Ötztal. In the Eastern Alps only, low μ_2-values are found in connection with mineralizations, like the scheelite deposits of Felbertal and the scheelite-bearing gold deposits of the Schellgaden type hosting in island arc rock suites. However, the main difference is the frequency of radiogenic lead (J-type), causing distinct inhomogeneities and anomalous negative model ages. The radiogenic leads are the mobilizates of young Alpidic metamorphism (around 30 Ma and 80 Ma) in the Eastern and Western Alps. The Hercynian granite intrusions of the Western Carpathians have not been seized by the „Tauern crystallization." The leads of the ore mineralizations connected with the young volcanism show relevant model ages or are slightly radiogenic.

In the Eastern Alps, strata-bound lead-zinc mineralizations have a tendency to model ages which are stratigraphically too old (B-type lead, named by the type locality Bleiberg). Such a lead isotope composition is also evident for the Devonian Pb-Zn-Ag-Ba ore mineralizations of the Graz Paleozoic (540 up to 570 Ma), and for most of the Triassic Pb-Zn- (F-Ba)-deposit there are age differences of 150 to 200 Ma years with respect to the stratigraphic ages. In the Eastern Alps, the lead isotope data of the Austrian carbonate-hosted Pb-Zn-ore mineralizations show model ages between 160 and 400 Ma. In the Western Carpathians, the lead isotope data of the few Anisian occurrences are unfortunate controversial, either comparable with the Alpine data or analogous with the ore lead from the ore mineralizations in the area of the Slovak neovolcanics.

However, the above mentioned model ages of the stratiform polymetallic massive sulphide deposits could be approximately real, as the physical dating of the host rocks indicates. Most of the ore mineralizations show model ages between 0 and 600 Ma. The
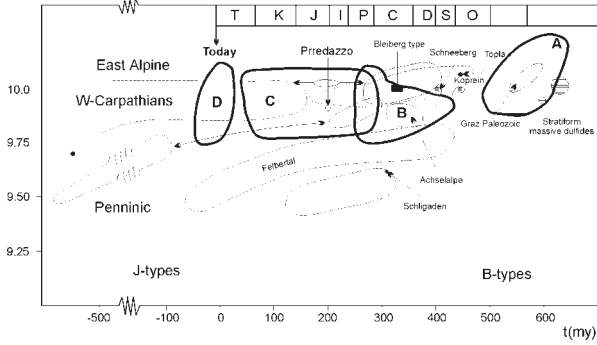
Fig. 1. Model age after Stacey & Kramers (1975) vs. μ_2-diagram comparing Eastern Alps (soft) and Western Carpathians (strong). Abbreviations: **A** — massive sulphide ore deposits (Gelnica Group), **B** — vein ore mineralizations (Gelnica Group), **C** — ore mineralizations of the Tatroveporide crystalline complex, **D** — ore mineralizations in the area of the Central Slovak neovolcanics (including some carbonate hosted sulphidic ore mineralizations).
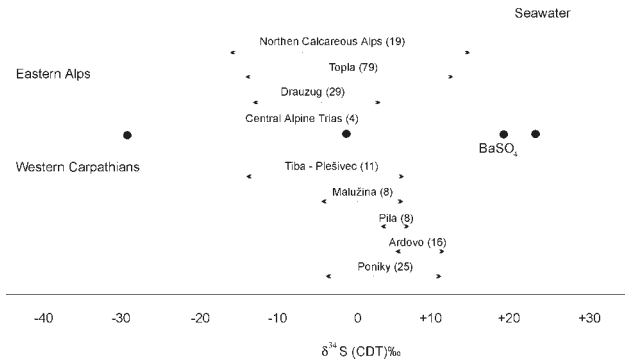

Fig. 2. Comparison of the sulphur isotope characteristic of Anisian carbonate hosted Pb-Zn-deposits (after Schroll 1997; Kantor 1997).
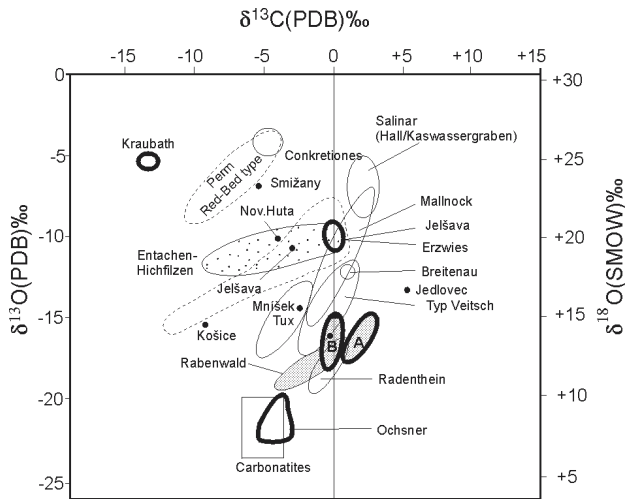

Fig. 3. C-O isotope diagram of magnesites of the Eastern Alps (soft) and Western Carpathians (after Schroll 1997; Turanová et al. 1996). Abbreviations: A — Košice, B — Jedlovec, excluding the outlayers.

μ_2-values vary between 8 and 10, corresponding to the average crust lead of the Hercynian granite complexes or to the thorogenic upper crust lead inherited from the pre-Cambrium clastic sedimentation (Data after: Schroll — including Köppel & Schroll 1997; Cernyšev, Cambel & Kodera 1984; Kantor & Rybár 1964).
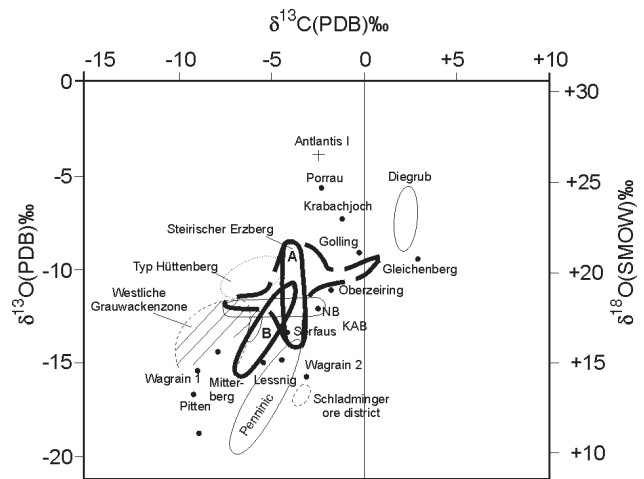

Fig. 4. C-O isotope diagram of siderites from the Eastern Alps (soft) — „Steirischer Erzberg" (dotted) — and of two selected siderite deposits of the Western Carpathians (strong): **A** — Rudňany, **B** — Rožňava (after: Schroll 1997; Grecula et al. 1995).

S-isotopes

The data base is well developed, although not in all cases sufficient. For example, the comparison is limited to the carbonate-hosted Pb-Zn deposits in respect to the problematic of biogenic and abiogenic sulphate reduction. The sulphide sulphur isotopes depend on the contemporaneous isotopic composition of the sea water sulphate. Therefore, differences in the sulphur isotope distribution are found between Anisian and Carnian Pb-Zn-mineralizations confirming different temporal origins. Fig. 2 presents the comparison of Pb-Zn occurrences hosted in Anisian carbonate rocks. Biogenic reduction processes are more typical in the Eastern Alps, although the inorganic origin of the sulphide sulphur is evident in some cases too. In the Western Carpathians, the acceptance of biogenic sulphide formation is conceivable only for the deposits of Poniky and of the vein range Herman–Tibor–Cipová (in Vyšná Slaná–Dobšiná region), as mentioned Kantor (1977). Ore mineralizations influenced by younger endogenic hydrothermal activities would be indicated by lead-lead model ages around zero (Černyšev et al. 1984).

C-O isotopes

Magnesites: Fig. 3 presents the comparison of the C-O isotope diagrams of magnesites. In the Western Carpathians, the Permian magnesites are in an adequate position. The Carboniferous-hosted magnesites are characterized by oxygen isotopes, the magnesites of Eugui in the Pyrenees (Spain) show a similar isotopic characteristic. In both cases, the sedimentary origin cannot be drawn in doubt considering the other facts too.

Siderites: The present state of the knowledge about the origin of siderites is not sufficient in all (Fig. 4). Recent sedimentary siderites are distinguishable clearly from those of deep seated veins or of a higher metamorphic environment. The siderites of the Rudňany deposit show affinity to the siderites of Erzberg. But the thermical history of the Erzberg is more complex. Rožňava and „Penninic" (Tauern gold veins) seem to be genetically analogous. But, the siderites of the „Penninic" are formed at higher temperatures.

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SULPHIDE OXIDATION PRODUCTS IN THE MALÉ KARPATY MTS. SW SLOVAKIA

S. TRTÍKOVÁ[1], M. CHOVAN[1], J. MADEJOVÁ[2],
M. KUŠNIEROVÁ[3] and I. ŠTYRIAKOVÁ[3]

[1]Department of Mineralogy and Petrology, Comenius University, Mlynská dolina G, 842 15 Bratislava, Slovak Republic
[2]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 842 26 Bratislava, Slovak Republic
[3]Geotechnical Institute, Slovak Academy of Sciences, Watsonova 45, 040 01 Košice, Slovak Republic

Key words: mine waters, iron oxyhydroxides, Malé Karpaty Mts.

Introduction

This paper deals with the hypergeneous products found in the area of Čmele, Augustín and Michal pyrite-pyrrhotite deposits and in the area of Kolársky Vrch and Pernek Sb-Au deposits. The precipitation and the deposition of the iron ochres is here the most distinctive manifestation of massive weathering. Our research involved the iron ochres deposition, the conditions of their formation, the role of microorganisms in the tailings and dumps environment, the identification and quantification of basic components — iron oxyhydroxides, the study of chemical composition and specification of some elements, structure ordering, morphology of particles and colour of precipitates.

Techniques and methods

The samples were taken from the mine drainage where the iron ochres precipitate and settle. pH in water was measured and water and solid secondary phases were sampled for further analysing. The secondary products were investigated by means of X-ray powder diffraction (XRD), atomic absorption spectrometry (AAS) (after selective dissolution), transmission electron micrography (TEM), scanning electron micrography (SEM), microprobe analyses, infrared spectroscopy (IR), Mössbauer spectroscopy (MS) and differential thermal and thermogravimetric analyses (DTA, TGA), as described by Bigham et al. (1990), Carlson & Bigham (1992), Bigham et al. (1996), Bigham et al. (1994). The identification of the chemolithotrophic bacteria in the mine drainage was accom-
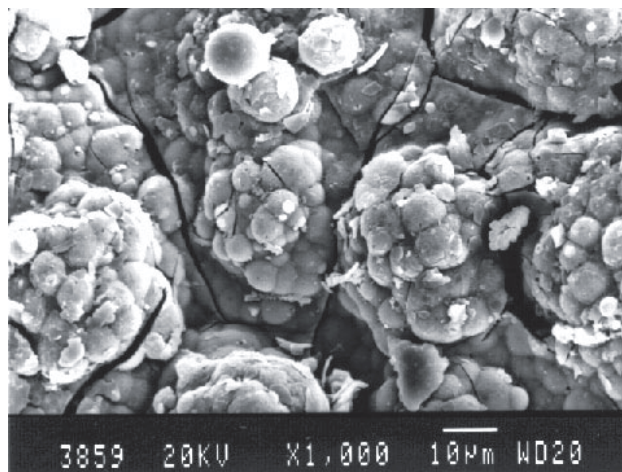

Fig. 1. Scanning electron micrograph (BSE mode) of goethite from FeS$_2$ deposit Augustín.

plished by isolation tests. Selective nutrient medium after Silverman, Lundgren and Vaksman (Silverman & Lundgren 1959) was applied in these tests.

Results and discussion

Intensive oxidation, dissolution and acidification takes place in the dumps and outcrops, in the pyrite-bearing black shales of the Augustín deposit (upper part of the Hrubá dolina valley). Lithotrophic bacteria *Thiobacillus ferrooxidans, Th. thiooxidans* and *Leptospirillum ferrooxidans* occur in the mine water at pH = 2.5–3 indicating their contribution to oxidation and precipitation processes. Only minor volumes of precipitates form at the bottoms of brooks. Precipitation and sedimentation of iron ochres prevails in the mine water with pH = 5.5–8 (Kolársky vrch, Michal and Pernek deposits). They occur in the form of fresh sediments at the bottom

Table 1: Chemical composition of fresh iron ochres, main major components, A11 and A12 — Augustín deposit, M1 — Michal deposit, K11 and K12 — Kolársky vrch deposit, PER1 and PER5 — Pernek deposit.

Sample	pH	Fe$_2$O$_3$	SiO$_2$	SO$_3$	Al$_2$O$_3$	As$_2$O$_5$
			wt. %			
A11	2.5-3	50.34	1.84	1.12	0.68	0.05
A12	2.5-3	46.33	2.52	0.82	0.59	0.02
M1	6.3-6.6	37.18	12.88	0.23	12.47	0.02
K11	7.5-8	34.68	2.57	13.31	0.32	24.07
K12	7.5-8	36.56	6.91	12.51	1.08	21.40
PER1	5.5-7	51.19	19.17	3.31	8.88	0.06
PER5	5.5-7	55.63	10.10	2.32	3.74	0.06

Table 2: Electron microprobe analyses (EDS) of goethite and opal rims from the oxidized zones of FeS$_2$ deposit Augustín, main major components.

	1.	2.	3.	4.	5.	6.	7.	8.
Number of analyses	3	2	1	3	1	2	1	2
FeO	88.02	3.90	27.94	3.09	69.51	93.77	90.06	67.02
SiO$_2$	1.57	88.91	64.64	90.68	0.69	1.33	6.28	20.29
S	7.03	0.39	0.79	0.51	18.77	3.32	0.97	0.85
Al$_2$O$_3$	1.04	5.59	5.99	3.52	0.36	0.00	2.10	8.12
P$_2$O$_5$	1.82	0.08	0.30	0.32	1.90	1.46	0.00	0.40
As$_2$O$_5$	0.00	0.75	0.00	1.00	0.00	0.00	0.00	0.00
Other components	0.42	0.40	0.34	0.48	8.77	0.12	0.59	3.33
				computed to 100 wt. %				

of mine drainage and locally they form in the marshes of large areal extent. Due to different formation conditions, their mineral composition varies widely. The hard pans of Fe oxide minerals solidify during the long-run repeated processes of drying and crystallisation of fresh precipitates in the mine waste environment. They were described as "limonite", a product of pyrite weathering (Cambel 1959).

The iron oxyhydroxides are basic components of fresh mine drainage ochres. The results of the above described methods indicate the presence of poorly crystallised ferrihydrite $Fe_5Ho_8.4H_2O$, schwertmannite $Fe_8O_8(SO_4)(OH)_6$, goethite α-FeO(OH) and ferric arsenate-sulphate(?) precipitates. Considerable sorption of Al_2O_3, SiO_2, As_2O_5 and SO_3 (Table 1) was recorded at the pyrite and stibnite deposits. All samples exhibit a moderate sorption of Ti, P, Sb, Zn, Pb, but in some samples Ca, K, Na, Mn, Cu were also recorded.

Goethite (stable form of iron oxyhydroxides, Fig. 1), opal, gypsum and jarosite form hard pans (Trtíková et al. 1996). These minerals either occur as rims of individual sulphide grains, or as massive coatings cementing the fragments of dump debris. At the microscale, coatings exhibit a stratification, in which the iron Fe-rich (goethite) alternate with laminae Si-rich (opal) ones (Table 2). The enrichment in S, P, Al, As (Table 2, as oxides), Sb, Na, K and Ca is a characteristic feature.

Toxic metal pollution causes more ecological problems in the studied area than the acidification. Iron ochreous muds represent a constant supply of toxic elements into the abandoned mine environment of the Malé Karpaty Mts. Therefore, a practical aim of our research was to investigate the transformation of ochres in time and/or on heating. These alterations may either lead to immo-bilisation, or to release of toxic elements (As, Al, Sb) sorbed on the surfaces of iron oxyhydroxides.

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