STIBNITE MINERALIZATION OF WESTERN CARPATHIANS AND EASTERN ALPS: GEOLOGICAL, MINERALOGICAL, AND GEOCHEMICAL FEATURES.

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Abstract: Stibnite mineralizations are situated in the Variscan basement and in Neogen volcanites in the Western Carpathians and in the Middle Austroalpine Crystalline complex and its post-Variscan sedimentary cover and in Jurassic limestone and shale, in the Eastern Alps. The succession of sulphidic mineral assemblages in the Variscan basement in the Western Carpathian and Eastern Alps is similar: *1st stage:* pyrite - arzenopyrite (±gold), *2nd stage:* Sb (Pb,Zn), stibnite, *3rd stage:* Cu, Sb, (Pb, Bi, Ag): tetrahedrite. Similar O and C isotopic features and two types of fluid inclusions have been identified from Sb deposits at Kreuzeck and Carpathians Variscan basement. Formation of antimony mineralizations are linked with variscan magmatic - metamorphic processes, peleoalpine rejuvenization and /or late Alpine period.

Key words: stibnite, geological setting, mineral assemblages, fluid inclusion and isotope study, origin, Alpine/Carpathian belt

The Western Carpathians and the Eastern Alps are part of the Alpine Mediterranean metallogenetic super province of the Alpine Himalayan orogenic collisional belt. Nevertheless, they form a distinct polycyclic province which is controlled by the particular geodynamic settings and remobilizations of pre-existing mineral concentrations during all (pre-Variscan, Variscan and Alpine) evolutionary stages (Ilavský, 1986, Ebner et al., 2000).

Geological setting

The most important stibnite mineralizations in the **Western Carpathians** are located in four structural and metallogenic zones: 1. Tatric unit (Pezinok, Dúbrava, Magurka), 2. Veporic unit (Ozdín), 3. Gemeric unit (Čučma) and in 4. Neovolcanic complexes (Kremnica).

1. The ***Tatric unit*** is an extensive thick-skinned crustal sheet composed of the pre-Alpine (generally Variscan) crystalline basement and its sedimentary cover. The Tatric basement has a generally well preserved Variscan structures without significant Alpine overprint. The basement is mainly composed of crystalline rocks: medium- to high- grade Early Paleozoic volcano - sedimentary complexes – paragneisses, micaschists, orthogneisses and amphibolites and phyllites (metamorphism in Devonian – 380 Ma, Rb-Sr) in the Malé Karpaty - and several suites of Variscan granitoides (360-320 Ma) intruding mostly the high-grade gneiss – migmatitic complexes. The crystalline basement complexes are incorporated into several thick - skinned Variscan nappe structures (Plašienka et al., 1997). Autochthonous Mesozoic sedimentary cover as well as the crystalline complex are overthrusted by the Mesozoic nappes. Today´s horst structure of the territory was created by Paleogene and Neogene fault tectonics. Fission track data are younger from the SE (Veporicum and S part of Tatricum) 90 – 50 Ma, to the N and NW (Považský Inovec, Vysoké Tatry) 20 – 10 Ma.

The *Malé Karpaty Mts.* Au-bearing arsenopyrite, pyrite as well as Sb mineralization are confined to the black shales embedded in actinolite schists and amphibolites and are exposed in form of lenses, quartz-carbonate veinlets, nests and disseminations in the host rocks. The most important Sb-mine of the Malé Karpaty Mts. was the Pezinok deposit.

The Lower Paleozoic (?) crystalline complex of the Tatric part of the *Nízke Tatry Mts.* consists of Variscan granitoids (granites to tonalites, 368 Ma) and medium- to high-grade metamorphic rocks like anatectic migmatites and various types of gneisses and amphibolites. The quartz veins (the most important is *Dúbrava* ore field) with Sb mineralization are located inside regional mylonite zones of N-S and E-W direction, accompanied by brittle fault structures cutting the whole crystalline complex. The preliminary $^{40}Ar/^{39}Ar$ results suggest Late Paleozoic (Variscan) tectonothermal activity: 332 and 322 Ma from muscovite of mylonitic orthogneises. The Alpine tectonothermal record appears to be restricted to discrete intermediate- or low- temperature ductile shear zones developed in basement elements, and a relatively low -temperature metamorphism and deformation in Permian – Mesozoic structural cover (80 – 100 Ma) (Dallmeyer et al. 1993).

2. The ***Veporic unit***. Paragneisses and migmatites, orthogneisses, amphibolites, frequently altered to various types of diaphtorized mica-schists and phyllonites during Variscan and Alpine metamorphic events, are regarded as the oldest rocks (Paleozoic to Proterozoic ?). The Variscan anatectic (S-types), magmatic (I-types) and less "autometamorphic" or metasomatic granites represent substantial part of the Veporic granitoids.

The South-Veporic region comprises *Ozdín* Sb – Au deposit. All occurrences are closely related to an Alpine (early/mid-Cretaceous, ca. 105-90 Ma, ^{40}Ar-^{39}Ar data on phengitic white micas, Dallmeyer et al. 1996) ductile shear zone dividing the Veporic and southerly located Gemeric domains.

3. Spiš-Gemer Rudohorie Mts. (with Sb – Au deposit Čučma) represent a marked mega-anticline. The ***Gemeric unit*** is mostly built up by Early Paleozoic low-grade metamorphic complexes. The mentioned magmatic-sedimentary groups now form the southvergent basement nappes which are cut by numerous Permian granites. Discordantly overlying Late Paleozoic (Carboniferous, Permian) and Mesozoic lithological sequences are preserved in the periphery of the Gemericum.

The Alpine thrust and later transpressional and extensional tectonics (like in the South-Veporic domain) played the decisive role also in metal vein forming processes. As an example of ore mineralization within the steep tectonic zone can be documented in the *Čučma* Sb – Au deposit. Original intrusive contact of a Permian granite porphyry with the metamorphic Gelnica Complex now has character of a narrow brittle-ductile fault zone infilled by ore-bearing veins.

4. The ***neovolcanic*** complexes in Central and East Slovakia are situated on the inner side of the Western Carpathian arc. Sb mineralization is characteristic for Kremnica and Zlatá Baňa deposits. The *Kremnica* precious-metal ore field is located in the northern part of the Central Slovak neovolcanites. During volcano-tectonic activity a stratovolcano was formed and later evolved to a caldera. Central part of the caldera in subvolcanic levels was intruded by diorites, granodiorites to gabbrodiorites. Badenian andesites, diorite and granodiorites porphyries and rhyolites form asymmetric dikes. Rhyolite dikes accompany later quartz Au-bearing veins with Sb mineralization in the Kremnica horst.

According to Weber (ed.) (1997) the major stibnite mineralizations were gathered as the naming elements in the following metallogenetic districts in the **Eastern Alps**: **A/** Kreuzeck-Goldeck Sb-(As, Au, Pb, Cu) (Rabant, Radlbergeralm, Lessnig, Guginock); **B/** Schlaining Sb-ore district .

A/ According to traditional tectonic concepts the Kreuzeck and Goldeck Mts. belong to the Middle Austroalpine Crystalline complex. Structural controlled polymetallic deposits are situated in the southern part of the Kreuzeck Mts. and the Goldeck Mts. Partley they are dominated by Sb (stibnite)-As-Au-Pb-Cu mineralization, partly by Au-As. Similar mineralizations are also known from the westernmost parts of the Drau-Range. The stibnite mineralization is bound to the meta psammopelitic unit and pyllitic units and the basement of the Drau range, which is regarded as an equivalent to the Paleozoic phyllitic complex.

The meta psammopelitic unit is a monotonous sequence of quartzitic paragneisses and micaschists (partly graphitic) with intercalations of amphibolites and marbles. Intrusions of granite, granodiorite and tonalite are of 443 and 427 Ma. The phyllite unit and the basement of the Drau Range (Gailtal crystalline) is of phyllite and micaschist with intercalations of amphibolite, metachert and marble. Locally, in the southern Kreuzeck area intrusions and dykes of granodiorite, quartz porphyrite and lamprophyre are known. K/Ar ages of 30 – 40 Ma indicate them as part of the peri-Adriatic intrusive rocks. The Alpine metamorphic overprint increases from very low grade conditions to greenschist facies metamorphic conditions in the south to amphibolite metamorphic facies in the central parts of the Kreuzeck Mts. The orientation of the vein-type mineralizations is parallel to a complex pattern of late Alpine shear and fault zones. Fission track data are significantly younger from the south (20,8 Ma) to the north (8 Ma). They display a post-Oligocene uplift along some fault systems.

Sb-Hg-formation was formerly postulated as a time and stratabound type. But mine outcrops, hydrothermal wall rock alteration and the position of mineralization in different lithologies proofed epignetic vein and impregnation character (Mali, 1996). At the western end of the Drau range (abandoned Abfaltersbach mine district) comparable Sb-mineralizations are situated in the Gailtal crystalline complex and its post-Variscan sedimentary cover (Gröden-Fm.).

B/ The Schlaining Sb-ore district (Weber (ed.), 1997) is situated in the Penninic Rechnitz window at the southeastern margin of the Eastern Alps. The low grade metamorphic volcanosedimentary hostrock (Cretaceous Rechnitz Group) is of oceanic origin and include tectonized relics of ophiolite complexes. During the Late Paleogene the Penninic oceanic domains were overridden by the Lower Austroalpine Crystalline complex. Final stages of Neogene uplift are documented by fission track data (Dunkl, 1992) with a cooling below 200^{o}C between 15 – 20 Ma. Sb mineralization is bound to the boundary of limestone/calcareous shale to the lower greenschists. Within this niveau the major mineralization occurred in at least 4 – 5 E/W to WNW/ESE striking ± vertical mineralized veins (“Gangspalten”).

Mineralogy and geochemistry

Formation of the Neogene hydrothermal mineralization in Kremnica deposit might have been related to the intrusion of diorite-granodiorite porphyries and exhibits a distinct pulsation character. Mineral assemblages are grouped into two phases. The earlier, Cu, Pb, Zn and Au, Ag bearing phase and the later Sb(Hg), which has been subdivided into quartz-carbonate and stibnite stages. Result of fluid inclusion studies on quartz and carbonates associated with precious metals indicate low salinity (0,9 – 4,5 wt.% NaCl equiv.) and low temperature aqueous solution (240-310 ^{o}C – base metal stage and 170-220 ^{o}C precious metal stage). Dispersion of values of the isotopic composition of sulphur (+5 to – 14‰) from sulphides and oxygen (+8,6 to –18,4‰) from quartz imply the mixing of magmatic and meteoric waters as well as a strictly magmatic source of the main ore elements (Maťo, 1994).

Epigenetic features in the Schlaining deposit are silicification alteration zones along the vein and stratiform mineralizations. Another epignetic argument is the typical hydrothermal calcite ^{87}Sr/^{86}Sr-ratio of 0,712 – 0,713 (Grum et al., 1992). Fluid inclusions in quartz indicate crystallization in a shallow crustal niveau between 210 – 280^{o}C and a pressure of < 1 kb (Belocky et al., 1991). The maximum age of mineralization can be estimated in account of the K/Ar cooling ages, zirkon fission track ages and the fluid inclusion temperature with approx. 17 – 19 Ma (Dunkl, 1992; Grum et al., 1992). The origin of the Sb is not yet clear. Ore sucession: a/ pre stage: pyrite, marcasite, arsenopyrite, sphalerite (quartz as gangart), b/ main stage: stibnite, arsenopyrite, sphalerite, pyrite (quartz and carbonatic gangart), c/ post stage: cinnabarite, fahlore, arsenopyrite, chalcopyrite, sphalerite (gangart calcite, ankerite).

The complete succession of sulphidic mineral assemblages in the Variscan basement in the Western Carpathian and Eastern Alps is similar: *1st stage:* **pyrite - arzenopyrite** (± invisible gold), **gold** occurs often in fissure in quartz and sulphides; *2nd stage:* Sb (Pb,Zn) sulphidic. The major mineral is **stibnite**, pyrite, sometimes berthierite; gudmundite, pyrrhotite, antimony, kermezite, gangue minerals are quartz and dolomite. Occasionally younger, but at other time older is the substage **sphalerite-sulphosalts** (füllöppite, zinckenite, robinsonite, plagionite, heteromorphite, semseyite, boulangerite, sometimes galena, jamesonite, ullmanite); *3rd stage:* Cu, Sb, (Pb, Bi, Ag): **tetrahedrite**, bournonite, chalcostibite; chalcopyrite, tintinaite, Bi-zinckenite?, horobetsuite, (sometimes also galena, Pb-Sb sulphosalts), gangue minerals quartz, carbonates, baryte and tourmaline in the Kreuzeck Mts.

Arsenopyrite-pyrite assemblage forms the oldest stage of the mineralizations at all investigated Sb-deposits. Second and third stage is not developed of all deposits in an equivalent time sequence. Older molybdenite or scheelite mineralization and younger mineralization with baryte, carbonates, strontianite, hematite, magnetite, and also quartz-hematite mineralization are sometimes present (Western Carpathians).

Sb-Au mineralisation in the Western Carpathians contains two contrasting types of mineral assemblages: An early, high temperature (300-400^{o}C) stage where arsenopyrite, pyrite and gold has formed from CO_2 rich aqueous fluids at increased pressures (1-2 kbar). The oxygen isotope signature of the equilibrium water indicates the presence of magmatic or metamorphic fluids. Later mesothermal sulphidic stages involving stibnite, berthierite, sphalerite, Pb-Sb(Bi) sulphosalts, tetrahedrite have crystallized from moderately saline (10-20 wt. % NaCl eq.) aqueous fluids devoid of CO_2. Isotopicaly lighter quartz reflex influx of meteoric water and marine or formation water during of crystallization of stibnite and tetrahedrite stages. Carbon isotope data indicate presence of organic carbon. (Chovan et al., 1995, Chovan et al., 1999, Majzlan et al., 2001).

Similar two types of fluid inclusions have been identified from Sb deposits at Kreuzeck and Goldeck Mts: inclusions with high CO_2 (CH_4,N_2) contents, (320-350 ^{o}C, 2-2,5 kbar) and medium to high saline aqueous fluid inclusions (180-270 ^{o}C, 0,5-1,5 kbar) (Mali,1996).

Conclusion

The high temperature assemblages pyrite – arsenopyrite and gold and most likely also substantial part of the stibnite are linked in the Western Carpathians with Variscan magmatic and/or metamorphic processes (neovariscan period, 340 – 290 Ma). The Alpine rejuvenization in the Variscan basement caused remobilization and/or crystallization of lower temperature sulphide assemblages, probably including antimony mineralization. Association with sulphosalts and stibnite crystallized from aqueous solutions predominantly of meteoric origin. Younger paleo Alpine (Jurassic-Cretaceous) carbonatic and sulphide mineralizations, often with barite, which sometimes accompany Sb-mineralizations, might be formed from non-equlibrial sea water, eventually from solutions mixed with meteoric water (Hurai et al., 2002). Weber (ed.)(1997) and Mali (1996) published a model of late Alpine formation of the Sb-mineralizations in the Eastern Alps (certainly, mentioning the assumption of pre-Alpine pre-concentration, Weber (ed.) 1997).

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