MINERALOGY AND GEOCHEMISTRY OF THE NIŽNÁ BOCA Sb-Au HYDROTHERMAL ORE DEPOSIT (WESTERN CARPATHIANS, SLOVAKIA)

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Abstract. Samples from hydrothermal Sb-Au mineralization in the area SE of Nižná Boca village in the Nízke Tatry Mountains were investigated using a variety of geochemical and mineralogical methods. Ore minerals typically occur in N-S striking quartz-carbonate veins hosted by an I-type biotite granodiorite to tonalite of Variscan Age (the Ďumbier Type). Paragenetic associations in the deposit are comparable to other mineralizations of the same type in the Ďumbierske Nízke Tatry Mountains. A quartz-arsenopyrite, pyrite stage of mineralization is the oldest with a calculated temperature of formation of about 445 ºC. It is followed by a quartz-carbonate-stibnite, zinkenite stage and, in turn, a quartz-carbonate-sphalerite-galena, boulangereite-gold stage. The gold typically contains between 9–18 wt.% Ag regardless of mineral association. No evidence for further generations of gold was found although it is possible that some gold was remobilized from the structure of auriferous arsenopyrite. The Au and Ag content of the bulk ore ranges from 0.53 g.t⁻¹ to 20.2 g.t⁻¹ and from 0.9 g.t⁻¹ to 31.2 g.t⁻¹, respectively. A tetrahedrite-chalcopyrite stage is followed by a barite-hematite stage – the youngest assemblage in the deposit. Fluid inclusions from the first mineralization stage are usually less than 3 µm in size and contain less than 3.6 wt.% CO₂; salinity, density and homogenization temperature range from 2.7–16.3 wt.% NaClₑₒₚ, 0.85–1.03 g.cm⁻¹ and 128–280 ºC, respectively.

Key-words: hydrothermal ore, gold, Nízke Tatry, Nižná Boca, stibnite, sulphosalts, Western Carpathians

INTRODUCTION

The village of Nižná Boca is located on the northern slopes of the Ďumbierske Nízke Tatry Mts, approximately 10 km south of Liptovský Hrádok in Slovakia. The geographical coordinates of the village are 48°57´00´´N and 19°46´00´´E. Boca (there is no distinction between Nižná and Vyšná Boca villages in the archives) was an important centre of gold mining in the Nízke Tatry Mountain in what is

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present-day Slovakia. The oldest mention of mining in the Boca Valley comes from 1271
(Bergfest 1952). At first, the gold was only gleaned from placer mines in alluvial sands
and gravels in the Boca River (north of the village). Only later was it mined under-
ground directly from ore veins; more than 70 adits were reported by Volko-Starohorsky
(1949). Throughout its history, the income from mining there fluctuated between profits
and losses. The annual gold production is estimated to have been 3–5 kg (Bergfest 1952;
Slavkay 1988). The last reports of gold mining there are from the second half of the 19th
century (Bergfest 1952).

With the notable exception of the Chopec mining field, N-NW of Vyšná Boca Village
(Ozdín, Chovan 1999), most of the gold mining activities were conducted in the area of
the present-day Nižná Boca village where numerous traces of the mining (e.g. mine
dumps, adits, surface explorations) are still visible to the SE of the village.

The occurrence of alluvial gold in the Boca River was recently evaluated by Smirnov
(1999) and Smirnov and Chovan (2003). The geochemistry and mineralogy of the primary
gold- and stibnite-bearing mineralization is the subject of this paper. As no such study of
the Nižná Boca deposit has ever been published, we hope that this contribution will
further the understanding of metallogenesis in the Nízke Tatry Mountains.

GEOLOGICAL SETTING AND MINERALIZATION

The surroundings of Nižná Boca village consist of two markedly different geological
environments: the Tatric Unit to the S of the village and the Hronic Unit – the Choč
Nappe – to the N (Fig. 1). The contact between these units is sharp due to the fact that,
during the Alpine Orogeny, the Hronic Unit was superimposed onto the lower Triassic
(Scythian) quartzites of the Lúžna Formation enveloping the Tatric Unit (Biely 1992;
Mišík, Jablonský 2000).

The Hronic Unit is represented by the Ipoltica Group and both its subunits: the
Malúžiná Group (Permian) and the Nižná Boca Group (Stephanian). The former con-
tains fluvial-lacustrine redbeds interbedded with dolomites, evaporates and mafic
lavas. The latter comprises turbiditic-, fluvial-, deltaic- and lacustrine sediments inter-
bedded with layers of intermediate- to felsic volcanic rocks (Vozárová, Vozár 1988;
Biely 1992; Dostal et al. 2003).

The Tatric Unit is represented in the area by the I-type biotitic granodiorite-tonalite –
the Žumbier Type – of Variscan (368±22 Ma, Rb/Sr) age. Macroscopically, the granitic
rocks are fine- to medium grained and locally porphyritic. Plagioclase is the most
abundant constituent, followed by quartz and biotite. Locally, the biotite crystals are
preferentially oriented and form an apparent “layered” texture. Common accessories
are zircon, apatite, zoisite and epidote (Lukáčik 1985; Biely 1992; Broska, Uher 2001).
The crystallization temperature was calculated to be 690–730°C (Cambel et al. 1990).
Metamorphic rocks occurring as xenoliths in the granitoid rocks are represented by
markedly foliated gneisses with, in some cases, migmatitic textures. They comprise
garnet, biotite, plagioclase, quartz, muscovite, kyanite and sillimanite with accessory
ilmenite, zircon and apatite. The P-T conditions of retrograde metamorphosis were
determined to be 620–660°C, 3.2–3.6 kbar (garnet rim) and 730°C, 4 kbar (garnet core) (Janák et al. 2000).

Occurrences of Sb-Au mineralization in the Tatric Unit of the Nízke Tatry Mts were extensively studied in the past, most notably those of Dúbrava (Chovan 1990; Chovan et al. 1995a; Chovan et al. 1998; Orvošová et al. 1998), Magurka (Chovan et al. 1995b; Bakos, Chovan 1999) and Mlynná Dolina (Majzlan, Chovan 1997). In the comprehensive review of Chovan et al., 1996), 10 discrete types of mineralization were identified, e.g., arsenopyrite-pyrite (frequently with “invisible” gold), gold (usually associated with quartz and sulphides) and antimony (typically associated with quartz, Sb-sulphosalts). More than one type of mineralization may occur in the same deposit.

The veins of hydrothermal Sb-Au at the Nižná Boca deposit are predominantly hosted by the Žumbier tonalite/ granodiorite; metamorphic host rocks (e.g., biotitic paragneisses, migmatites) are rare. According to Koděra (1990), the hydrothermal Au-Sb veins have a N-S strike and dip 50° to the E. The most exploited vein – the Margaréta Vein – is 160 m long with an average thickness of 1.2–1.6 m (Slavkay 1988). Other ore bodies mentioned in the compilation of Slavkay (1988) are Pavol, Tobiáš,
Prior to sample collection, reconnaissance field trips were conducted to map out the extent of the old mining activities. Samples collected from mine dumps were carefully examined for textural evidence of crystallization episodes. In total, 125 polished sections were prepared and inspected in polarized reflected light. Close attention was paid to ore structures and the relative age relationships of the ore minerals. The chemical compositions of the primary minerals (excepting the sulphosalts) were determined by electron probe microanalysis (EPMA) using a JEOL Superprobe 733 (Geological Survey of Slovak Republic, Bratislava, Slovakia) and a JEOL JXA 840A (Comenius University, Bratislava, Slovakia) using 20 kV, 15 nA and 2–5 μm beam diameter. Standards were as follows: arsenopyrite–Fe, As, S; PbS–Pb; HgS–Hg; Bi, Sb, Au, Ag, Zn, Cu, Te as pure metals. Sulphosalts were analysed using a JEOL Superprobe 733 (Geologisk Institut, University of Copenhagen, Denmark) using 20 kV, 20 nA, 5 μm beam diameter and the following standards: PbS – Pb; Bi₂S₃ – Bi; CuFeS₂ – S, Cu, Fe; Ag, Sb as pure metals.

Fe secondary minerals were analysed by X-ray diffraction (XRD) using a DRON-3 diffractometer (Comenius University, Bratislava, Slovakia) under the following conditions: CuKα radiation, Ni filter, step 0.02, 0.1° pm. Arsenopyrite was analysed on a PHILIPS diffractometer (Slovak Academy of Sciences, Bratislava, Slovakia) using CoKα radiation, no monochromator, step 0.02, 2° pm with quartz as an internal standard. XRD analyses of Sb secondary minerals were performed using a STOE diffractometer (Masaryk University, Brno, Czech Republic) under the following conditions: CuKα radiation, Ge crystal monochromator, PSD detector, step 0.01°, 2° pm. The Au content in arsenopyrite was determined using a Carl-Zeiss optical emission spectrometer (Slovak Academy of Sciences, Banská Bystrica, Slovakia) using a 7A current and 120 s exposition time.

The Au contents in bulk ore samples (0.1–1000 g.t⁻¹) were analysed using a VARIAN AA-20 flame atomic absorption spectrometer (Geoecological Laboratories Ltd., Spišská Nová Ves, Slovakia). Samples were dissolved in HCl/HNO₃ solution and analysed using an acetylene/air flame and selecting Ag and Au absorption bands at 328.1 nm and 242.8 nm, respectively. Smaller concentrations (0.005–0.1 g/t) of Au were analysed using a SPECTR AA-400 atomic absorption spectrometer with a GTA-96 electrothermal atomiser (Geoecological Laboratories Ltd., Spišská Nová Ves, Slovakia) under the following conditions: Au absorption band = 242.8 nm, Tcombustion = 600°C, Tatomization = 2400°C.
The fluid inclusion study was performed using a microthermometric LINKAM THMS 600 (freezing – heating) stage coupled with a NIKON Optiphot-2 microscope (Geological Survey of Slovak Republic, Bratislava). A CCD camera coupled with a computer monitor enabled observations of phase transition in fluid inclusions as small as ~3 μm. The microthermometric stage was calibrated using synthetic fluid inclusions and pure $K_2Cr_2O_7$. The phase transitions measured in our samples were: total homogenization temperature ($T_h$), eutectic temperature ($T_e$) and the temperature of ice melting ($T_{m_{ice}}$). The precision of the measurements was ±0.1°C.

RESULTS

A map of old mining activities in the Nižná Boca area, as confirmed by field reconnaissance is shown in Figure 2. Not all of the discovered traces of mining are
shown in the map, only prominent mine dumps. Based on the mineralogy of dump material, we conclude that Sb-Au mineralization was predominantly exploited in the Zach and Geplové mining field. Several mine dumps with abundant siderite ore samples are located at Fišiarka in the Kralovská Dolina valley where the only accessible adit (Okrúhla štôľňa) in the Nižná Boca area was discovered. It is unclear whether the adit was dug for exploratory or exploitation purposes (total length ~ 35 m) as no signs of exploitable ore were found inside or near the adit. There are some surface exploration digs and mine dumps on the slope directly above the mine; however, excepting altered granitoid rocks with occasional disseminated arsenopyrite, pyrite and tetrahedrite, no ore samples were found. Though the increased presence of sedimentary quartzites of the Lúžna Formation in this area reflects the proximity of the stratigraphic boundary between the Tatric crystalline massif and its quartzite envelope, no ore veins intersecting the quartzites were found.

The NW-SW arrangement of old mining activities at Jedlinská (Fig. 3) appears to have been exploiting the Weise Kluft vein (Fig. 2). However, we were unable to
determine the type of mineralization exploited because of the scarcity of ore samples. Regrettably, the only sulphides identified were arsenopyrite and pyrite disseminated in the altered granitic host rock.

**Primary minerals**

**Arsenopyrite**, one of the most abundant ore minerals in the deposit, is present in virtually all of the ore occurrences in the Nižná Boca area. Macroscopically, it forms clusters, nests and veinlets in quartz and hydrothermally-altered wallrock. Most crystals (< 3 mm) are euhedral to subhedral, and with fractures that are cemented by other minerals, especially boulangerite, galena and gold (Fig. 4A, D, E; Fig. 7). The Au contents of monomineralic arsenopyrite crystals in five randomly selected ore samples, NB-Z24/25, NB-F2, NB-Z35/36, NB-Z4, NB-Z7, were 31.2, 10.7, 1166.7, 13.5, 5.4 and 25.3 ppm, respectively. The anomalously high Au content in sample NB-Z35/36 is likely due to the presence of particulate gold which commonly forms intimate intergrowths with arsenopyrite (Fig. 7). Older Ti ± Fe minerals are frequently enclosed as relics in arsenopyrite grains. Arsenopyrite is very closely associated with pyrite. Their common grain contacts indicating equivocal relative ages combined with the lack of optical and chemical (BSE) zonality suggest that they were in equilibrium and at buffered $S_2$ values at the time of deposition (Kretschmar, Scott 1976). The assumption of equilibrium along with the low (< 1 wt.%) content of minor elements, e.g., Ni, Co and Cu (Table 1), the suitable Fe content (within 33.3±0.7 at.%) and an As content typical for arsenopyrite + pyrite parageneses (< 33.3 at.% As) allows for the use of a thermometer determining the temperature of origin (Kretschmar, Scott 1976). After the chemical composition was determined by electron microprobe, a $d_{131}$ value of 1.6325, directly correlatable with the arsenopyrite As content, was obtained by XRD. The $d_{131}$ value was subsequently used to calculate the crystallization temperature of approximately 445°C.

**Barite** occurs as a part of what is presumably the youngest mineral paragenesis together with hematite and pyrite (Fig. 4G). No luminescence in UV light was observed.

**Carbonates** are abundant in virtually all samples. All analysed carbonates are ferroan dolomite to ankerite (10.65–21.61 mol% FeCO₃; Fig. 5, Table 2) which frequently exhibits chemical zoning (Fig. 6). Concentric alternation of lighter and darker zones in BSE images likely reflects fluctuations in the Fe and Mn contents; lighter zones are typically enriched in Fe and/or Mn (Table 2). Carbonates are always younger than quartz and typically older than ore minerals within the same mineralization paragenesis. It is likely that several (up to three) generations of chemically similar carbonates associated with different ore mineral assemblages occur in the deposit. In some cases, a weak reddish luminescence was observed in the UV light.

**Chalcopyrite** is found only in a few samples. It occurs only as anhedral grains with older tetrahedrite in carbonate, rarely in quartz. It unclear; however, if it is a part of the Sb-Au or siderite mineralization.

**Galena** is one of the most abundant ore minerals, commonly forming accumulations of high-luster silver-white grains up to few mm in size. Most of the galena from Nižná
Fig. 4. BSE photographs of common ore mineral associations:
A – arsenopyrite (asp) replaced by younger galena, B – needle-shaped crystals of boulangerite (boul) replaced by younger galena, C – gold (Au) replacing older boulangerite in a quartz (qtz) and carbonate (carb) matrix, D – gold replacing and enclosing older arsenopyrite grains, E – gold replacing and enclosing older arsenopyrite, carbonate and galena, F – anhedral gold grains dispersed in a carbonate matrix, G – hematite (hem) crystals with pyrite (py) in a quartz and barite (bar) matrix, H – stibnite (stb) enclosing older anhedral quartz grains
**TABLE 1**

Representative electron microprobe analyses (in wt.%) of ore minerals from the Nižná Boca Deposit

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TABLE 1 cont.

<table>
<thead>
<tr>
<th>wt.%</th>
<th>ttd</th>
<th>ttd</th>
<th>ttd</th>
<th>ttd</th>
<th>ttd</th>
<th>Zink**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>NB-F1</td>
<td>NB-F1</td>
<td>NB-F1</td>
<td>NB-Z6</td>
<td>NB-Z6</td>
<td>NB-Z36</td>
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<tr>
<td>S</td>
<td>25.7</td>
<td>25.65</td>
<td>26.73</td>
<td>26.70</td>
<td>26.19</td>
<td>23.05±0.29</td>
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<td>Pb</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>32.13±0.37</td>
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<tr>
<td>Sb</td>
<td>24.56</td>
<td>23.82</td>
<td>16.2</td>
<td>18.30</td>
<td>19.35</td>
<td>45.30±0.45</td>
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<tr>
<td>Ag</td>
<td>2</td>
<td>1.6</td>
<td>1.15</td>
<td>0.08</td>
<td>0.30</td>
<td>0.18±0.05</td>
</tr>
<tr>
<td>Fe</td>
<td>3.0</td>
<td>2.85</td>
<td>3.86</td>
<td>2.77</td>
<td>2.63</td>
<td>0.05±0.05</td>
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<tr>
<td>Bi</td>
<td>0.64</td>
<td>0.45</td>
<td>0.76</td>
<td>0.40</td>
<td>0.78</td>
<td>0.04±0.07</td>
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<tr>
<td>Zn</td>
<td>3.5</td>
<td>3.32</td>
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<td>4.37</td>
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<tr>
<td>As</td>
<td>2.67</td>
<td>2.64</td>
<td>6.89</td>
<td>7.11</td>
<td>6.51</td>
<td>n.a.</td>
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<tr>
<td>Hg</td>
<td>0.27</td>
<td>0.48</td>
<td>0.27</td>
<td>0</td>
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<td>Cu</td>
<td>38.56</td>
<td>38.32</td>
<td>40.54</td>
<td>39.57</td>
<td>38.37</td>
<td>0.38±0.05</td>
</tr>
<tr>
<td>Total</td>
<td>100.9</td>
<td>99.14</td>
<td>99.42</td>
<td>99.30</td>
<td>98.86</td>
<td>101.1±0.51</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
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<tbody>
<tr>
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<td>Bi</td>
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<td>Zn</td>
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<tr>
<td>As</td>
</tr>
<tr>
<td>Hg</td>
</tr>
<tr>
<td>Cu</td>
</tr>
</tbody>
</table>

* and ** denote the mean of 15 and 11 EPMA analyses, respectively. Formulae were calculated on the basis of total number of cations. Mineral names abbreviated as follows: asp – arsenopyrite, boul – boulangerite, bour – bournonite, gal – galena, stb – stibnite, ttd – tetrahedrite, zink – zinkelite.
TABLE 2

Chemical composition of carbonates (in mol %) determined by standardized EDS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Place of analysis</th>
<th>FeCO₃</th>
<th>MgCO₃</th>
<th>MnCO₃</th>
<th>CaCO₃</th>
<th>SrCO₃</th>
<th>Total</th>
</tr>
</thead>
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<tr>
<td>NB-Z35b</td>
<td>homogenous grain</td>
<td>17.51</td>
<td>28.95</td>
<td>0.97</td>
<td>52.06</td>
<td>0.23</td>
<td>99.73</td>
</tr>
<tr>
<td>NB-Z35b</td>
<td>homogenous grain</td>
<td>17.61</td>
<td>29.02</td>
<td>0.79</td>
<td>51.28</td>
<td>0.46</td>
<td>99.15</td>
</tr>
<tr>
<td>NB-Z35e</td>
<td>light zone</td>
<td>15.95</td>
<td>27.28</td>
<td>1.85</td>
<td>54.51</td>
<td>n.a.</td>
<td>99.58</td>
</tr>
<tr>
<td>NB-Z35e</td>
<td>dark zone</td>
<td>11.26</td>
<td>33.41</td>
<td>0.79</td>
<td>53.04</td>
<td>n.a.</td>
<td>98.5</td>
</tr>
<tr>
<td>NB-Z35e</td>
<td>light zone</td>
<td>16.37</td>
<td>29.1</td>
<td>0</td>
<td>53.38</td>
<td>n.a.</td>
<td>98.85</td>
</tr>
<tr>
<td>NB-Z35e</td>
<td>dark zone</td>
<td>13.14</td>
<td>31.69</td>
<td>0.83</td>
<td>53.17</td>
<td>n.a.</td>
<td>98.83</td>
</tr>
<tr>
<td>NB-Z36k</td>
<td>dark zone</td>
<td>11.69</td>
<td>33.83</td>
<td>0.49</td>
<td>53.79</td>
<td>n.a.</td>
<td>99.8</td>
</tr>
<tr>
<td>NB-Z36k</td>
<td>light zone</td>
<td>21.61</td>
<td>24.71</td>
<td>1.57</td>
<td>52.95</td>
<td>n.a.</td>
<td>100.84</td>
</tr>
<tr>
<td>NB-Z36k</td>
<td>dark zone</td>
<td>10.65</td>
<td>34.84</td>
<td>0.42</td>
<td>53.95</td>
<td>n.a.</td>
<td>100.16</td>
</tr>
<tr>
<td>NB-Z36k</td>
<td>light zone</td>
<td>15.53</td>
<td>29.85</td>
<td>0.5</td>
<td>53.1</td>
<td>n.a.</td>
<td>98.98</td>
</tr>
</tbody>
</table>

Fig. 5. Standardized EDS analyses of carbonates
A – correlation between Fe and Mg content of the carbonates, B – position of the Nižná Boca carbonates close to the dolomite (MgCaCO₃) – ankerite (CaFeCO₃) solid solution
Boca is anhedral and occurs in interstices, fissures and weakened cleavage zones in vein carbonates (Fig. 6) and quartz. As a younger mineral, galena very often replaces arsenopyrite, pyrite and sphalerite, penetrates along fissures and encloses entire grains of older minerals. Galena also commonly contains small anhedral inclusions of boulangerite and thus it appears that their crystallization periods overlapped and/or closely followed to each other. Galena only contains trace amounts of Bi (0.3–0.6 wt.%; Table 1) and is optically and chemically homogenous.

Gold occurs scarcely but regularly in three microscopically distinct host settings:
1) replacing older sulphides, forming inclusions in arsenopyrite, pyrite, boulangerite and bouronite (Fig. 4C, E, D);
2) anhedral grains and veinlets in milky-white to smoky-grey quartz and, to a lesser extent, carbonate notably devoid of sulphides (Fig. 4F);
3) as arsenopyrite crystals filling microfractures (e.g., micro stringers < 1 µm thick), possibly due to remobilization of “invisible” gold from the arsenopyrite structure (Fig. 7).

Analyses of gold from the Nižná Boca deposit show no differences in chemistry between the type 1 and type 2 gold (Fig. 8, Table 3). Type 3 gold was not analysed because its grain size proved prohibitively small for microprobe analysis. The size of gold grains varies from 0.002–2 mm with an average of 0.05 mm (n = 252). Its chemical composition is typically high in Ag (min. 13.37 wt.%) and low concentrations of admixed elements (< 0.4 wt.%). True fineness ($F_T = \frac{[\text{Au}]}{[\text{Au} + \text{Ag}]} \cdot 1000$) values vary between 815–906. The Au and Ag contents of bulk ore samples are presented in Table 4.

Hematite is one of the youngest minerals in the deposit and is probably not related to the Sb-Au mineralization. Lamellae observed in reflected polarized light intersect is multiple grains and may indicate post-depositional stress. Hematite occurs in two
distinct forms: 1) with barite as cement in older cataclasized quartz and 2) anhedral to subhedral lath-like crystals in barite and carbonate, commonly in brush-like aggregates (Fig. 4G). Hematite often occurs together with pyrite; however, their relative age relationship is difficult to determine.

Fig. 7. BSE images of arsenopyrite crystals (asp) with micro-stringers of gold (Au). It is possible that two generations of gold are present (see text)

Fig. 8. Chemical composition of primary gold. Note the lack of systematic compositional variations in gold associated with quartz and carbonates versus sulphide minerals
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.34</td>
<td>0.24</td>
<td>0.27</td>
<td>0.23</td>
<td>0.25</td>
<td>0.26</td>
<td>0.22</td>
<td>0.22</td>
<td>0.23</td>
<td>0.26</td>
<td>0.25</td>
<td>0.26</td>
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</tr>
<tr>
<td>Te</td>
<td>0.14</td>
<td>0.08</td>
<td>0.01</td>
<td>0.14</td>
<td>0.02</td>
<td>0.11</td>
<td>0.14</td>
<td>0.04</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.10</td>
<td>0.25</td>
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<tr>
<td>Sb</td>
<td>0.04</td>
<td>0.03</td>
<td>0.11</td>
<td>0.09</td>
<td>0.07</td>
<td>0.06</td>
<td>0.20</td>
<td>0.20</td>
<td>0.04</td>
<td>0.14</td>
<td>0.02</td>
<td>0.16</td>
<td>0.12</td>
</tr>
<tr>
<td>Ag</td>
<td>10.94</td>
<td>9.40</td>
<td>11.00</td>
<td>13.23</td>
<td>13.52</td>
<td>12.85</td>
<td>14.27</td>
<td>14.27</td>
<td>12.91</td>
<td>11.12</td>
<td>11.44</td>
<td>12.61</td>
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<td>0.63</td>
<td>0.33</td>
<td>0.34</td>
<td>0.56</td>
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<td>0.25</td>
<td>0.47</td>
<td>0.41</td>
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<td>Au</td>
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<td>86.65</td>
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<td>84.35</td>
<td>84.35</td>
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<tr>
<td>Cu</td>
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<td>0.05</td>
<td>0.23</td>
<td>0.10</td>
<td>0.12</td>
<td>0.06</td>
<td>0.12</td>
<td>0.09</td>
<td>0.12</td>
<td>0.10</td>
<td>0.08</td>
<td>0.10</td>
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<tr>
<td>Bi</td>
<td>0.39</td>
<td>0.25</td>
<td>0.29</td>
<td>0.38</td>
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<td>0.46</td>
<td>0.45</td>
<td>0.45</td>
<td>0.46</td>
<td>0.42</td>
<td>0.29</td>
<td>0.46</td>
<td>0.43</td>
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<tr>
<td>Total</td>
<td>101.32</td>
<td>101.54</td>
<td>99.37</td>
<td>101.29</td>
<td>100.54</td>
<td>101.62</td>
<td>99.94</td>
<td>99.94</td>
<td>100.79</td>
<td>99.16</td>
<td>99.90</td>
<td>100.75</td>
<td>98.87</td>
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<tr>
<td>$F_T$</td>
<td>890</td>
<td>906</td>
<td>888</td>
<td>868</td>
<td>864</td>
<td>872</td>
<td>855</td>
<td>855</td>
<td>870</td>
<td>886</td>
<td>885</td>
<td>873</td>
<td>815</td>
</tr>
</tbody>
</table>
Marcasite is very rare, usually forming anhedral grains in quartz and in the wall-rock, and shows no specific relationship to other ore minerals.

Pb-Sb-(Cu)-(Fe) sulphosalts occur commonly in two distinctive paragenetic settings depending on their Pb/Sb. For example, boulangerite and bournonite (high Pb/Sb) occur in the same paragenesis as galena, whereas zinkenite and berthierite (low Pb/Sb) are associated with stibnite (Fig. 9). The high Pb/Sb paragenesis is younger than the low Pb/Sb paragenesis (Fig. 10). Berthierite is rare, forming minute lath-like crystals enclosed in zinkenite and stibnite. Boulangerite, one of the most abundant sulphosalts in

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Au (g·t⁻¹)</th>
<th>Ag (g·t⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB-Z3</td>
<td>First mineral paragenesis with dominant quartz and disseminated arsenopyrite and other sulphides</td>
<td>1.91</td>
<td>0.9</td>
</tr>
<tr>
<td>NB-Z35</td>
<td>Second mineral paragenesis with quartz, carbonate and abundant coarse- to fine-grained stibnite</td>
<td>3.95</td>
<td>24.8</td>
</tr>
<tr>
<td>NB-Z50</td>
<td>Second mineral paragenesis with dominant quartz, carbonate and disseminated needles and grains of ore minerals</td>
<td>0.47</td>
<td>10.5</td>
</tr>
<tr>
<td>NB-Z9</td>
<td>Third mineral paragenesis with smoky to milky white quartz with frequent disseminated sulphides</td>
<td>20.2</td>
<td>31.2</td>
</tr>
<tr>
<td>NB-Z14</td>
<td>Milky white quartz with rare disseminated sulphides</td>
<td>0.53</td>
<td>21.1</td>
</tr>
</tbody>
</table>

**Fig. 9.** Comparison of Pb-Sb sulphosalts from the Nižná Boca deposit to known theoretical compositions
the deposit, occurs in smoky- to milky white quartz and in carbonates; it is usually associated with galena, sphalerite and gold. It usually forms small anhedral grains in galena, quartz and carbonates or needle-like crystals in quartz and carbonates (Fig. 4B, C) and commonly fills carbonate cleavage planes or fissures penetrating several host-mineral grains. Boulangerite often replaces older minerals, mainly arsenopyrite, pyrite and sphalerite. Its formula based on 15 analyses (Table 1) is Pb_{5.17}Sb_{3.81}S_{11.08}. Bournonite is rare and always in the form of small anhedral grains in quartz, carbonates and, in occasional instances, boulangerite. Analyses of bournonite are given in Table 1 and its formula based on three analyses is near stoichiometric Cu_{0.99}Pb_{1.00}Sb_{0.99}S_{3.01}. Zinkenite is abundant, forming veins and aggregates in quartz, carbonates and, rarely, in the hydrothermally altered wall-rock. Its anhedral or euhedral needle-like crystals also commonly associate with stibnite (age relationship unclear) or replace older sulphides, especially pyrite and arsenopyrite. The average formula, based on 11 microprobe analyses, was calculated to be Cu_{0.35}Ag_{0.09}Pb_{8.97}Fe_{0.05}Sb_{21.53}Bi_{0.01}S_{41.60} (Table 1). Cu likely enters the structure by the “aikinite” type of substitution Cu + Pb → Sb + □.

Fig. 10. Photograph (A) and a schematic sketch (B) of the 3rd mineral paragenesis (stibnite, zinkenite-rich, low Pb/Sb) cutting a veinlet of the older 2nd mineral paragenesis (galena, sphalerite, boulangerite-rich, high Pb/Sb)
Fe by the simple Fe → Pb substitution and Ag by the “lillianite” type of substitution Ag + Sb → 2Pb (Makovický 1989). Taking into account these substitutions, the simplified formula could be written as Pb$_{8.85}$Sb$_{21.80}$S$_{41.60}$.

**Pyrite**, as anhedral to euhedral crystals < 3 mm in size, is one of the most abundant minerals in the Nižná Boca area. It occurs both in hydrothermal veins and in wall-rock alteration zones, and is commonly weathered to secondary Fe minerals such as goethite or jarosite. Based on microscopic observation, three generations of pyrite in different mineral parageneses can be recognised. Pyrite I (oldest) is associated with arsenopyrite in quartz veins and wall-rock alteration zones, often forming banded textures. It usually forms chemically- and optically homogenous subhedral to euhedral crystals that are commonly cataclased and cemented by younger minerals (e.g., Pb-Sb sulphosalts, galena, gold). Inclusions of Ti-minerals (rutile, ilmenite) are sporadic. Pyrite II is associated with sphalerite, galena, boulangerite, bournonite and gold, often filling fractures in quartz and carbonate. It usually forms subhedral to euhedral homogenous crystals. Pyrite III (the youngest), associated with hematite and barite, often forms euhedral crystals (Fig. 4G).

**Pyrrhotite** is very rare as anhedral grains in wall-rock alteration zones and in the host rock. Relationships to other ore minerals are unclear.

**Quartz**, the dominant gangue mineral, occurs in several generations distinguished on the basis of textural and structural observations. Quartz I is usually coarse-grained and associated with arsenopyrite and pyrite I. Its colour is sometimes influenced by finely dispersed sulphides and by coatings of secondary Fe-minerals. It is often intensely fractured and replaced by younger mineral parageneses, including quartz. As the most reliably identifiable, Quartz I was chosen for fluid inclusion studies (see below). Quartz II is milky-white and associates with younger ferroan dolomite, stibnite and zkenite. Quartz III usually occurs closely intergrown with younger ferroan dolomite, pyrite II, sphalerite, galena, boulangerite and gold (Fig. 4C, F).

**Sphalerite** commonly forms aggregates of brown red anhedral grains in quartz and carbonate vein fillings. It is often associated with, and replaced by, younger minerals, especially boulangerite, galena and gold.

**Stibnite** is rare. It forms veins (< 4 cm) and aggregates with minor coarse-grained milky-white quartz and rare carbonate in the hydrothermally-altered host tonalite. Microscopically, needle-like crystals are scarce; the dominant anhedral grains often cement brecciated quartz grains, fill cracks and cavities, and replace older arsenopyrite and pyrite (Fig. 4H). Deformation lamellae are common but any indication of recrystallization (e.g., fine-grained veinlets) is lacking. An analysis is given in Table 1.

**Tetrahedrite** is very rare. It is seen only microscopically as anhedral grains in quartz and carbonates with younger chalcopyrite. Sporadically, it replaces pyrite, galena and boulangerite. Tetrahedrite from both the siderite mineralization (Fišiarka – sample NB-F1) and the Sb-Au mineralization (Zach – NB-Z6) is included in Table 1. Even though limited As-Sb substitution (up to 7.1 wt.% As) and a low Ag content (< 2 wt.%) characterizes tetrahedrite from both samples, their accessory nature inhibited further analysis and comment on their chemical differences. The average formula based on 5 EPMA analyzes can be written as Cu$_{10.07}$Ag$_{0.16}$Zn$_{0.94}$Fe$_{0.89}$Sb$_{2.75}$As$_{1.12}$Bi$_{0.05}$S$_{13.38}$.
Ti-minerals (rutile, ilmenite) occur commonly, predominantly as anhedral, deformed grains in the oldest sulphides (arsenopyrite, pyrite I), quartz, carbonates, wall-rock and the host rock.

**Secondary minerals**

Secondary Fe minerals in the deposit are represented by goethite, jarosite, rosenite and possibly other phases lacking long-range structural order detectable by XRD. They usually occur together in a mixture of brownish to yellowish colour which forms coatings and accumulations (nests) of various thickness and size on primary Fe-bearing minerals, typically pyrite and carbonates.

Secondary Sb minerals are represented only by stibiconite (detected by XRD), which forms pale- to dark yellow powder accumulations on weathered stibnite and Pb-Sb sulphosalts.

**Fluid inclusions**

Fluid inclusions irregularly disseminated in quartz from the first mineral paragenesis (quartz – arsenopyrite, pyrite) were studied by optical microthermometry. The quartz matrix from subsequent parageneses and carbonates were not suitable for fluid inclusion study because of complicated genetic relationships, fine mutual intergrowths and/or small inclusion sizes. Only primary inclusions were studied though, in some cases, their designation as primary (sensu Roedder 1984) was ambiguous. The inclusions are predominantly irregular in shape with sizes ranging from < 2–17 µm with an
average of 4.5 µm (n = 51). All inclusions examined are two-phase (liquid + gas) with the liquid phase predominant (Fig. 11). Melting of totally frozen inclusions was observed to start between −23.9 and −21.2°C. Owing to their small size, the eutectic temperature ($T_e$) was not measured in all inclusions. The $T_e$ values relate to the H$_2$O-NaCl-(KCl?) system (Borisenko, 1977 in Shepherd et al. 1985). Double freezing of aqueous liquid indicative of the presence of CO$_2$ was not observed. Therefore, the CO$_2$ concentrations were < 3.6 wt.%. Temperatures of ice melting ($T_{m_{\text{ice}}} = −1.6$ to $−12.4°C$) correspond to salinities between 2.7–16.3 wt.% NaCl$_{\text{eq}}$ (Fig. 12A; Hall et al. 1988). Occasionally, metastable

![Fig. 12. Calculated salinities (A); homogenization temperatures (B) and (C) correlation ($R^2 = −0.36$) between homogenization temperature and salinity in fluid inclusions (n = 51) from quartz I (stage I).]
superheated ice melted at temperatures as high as +8.4°C in inclusions with extremely small vapor bubbles. All inclusions homogenized to liquid at temperatures between 128–280°C (Fig. 12B) corresponding to liquid densities between 1.03–0.85 g cm⁻³, by reference to a H₂O-NaCl system (Hurai 1988). Poor correlation (R² = –0.36) between the homogenization temperature and salinity does not permit a distinction between fluid boiling and mixing, i.e., two possible mechanisms which could account for the wide range of observed salinities (Fig. 12C).

PARAGENETIC CONSIDERATIONS AND DISCUSSION

Based on our macroscopic and microscopic observations, we propose a model with 5 main stages of mineralization for the Nižná Boca deposit. It is important to note that all samples on which the model is based were collected ex-situ from mine dumps and, therefore, it cannot be considered complete and unequivocally correct. The model comprises the following depositional sequence (ordered from oldest to youngest relative age of minerals):

I. Quartz I – arsenopyrite, pyrite I, marcasite(?), pyrhotite(?) – gold(?).
II. Quartz II – ferroan dolomite/ankerite – stibnite, zinkenite, berthierite.
IV. Quartz(?) – carbonate(?) – tetrahedrite – chalcopyrite.
V. Barite – hematite, pyrite.

The first mineral paragenesis (oldest) is usually disseminated in the hydrothermally altered granitic host rock although discrete veinlets also occur. Brittle deformation of the 1st stage is documented by arsenopyrite and pyrite I cataclasis followed by the healing of fractures by other minerals, most commonly gold and boulangerite. It is possible that native gold also formed during this stage; however, due to the lack of distinctive chemistry we are unable to differentiate it from gold in younger mineralization stages (Fig. 8). The most common basis for such distinction is the Ag content of gold as has been shown in other deposits in the Nízke Tatry Mountains (e.g., Chovan et al. 1995b; Bakos, Chovan 1999) and elsewhere (e.g., Dill et al. 1995; Mikuš, Chovan 2003). In other deposits, however, such a systematic variation in Ag content may be missing entirely (e.g., Majzlan, Chovan 1997; Oberthür et al. 1997; Uemoto et al. 2002; Helmy et al. 2004). Because arsenopyrite from Nižná Boca is gold-bearing, we hypothesize that it may have served, to some extent, as the source of the native gold remobilized during high temperature/pressure events. This remobilized gold was deposited as minute (< 1 µm) stringers in arsenopyrite crystals or in their close vicinity (Fig. 7). Such a mechanism has been proposed for some deposits in southern India (Saha, Venkatesh 2002), Canada (Larocque et al. 1995), Ghana (Mumin et al. 1994; Helmy et al. 2004), Western Australia (Vaughan, Kyin 2004), Bolivia (Dill et al. 1995) and the Balkans (Mladenova et al. 2004). Further useful comment awaits appropriate chemical analyses.

The second, stibnite-bearing (high Sb) paragenesis forms veins < 4 cm thick and comprises coarse-grained milky-white quartz II, ferroan dolomite, stibnite, zinkenite
and berthierite. The stibnite is fine- to coarse grained without any recrystallization fe-
atures. Though zinkenite was the only Pb-Sb sulphosalt found in this paragenesis, it is
possible that other sulphosalts with high Sb/Pb, e.g., fullöppite, plagionite, occur (Fig. 9).

The third (high Pb) paragenesis is the most abundant in the deposit. Milky-white to
smoky-grey quartz III and ferroan dolomite host pyrite II, sphalerite, galena, boul-
gerite, bournonite and gold. Other sulphosalts with high Pb/Sb, e.g., semseyite, may be
also present in this paragenesis. Analyses of the boulangerite (Table 1) show a higher Pb
content than its ideal composition (Pb₅Sb₄S₁₁) and, thus, it plots between boulangerite
and falkmanite (Pb₃.₅Sb₃.₆S₁₁) on the Pb vs. Sb chart (Fig. 9). Because they are members
of the same boulangerite homologous series (Me₉S₁₁) (Mozgova et al. 1983) and have
very similar chemical compositions, their XRD powder diffraction patterns exhibit only
negligible differences. A single crystal XRD analysis is therefore required for definite
identification. Interestingly, boulangerite non-stoichiometry is a commonly observed
phenomenon in Sb-Au deposits across the Žumberk Nízke Tatry Mountains (Pršek –
pers. comm).

In one macroscopic sample, an ore veinlet (~2 cm thick) of this paragenesis was
observed to intersect a veinlet of the older, second stibnite-bearing paragenesis –
unequivocally establishing their relative ages. The mutual age relationship of the Sb-
and Pb-rich parageneses in Nižná Boca is similar to that in deposits at Magurka
(Chovan et al. 1995b), Klačianka, Krámeck and Veľké Oružné (Bakos et al. 2000), Malé
Železné (Pršek – pers. comm.), but the reverse of that in the Dúbrava Deposit (Chovan
1990).

The fourth mineral paragenesis occurs sparsely – replacing boulangerite from the
previous mineral paragenesis. The fifth paragenesis with barite, hematite and pyrite is
probably not genetically linked to the Sb-Au hydrothermal mineralization but is of
younger relative age (Chovan et al. 1996; Bakos et al. 2000).

CONCLUSIONS

In spite of abundant records of Boca gold mining in the archives (e.g., Central
Mining Archive in Banská Štiavnica, Slovakia), detailed field reconnaissance and miner-
alogical research has not been conducted there since the decline of gold mining in the
late 19th century. Presumably due to its small size and lesser economic importance, it
was not even included in the comprehensive work on stibnite deposits in the Nízke
Tatry Mountains by Hak (1966). Based on our field research, we have confirmed
occurrences of Sb-Au mineralization over an area of about 2 km² in the mine field Zach
(Fig. 2) in workings striking N-S to NW-SE. Several new occurrences of siderite minera-
lization (sensu Chovan et al. 1996) were also discovered. The Sb-Au mineralization is
hosted by biotite tonalities to granodiorites of the Žumberk Type which is in agreement
with the archive data (e.g., Slavkay 1988) and the geological map of the Nízke Tatry
Mountains (Biely 1992). The results presented here expand our knowledge of the
deposit, most notably its mineralogy and depositional sequence, and contribute to our
understanding of metallogenesis in the Nízke Tatry Mountains.
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Mineralogia i geochemia hydrotermalnego złoża Sb-Au Niżná Boca
(Zachodnie Karpaty, Słowacja)

Streszczenie

Złoże hydrotermalne Sb-Au, położone na SE od wsi Nižná Boca w Małych Tatrach, było eksploatowane do końca XIX wieku. Sporządzono mapy występowania żyl rudnych, a próbki pobrano z licznych hałd. W badaniach laboratoryjnych zastosowano mikroskopię w świetle odbitym, mikrosondę elektronową, dyfraktometrię rentgenowską, optyczną spektrometrię emisyjną, atomową spektroskopię absorpcyjną i analizę inkluzy ciekłych. Minerały kruszcowe są najczęściej zawarte w żyłach kwarcowo-węglanowych o przebiegu N-S, występujących w biotytowych granodiorytach-tonalitach typu I wieku waramcowego (tzw. typ Dumbierski). Paragenesy w złożu są zbliżone do innych przejawów mineralizacji tego samego typu w Niżnych Tatrach Dumbierskich. Najstarszym jest etap kwarco-arsenopyrytowy z pirytem, utworzony w temperaturach około 445°C. Następnie tworzyły się żyły kwarcowo-węglanowo-antymonitowe z zinkiem, a po nich żyły kwarcowo-węglanowo-sfalerytowo-galenowe z boulange-rytem i złotem. Złoto zawiera przeważnie 9–18% wag. Ag, niezależnie od współwystępujących z nim minerałów. Nie znaleziono złota innych generacji, chociaż nie można wykluczyć, że część jego ziaren powstała w wyniku remobilizacji złota ze struktury złotoośnego arsenopyrytu. Zawartość Au w rudzie waha się w granicach 0,53–20,2 g t⁻¹, a Ag w granicach 0,9–31,2 g t⁻¹. Najsłodszymi paragenesami kruszcowymi w złożu są tetraedryt z chalkopyrytem oraz baryt z hematytą. Ciekłe inkluzy zawarte w minerałach reprezentujących pierwszy etap powstania złoża mają zwykle rozmiary poniżej 3 µm i zawierają mniej niż 3,6% wag. CO₂; ich zasolenie, gęstość i temperatury homogenizacji wahają się odpowiednio w granicach 2,7–16,35% wag. NaCl(eq), 0,85–1,03 g cm⁻³ i 128–280°C.