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Copper mineralization in the Permian basalts of the Hronicum Unit, Slovakia

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ABSTRACT: Two types of copper mineralization occur in volcanic rocks of the Malu•iná Formation in the Kozie Chrbty Mts, and the Malé Karpaty Mts. Disseminated copper mineralization is related to carbonate-chlorite-quartz amygdales and veinlets. The younger vein type mineralization is bound to barite, barite-carbonate and quartz-carbonate veins. Both types of mineralization are hosted in basalts and andesites. The disseminated copper mineralization was formed due to the Permian post-volcanic hydrothermal activity. The vein type of mineralization is bound to faults formed during the Alpine overthrust of the Hronicum Unit. The mineral association represent chalcopyrite and bornite, accompanied by chalcocite, pyrite, covellite, digenite, tetrahedrite, tennantite, galena, sphalerite, arsenopyrite, gersdorffite, siegenite, carrollite, calcite, quartz, opal and chlorite.

KEY WORDS: basalt, copper minerals, barite, Slovakia, disseminated and vein mineralization.

Introduction

The Permian basic volcanism of the Hronicum Unit is characterized by barite and copper mineralization. The chemical composition of basic volcanic rocks corresponds to tholeiite and partly to calc-alkaline trend of volcanism (Vozár 1977). They underwent of the low grade regional metamorphism indicated by the presence of pumpellyite (Vrána 1965).

A disseminated copper mineralization hosted in basalts and andesites occurs in the uppermost part of the Malu•iná Formation at Kvetnica (Kantor 1951; Antaš 1963; Rojkovič 1990), Sološnica, Lošonec (Varček and Regásek 1962; Rojkovič 1990) and Malu•iná (Turan 1962; Petro 1974; Friedl 1985). Antaš (1963) distinguished at Kvetnica the older chalcopyrite mineralization within amygdales of the basalt and the younger vein quartz-chalcopyrite mineralization. Chalcopyrite is accompanied by chalcocite, bravoite, chalcedony and carbonate in amygdales and by calcite, pyrite, bornite, galena, sphalerite and gold in veinlets.

Methods

The optic and chemical characteristics of minerals were studied under the microscope in transmitted and reflected light, by scanning electron microscope (SEM), by wave-dispersion X-ray microanalysis (WDX), energy-dispersion X-ray microanalysis (EDX) and by X-ray diffraction analysis (XRD). Carbonates were analysed by volumetric and thermal analysis. The studies of fluid inclusions in barite provided homogenization temperatures. The rock analyses were carried out by X-ray fluorescence analysis (XFA), optical emission spectroscopy (OES) and instrumental neutron activation analysis (INAA).

Copper mineralization in the Malé Karpaty Mts.

The green amygdaloidal basalts is composed predominantly by plagioclases and chlorite. They are accompanied by relics of chloritized augite, epidote and apatite. Mineralized amygdales (up to 6 mm in size) are filled by calcite and chlorite, less by quartz. Magmatic ore minerals, as magnetite, ilmenite, are often altered to hematite, rutile and leucoxene. The copper mineralization is formed by bornite, chalcocite and pyrite. They are accompanied by chalcopyrite, digenite, covellite, idaite, sphalerite and galena.

Euhedral grains and aggregates of pyrite (up to several mm in size) are often cataclased. Chalcopyrite aggregates occur within amygdales or they are disseminated in quartz veinlets. Chalcopyrite is replaced by bornite aggregates of several mm in size. Bornite forms graphic intergrowths with chalcocite (Fig. 1) and veinlets in pyrite. The graphic intergrowths of bornite and chalcocite might document a disintegration of solid solution (Kostov et al. 1984). Bornite is close to stoichiometric composition with Cu/Fe atomic ratio 5.796. It does not correspond to a wide

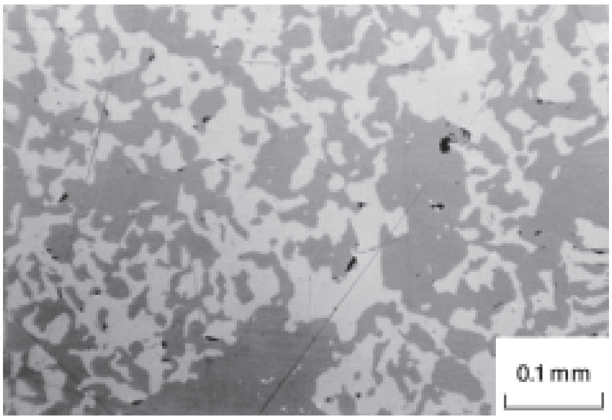

Fig.1. Graphic intergrowth of bornite (dark grey) and chalcocite (light grey). Lošonec, reflected light, parallel nicols.

Mineral Sample	chalcopyrite Kv 1	bornite MKL2	digenite MKL5.3	idaite MKSo3.2
		Weight %		
Cu	35.00	64.22	77.42	56.64
Ag		0.20		
Fe	30.50	9.74		10.98
S	34.90	25.82	22.58	32.38
Total	100.40	99.98	100,00	100.00
		Atomic proportion		
Cu	1.008	5.073	1.901	5.098
Ag		0.010		
Fe	1.000	0.875		1.124
S	1.992	4.042	1.099	5.777
Total	4.000	10.000	3.000	12.000

Tab. 1. Chemical composition of copper sulphides (Kv-Kvetnica, MKL-Malé Karpaty Mts.-Lošonec, MKSo-Sološnica).

compositional range of bornite in equilibrium with chalcopyrite as well as to Cu/Fe ratio 8.0 for bornite composition in equilibrium with chalcopyrite and idaite at 300 °C (Sagaki et al. 1975).

Digenite replaces bornite. Its composition $Cu_{1.730}S$ corresponds to low temperature Cu-poor digenite as Cu-rich limit changes to $Cu_{1,83}S$ at 83 °C (Roseboom 1966). Blades of secondary chalcopyrite (up to 0,05 mm long) replace bornite along the cleavage and fissures. Disseminated sphalerite aggregates (several mm in size) with tiny exsolutions of chalcopyrite are cut by galena veinlets. Covellite replaces bornite and digenite along the fissures and at the margins of their grains. Bornite is replaced in some places by idaite. Thin plates (about 0.1 mm long) of idaite have a characteristic strong bireflection and anisotropy identical to those described by Uytenbogaardt and Burke (1971). Synthesized idaite with formula $Cu_{5.5x}Fe_xS_{6.5x}$ proposed by Yund (1963) can coexist with covellite and bornite at 350 °C and 300 °C (Sagaki et al. 1975). Formula Cu_3FeS_4 represents supergene idaite according to Sillitoe and Clark (1969). Mineral with the same composition Cu_3FeS_4 corresponds according to Rice et al. (1979) to nukundamite. Analyzed mineral with composition $Cu_{5.098}Fe_{1.124}S_{5.777}$ is closer to Strunz's (1970) formula Cu_5FeS_6. It represents the initial product of supergene oxidation of bornite. Chemical composition of some copper sulphides illustrates Table 1.

Malachite and goethite are abundant in the oxidation zone. They fill fissures and cavities of the rock and interstitial spaces in carbonates. Goethite replaces pyrite, chalcopyrite, bornite and idaite.

Copper mineralization in the Kozie Chrbty Mts.

Kvetnica represents the best known occurrence of copper mineralization in the Permian basalts of the Hronic Unit. A few occurrences of copper mineralization with barite were found recently in basalts of the Kozie Chrbty Mts. They appear in an E-W zone running from the Lopušná valley in the west, to Kvetnica in the east. All these occurrences were mined in past (adits up to 110 m long). Two types of copper mineralization were distinguished in the Kozie Chrbty Mts:

- disseminated type of copper mineralization occurring within the matrix of basalts, filling amygdales or occurring in small quartz-carbonate lenses (up to 2 m long and 20 cm thick),
- vein type of copper mineralization related to barite, barite-carbonate, quartz-carbonate and quartz veins that are generally of E-W direction (up to 100 m long and 1 m thick).

The disseminated type of copper mineralization is wide spread in the whole area. The vein type of copper mineralization is typical for the western part of the Kozie Chrbty Mts. Chalcopyrite and bornite are predominant ore minerals. Chalcopyrite forms anhedral grains (0,1 to 3 mm in size) and veinlets in basalts and in quartz-carbonate lenses as well. It replaces plagioclase crystals along their cleavage. Massive chalcopyrite aggregates can be observed in barite-carbonate and quartz-carbonate veins. They fill interstices between quartz and carbonate grains. Chalcopyrite and bornite often forms graphic intergrowths. Blades of secondary chalcopyrite (1 to 6 µm thick) are frequent in bornite (Fig. 2). Lamellas of chalcopyrite in bornite are originated either by low temperature replacement of bornite, or by exsolution of chalcopyrite lamellas from "anomalous" bornite heated to around 200–250 °C during mild metamorphism (Durazzo and Taylor 1982). The Permian rocks of Hronicum Unit underwent metamorphism below 150 °C (Šucha and Eberl 1992). This exclude possible metamorphic origin of the lamellas. They were formed probably by low temperature

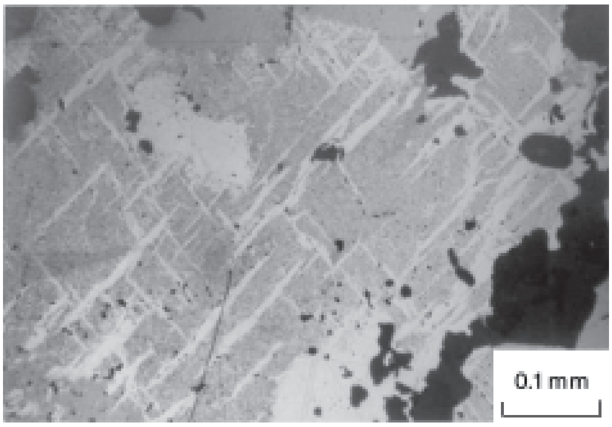

Fig. 2. Blades of secondary chalcopyrite (light grey) in bornite (dark grey). Kvetnica, reflected light, parallel nicols.

replacement of bornite I. Tetrahedrite-tennantite group minerals are abundant at Kvetnica locality. Veinlets and grains of tennantite are intimately associated with tetrahedrite. The As content in tetrahedrite ranges from 8.31 to 9.86 wt % (17,13 to 17,66 in tennantite), and Sb content ranges from 19.32 to 21.7 wt. % (6,69 to 7,48 in tennantite; Fig. 3, Tab. 2). The variability of As and Sb contents reflects a substitution of As^{+3} by Sb^{+3} and vice versa (Breskovska and Tarkian 1994).

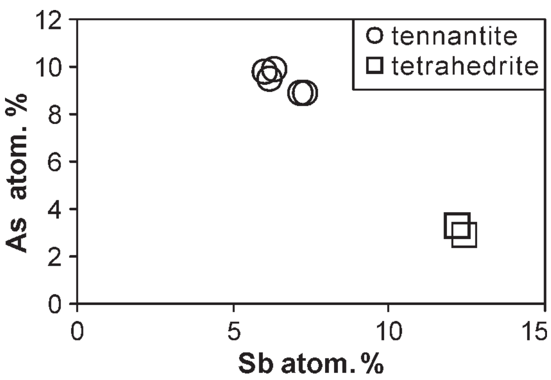

Fig. 3. X-Y plot of Sb and As contents in tetrahedrite-tennantite series.

Analyse	1	2	3	4
		Weight %		
S	52.00	53.60	52.20	54.05
Fe	47.00	43.40	42.50	45.63
As	0.80	2.50	5.30	0.00
Cu	0.00	0.00	0.00	0.55
Ni	0.00	0.00	0.00	0.02
Total	99.8	99.5	100.00	100.24
		Atomic proportion		
S	1.97	2.02	1.99	2.01
Fe	1.02	0.94	0.93	0.98
As	0.01	0.04	0.09	-
Cu	-	-	-	0.01
Ni	-	-	-	-
Total	3.00	3.00	3.00	3.00

Tab. 2. Chemical composition of the minerals of the tetrahedrite-tennantite serie from Kvetnica.

Pyrite and marcasite belong to the oldest minerals of both disseminated and vein types of copper mineralization. Their grains and crystals are disseminated in basalts and they are often enclosed in younger minerals (Fig. 4). Pyrite contains As up to 5 wt. %(Tab. 3). Gersdorffite is very rare mineral in both types of copper mineralization. More abundant gersdorffite grains and veinlets were observed at Kvetnica only, in quartz and carbonate gangue with chalcopyrite and tetrahedrite (Fig. 5). Gersdorffite shows a high Co-content and a low Fe-content (Fig. 6, Tab. 4). Compositional range of gersdorffite $MeAs_{1.05-1,42}S_{0.88-0.59}$ does not exceed extreme values of natural gersdorffites $MeAs_{0,96-1.63}S_{1.04-0.37}$ described by Rosner (1970). Siegenite with chemical composition corresponding to formula $(Co_{1,37}Ni_{1,23}Cu_{0,24}Fe_{0,10})_{2,94}S_{4,06}$, and mineral with composition approach-

	1	2	3	4	5	6	7
				Weight %			
S	25.17	26.80	27.03	26.98	26.89	27.53	24.86
Fe	2.39	2.26	2.58	3.11	2.16	3.10	3.95
Cu	38.66	37.76	37.99	40.99	38.45	41.57	37.30
Zn	2.68	3.62	3.41	2.89	3.82	2.74	1.51
As	9.75	9.16	8.43	17.13	9.86	17.66	8.31
Ag	0.00	0.06	0.07	0.08	0.08	0.05	0.08
Sb	19.32	21.71	21.23	7.48	19.85	6.69	21.11
Hg	0.52	0.34	0.60	0.20	0.15	0.04	0.72
Bi	0.53	0.86	0.34	0.00	0.61	0.53	0.75
Tot.	100.01	101.56	101.67	98.87	101.85	99.91	98.58
				Atomic proportion			
S	12.85	13.23	13.35	12.99	13.22	13.08	12.86
Fe	0.70	0.64	0.73	0.86	0.61	0.85	1.17
Cu	9.96	9.40	9.47	9.96	9.54	9.96	9.74
Zn	0.67	0.88	0.83	0.68	0.92	0.64	0.38
As	2.13	1.93	1.78	3.53	2.07	3.59	1.84
Ag	-	0.01	0.01	0.01	0.01	0.01	0.01
Sb	2.60	2.82	2.76	0.95	2.57	0.84	2.88
Hg	0.04	0.03	0.05	0.02	0.01	-	0.06
Bi	0.04	0.07	0.03	-	0.05	0.04	0.06
Tot.	29.00	29.00	29.00	29.00	29.00	29.00	29.00

Tab. 3. Chemical composition of pyrite from the Malé Karpaty and Kozie Chrbty Mts. (1-3 Malé Karpaty Mts., Lošonec, 4 Kozie Chrbty Mts., Kvetnica).

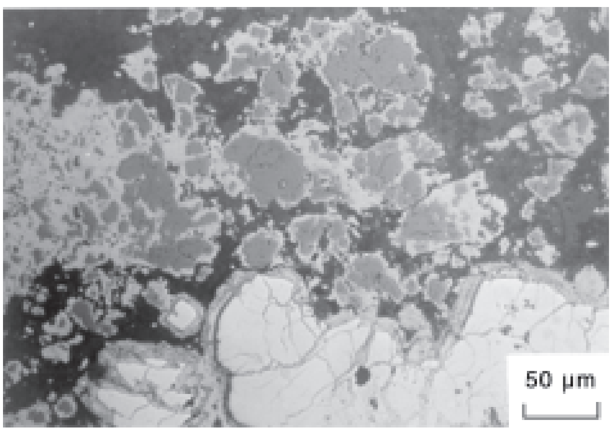

Fig.4. Pyrite crystals and aggregates filling amygdales (white) are rimmed by galena (light grey) and sphalerite (dark grey). Kvetnica, reflected light, parallel nicols.

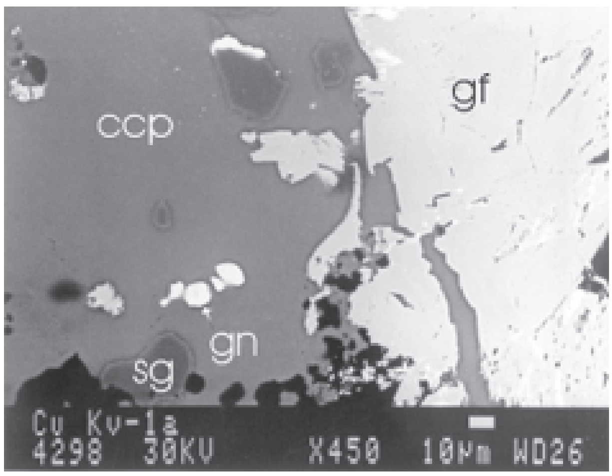

Fig.5. Chalcopyrite (ccp) with gersdorffite (gf), siegenite (sg) and galena (gn) inclusons. Kvetnica, SEM-BEI.

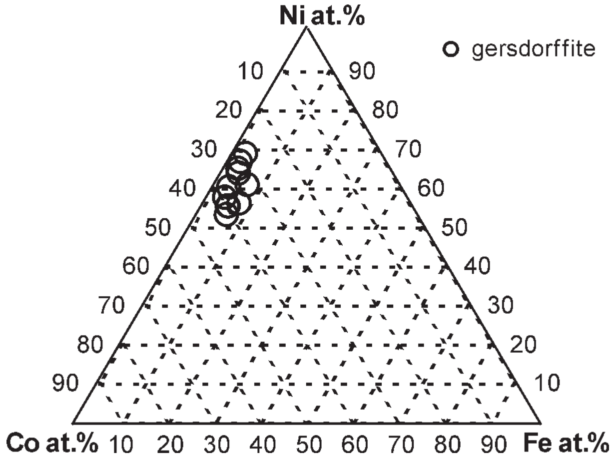

Fig. 6. Fe-Co-As atomic ratios of gersdorffite.

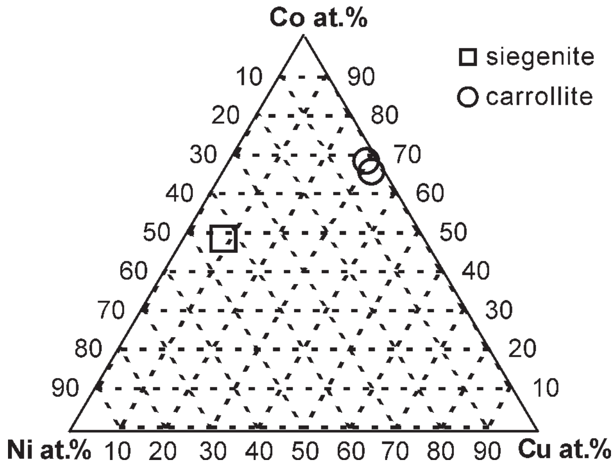

Fig. 7. Co-Cu-Ni atomic ratios of carollite and siegenite.

ing to carrollite $(Cu_{0,92}Co_{2,12}Ni_{0,07})_{3,11}S_{3,89}$ were found only scarcely as microscopic grains enclosed in chalcopyrite and bornite (Figs. 5 and 7, Tab. 5). Galena and sphalerite belong to the youngest ore minerals. The aggregates of galena are more abundant at Kvetnica. They are associated with chalcopyrite and enclose pyrite and sphalerite grains (Fig. 4, Tab. 6). Hematite, rutile and leucoxene accompany the copper mineralization. Small grains of hematite are disseminated in basalts or they are concentrated around amygdales. The shape of some hematite aggregates indicates pseudomorphs after magnetite (martite). Rutile and leucoxene, disseminated in basalts are alteration products of former magmatic magnetite and ilmenite.

Chalcopyrite, bornite, covellite, malachite, azurite, iron hydroxides, jarosite and gyps represent supergene minerals.

Gangue minerals are represented by carbonates (calcite, dolomite, ankerite) barite and quartz Carbonates are often intergrown with quartz. The textural relationship indicates simultaneous precipitation of ore minerals and carbonates, while barite is younger. Fluid inclusions studies in barite from the in the western part of the Kozie Chrbty Mts. confirmed two phases, with volume of gaseous phase less than 10 vol. % (at the room temperature). The homogenization temperatures (Th) varies from 138.4 to 257 °C and the melting temperatures of the last solid phase (Tmi) varying from −36.9 to −10,6 °C. The eutectic temperatures (Te) of inclusions attained over −70 °C. The fluid inclusions indicate presence of $CaCl_2$ and $MgCl_2$.

Geochemical characteristic of volcanic rocks

Trace element analyses of mineralized rocks show distinct increase in metallic elements (over 1000 ppm) forming the copper mineralization (Cu, Pb and Zn) compared to non-mineralized rocks (MKL 18 and KCHKv 5). Their content in the non-mineralized rocks corresponds to data for tholeiitic basalts (Wedepohl 1978). Ag bound in copper minerals accompanies increased content of Cu. Gold described by Antaš (1963) was not observed in microscope, and INAA confirmed only very low content of Au (Tab. 7). The sulphide mineralization is ac-

Analyse	1	2	3	4	5	6	7	8	9	10	11
					Weight %						
S	10.05	10.32	14.30	14.89	13.28	15.00	17.7	20.0	16.41	15.84	14.28
Fe	0.66	0.62	0.90	1.08	1.00	0.75	2.30	2.10	1.94	1.69	1.62
Co	9.17	9.64	12.14	12.93	10.48	10.27	12.60	11.2	13.50	13.09	13.03
Ni	21.83	20.73	19.92	19.13	20.37	20.56	19.30	20.90	17.65	18.51	18.35
Cu	0.29	0.47	0.42	0.26	0.41	0.24	0.00	0.00	3.89	3.95	3.14
As	55.94	57.45	50.55	51.19	53.35	51.86	47.70	46.00	46.20	47.70	49.35
Sb	0.09	0.02	0.01	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Au	0.00	0.16	0.00	0.00	0.06	0.04	0.00	0.00	0.00	0.00	0.00
Total	98.30	99.41	98.24	99.55	98.96	98.72	99.60	100.20	99.59	100.78	98.78
					Atomic proportion						
S	0.59	0.59	0.79	0.81	0.74	0.82	0.56	0.59	0.88	0.84	0.78
Fe	0.02	0.02	0.03	0.03	0.03	0.02	0.07	0.06	0.06	0.05	0.05
Co	0.29	0.30	0.27	0.38	0.32	0.31	0.36	0.31	0.39	0.38	0.39
Ni	0.70	0.65	0.60	0.57	0.62	0.62	0.56	0.59	0.51	0.54	0.55
Cu	0.01	0.01	0.01	0.01	0.01	0.01	-	-	0.10	0.11	0.09
As	1.40	1.42	1.20	1.19	1.27	1.22	1.08	1.01	1.05	1.08	1.15
Sb	-	-	-	-	-	-	-	-	-	-	-
Au	-	-	-	-	-	-	-	-	-	-	-
Total	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00

Tab. 4. Chemical composition of gersdorffite from the Kozie Chrbty Mts. (1–8 Kvetnica. 9–11 Kozí Kameň)

Mineral	siegenite	siegenite	carrollite
Analyse	1	2	3
	Weight %		
Co	26.80	27.00	39.91
Ni	23.90	24.10	1.31
Fe	2.00	1.60	0.04
Cu	5.30	5.10	18.64
S	43.20	43.50	39.59
Total	101.20	101.30	99.49
	Atomic proportion		
Co	1.37	1.37	2.12
Ni	1.22	1.23	0.07
Fe	0.11	0.09	-
Cu	0.25	0.24	0.92
S	4.05	4.07	3.89
Total	7.00	7.00	7.00

Tab. 5. Chemical composition of siegenite (Kvetnica) and carrollite (Lopušná Dolina).

Analyse	1	2
	Weight %	
S	13.74	13.86
Pb	86.75	86.47
Ag	0.00	0.00
Fe	0.14	0.13
Bi	0.00	0.00
Cu	0.28	0.33
Total	100.90	100.79
	Atomic proportion	
S	1.00	1.01
Pb	0.98	0.97
Ag	-	-
Fe	0.01	0.01
Bi	-	-
Cu	0.01	0.01
Total	2.00	2.00

Tab. 6. Chemical composition of galena from the Kozie Chrbty Mts. (1 – Kvetnica, 2 – Lopušná Dolina).

companied by silicification (HMKL 2) as shown by high SiO_2 content (up to 68 weight %). Increased concentrations of CO_2, CaO (up to 22 wt. %) and of ignition loss (LOI, up to 7 wt. %) are due to the presence of carbonates (KCHKv 1). Mafic minerals like pyroxenes were probable source of Ni and Co. Increased contents of Ni and Co in some mineralized rocks reflect their local remobilization and accumulation in Ni-Co minerals (gersdorffite, siegenite) with assistance of arsenic from hydrothermal solutions. Al_2O_3, Fe_2O_3, TiO_2 and Sr, bound to rock forming minerals (plagioclases, magnetite) are on the contrary relatively decreased in the mineralized rocks due to increased ratio of carbonates, quartz and other mineral formed during hydrothermal phase (Tab. 7).

Discussion

Our study permits to distinguish two generations of copper mineralization in the Permian basalts of the Kozie Chrbty Mts. and the Malé Karpaty Mts. The older copper mineralization is disseminated in basalts, within amygdales and in quartz-carbonate lenses. It is represented by:

1) hematite, rutile, leucoxene,
2) pyrite, marcasite, siegenite, gersdorffite,
3) chalcopyrite, bornite, chalcocite,

This type of copper mineralization was formed from ore-bearing fluids circulating in pores of cooling basalts. Copper mineralization was accumulated similarly during hydromagmagmatic phases in the Keweenawan basalts of the Michigan copper deposits (Amstutz 1977).

The younger vein type of copper mineralization occurs closely related to barite, barite-carbonate and quartz-carbonate veins. It is represented by:

1) pyrite, marcasite,
2) chalcopyrite, bornite, tetrahedrite-tennantite,
3) gersdorffite, carrollite,
4) galena, sphalerite.

This vein type of copper mineralization is related to the fault system formed during the overthrust of the Hronicum Unit. There are several hypotheses on the origin of barite veins in the Permian volcanic rocks of the Hronicum Unit. Turan (1962) suggested the Permian age of barite filling contraction fissures of the cooling basalts. On the contrary Petro (1974) related barite veins to tectonic zones of the Alpine age. Barite occurrences at the faults cutting the basalts as well as the Permian sandstone overlying basalt suggest the Alpine age of barite according our observations.

Low temperature chalcopyrite, bornite, digenite, covellite, idaite, malachite, azurite, iron hydroxides, jarosite and gyps represent supergene minerals.

Sample	MKL2	MKL5	MKSo4	MKL18	KCHKv1	KCHKv5
SiO_2	68.04	53.22	53.78	51.77	34.61	46.92
TiO_2	0.41	1.22	1.50	2.55	0.83	1.84
$Al2O_3$	8.83	18.53	18.04	14.31	9.68	17.07
Fe_2O_3 tot	2.90	6.11	6.34	12.83	6.85	9.48
MnO	0.05	0.05	0.05	0.09	0..54	0.14
MgO	1.49	7.31	6.16	3.66	4.37	5.45
CaO	5.84	2.23	2.16	4.22	22.04	6.13
Na_2O	1.09	6.51	4.82	4.33	2.18	3.43
K_2O	5.07	0.31	2.54	2.59	0.45	1.48
LOI	5.85	3.85	3.90	2.28	17.76	7.17
H_2O	0.36	0.43	0.42	0.70	0.05	0.17
P_2O_5				0.55	0.18	0.19
Total	99.93	99.77	99.71	99.88	99.36	99.28
Ag*	98.00		61.00	1.60		0.40
As*	106.00		30.00	13.00		13.00
Au*	0.025		0.019	0.152		0.063
B	22.40	13.20	76.00	28.80	19.00	52.00
Ba	162.00	138.00	257.00	200.00	<30.00	147.00
Co	32.00	24.00	42.00	25.00	210.00	40.00
Cr	104.00	78.00	4.20		50.00	114.00
Cu	>3000.00	>3000.00	2240.00	41.00	>3000.00	97.00
La	23.00	23.00	32.00	60.00	52.00	37.00
Mo	31.00	0.70	0.70	6.30	6.00	2.00
Ni	59.00	56.00	2.00	18.30	144.00	58.00
Pb	251.00	11.00	1010.00	20.00	>3000.00	28.00
Sr	36.00	76.00	76.00	260.00	77.00	173.00
U	0.90		0.90	2.00		5.60
V	112.00	195.00	138.00	151.00	132.00	173.00
Y	24.00	24.00	40.00	60.00	21.00	12.00
Yb	4,20	3.00	6.00	6.90		
Zn*	2020.00		1360.00	225.00		
Zr	191.00	95.00	490.00	360.00	148.00	114.00

oxides above total – XFA , * – INAA, other elements – OES.

Tab. 7. Chemical composition of basalts from Malé Karpaty Mts. (MKL–Lošonec, MKSo–Sološnica) and Kozie Chrbty Mts. (KCHKv–Kvetnica).

Conclusions

The disseminated copper mineralization is related to the Permian postvolcanic hydrothermal activity of basaltic volcanism. The association of minerals reflects composition of wall-rocks, as confirmed by the presence of Ni-Co minerals (siegenite, gersdorffite and carollite).

The vein copper mineralization is associated with faults formed during the Alpine overthrust of the Hronicum Unit. These structures allowed the circulation of the hydrothermal fluids. More data are needed to explain the origin of these fluids. Metallic elements might be mobilized from disseminated preconcentrations, and subsequently transported and deposited into the structurally favourable milieu.

Low temperature chalcopyrite, digenite, covellite, idaite, malachite, azurite, iron hydroxides, jarosite and gypsum represent supergene association of minerals.

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Hydrothermal Carbonate and Sulphide Mineralization in the Late Paleozoic Phyllites (Bacúch, Nízke Tatry Mts.)

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ABSTRACT: Two significant occurrences of Fe-carbonate mineralization in the vicinity of Bacúch village, are hosted by metamorphosed volcanosedimentary rocks of the Jánov grúň complex in the Veporic Unit of Nízke Tatry Mts. The occurrences are paragenetically close to other Fe-carbonate deposits in the region. At the locality Jánov grúň Hill occurs carbonate and quartz--sulphide stages. At the locality Sokolova dolina Valley is older carbonate stage cut by younger quartz-sulphide stage. Quartz--sulphide mineralization consists of two generations of pyrite, sphalerite, and chalcopyrite Galena occurred with PbBi, CuPbBi