PŮVODNÍ PRÁCE/ORIGINAL PAPER

Nesquehonite from the Pezinok-Kolársky vrch antimony deposit, Malé Karpaty Mts. (Slovak Republic)

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Abstract

An uncommon post-mining mineral assemblage with nesquehonite, Sr-rich brandholzite and hörnesite was recently discovered at the Kolársky vrch antimony deposit near Pezinok, Malé Karpaty Mts., Slovakia. Nesquehonite occurs as white opaque pseudomorphs after pre-existing flattened crystals and crystalline aggregates of lansfordite up to 18 mm in size associated with aragonite, gypsum, brandholzite and hörnesite. Its refined unit-cell parameters (for the monoclinic space group $P2_1/n$) are: *a* 7.694(1) Å, *b* 5.364(1) Å, *c* 12.118(2) Å, *β* 90.33(2)° and *V* 500.2(1) Å^3. Except of dominant content of Mg only minor amounts of Si were detected in studied nesquehonite. Sr-rich brandholzite occurs as colourless, well developed, tabular pseudohexagonal crystals up to 3 mm in size and its empirical formula based on (Sb+As = 2 *apfu*) is $(Mg_{0.72}Sr_{0.21})_{\Sigma 0.93}(Sb_{1.95}As_{0.05})_{\Sigma 2.00}(OH)_{12}\cdot 6H_2O$. Hörnesite forms microscopic spherical aggregates up to 70 μm enclosed in nesquehonite. It has near end-member composition with empirical formula $(Mg_{3.24}Fe_{0.01})_{\Sigma 3.25}(AsO_4)_{1.93}(SiO_4)_{0.04}(SO_4)_{0.03}\cdot 8H_2O$ (based on As+Si+S = 2 *apfu*). The whole supergene assemblage is a product of post-mining weathering of stibnite and arsenopyrite in carbonate (dolomite) rich environment under near-neutral conditions.

Key words: *nesquehonite, brandholzite, hörnesite, X-ray powder data, chemical composition, Kolársky vrch deposit, Pezinok, Slovak Republic*

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Introduction

Nesquehonite, $MgCO_3\cdot 3H_2O$ is relatively rare species, which may form as a dehydration product of lansfordite, $MgCO_3\cdot 5H_2O$. The type locality of nesquehonite is No. 1 Tunnell at Nesquehoning anthracite mine, Nesquehoning near Lansford, Pennsylvania, USA, where it forms pseudomorphs and crystals formed by dehydration of lansfordite (Genth, Penfield 1890). Other well-known localities of nesquehonite are Brosso pyrite mine in Piedmont (Campostrini 2001) or Cogne iron mine in Aosta Valley, Italy (Fenoglio 1935), Suonion mine No. 19 in Lavrion District, Greece (Giester et al. 2000), Sommergraben near Leoben in Styria, Austria (Meixner 1950), Mt. Moore in Western Antarctica (Vennum 1986), Eibengrotte cave near Wiessenthal, Germany (Fischbeck, Müller 1971) or Wolkberg cave in Capricorn District, South Africa (Martini, Kavalieris 1978).

Genth and Penfield (1890) and later also Fonoglio (1935) proposed that nesquehonite has orthorhombic symmetry (space group *Pmmm*), but Pepinsky (1941) and later Kinsolving et al. (1950) proved that nesquehonite is actually monoclinic and pseudoorthorhombic symmetry is caused by intense twinning on (001) plane. The crystal structure of natural nesquehonite was solved by Geister et al. (2000) and it is characterized by infinite chains along [010], formed by corner sharing MgO_6 octahedra. Within the chains, CO_3 groups link three MgO_6 octahedra by two common corners and one edge, which causes strong distortions of the involved polyhedra. These chains are interconnected via hydrogen bonds only. Each Mg atom is coordinated by two H_2O ligands, and one free water molecule is situated between the chains.

The aim of this short paper is description and complex mineralogical study of nesquehonite and associated supergene minerals from the recently discovered locality, the Kolársky vrch antimony deposit, Malé Karpaty Mts., Slovakia.

Geological setting and occurrence

The Kolársky vrch antimony deposit is located around 5 km NW of Pezinok town, in the Malé Karpaty Mts., Western Slovakia. It was exploited for Sb ores from 1790 until 1992, with overall production of 20 000 tons of antimony. Both open-pit and underground mining methods were used. GPS coordinates of the Kolársky vrch deposit are: 48°19'10.94"N and 17°13'39.71"E.

Hydrothermal quartz-carbonate mineralization with stibnite is hosted in Lower Paleozoic metamorphic rocks of the Pezinok-Pernek crystalline complex. The so-called "productive" zones with the Sb±Au ores are embedded in a Devonian volcano-sedimentary formation, metamorphosed during the Variscan orogeny to actinolite schists and amphibolites (Cambel 1959; Cambel, Khun 1983; Chovan et al. 1992, 1994; Ivan et al. 2001; Putiš et al. 2004). The ores at the Kolársky vrch deposit are bound to black shales in the NW - SE trending productive zone, which is more than 1 km long, 50 to 70 m wide and reaching vertical depth of around 100 m (Cambel 1959; Chovan et al. 1994). The Sb ore mineralization occurs in quartz-carbonate (mostly Fe-rich dolomite) lenses or as veinlets, nests, and impregnations in the host rocks. The hydrothermal ores contain mainly pyrite, arsenopyrite, stibnite, as well as the relatively abundant berthierite, gudmundite, primary kermesite, valentinite and native antimony (Cambel 1959; Chovan et al. 1992, 1994; Uher et al. 2000; Andráš et al. 2002). Števko et al. (2012) and Majzlan et al. (2016) recently described presence of post-mining supergene mineralization with abundant brandholzite from the abandoned mines at the Kolársky vrch deposit.

Nesquehonite was found on the walls of abandoned stope, at the Antimónová adit level, which is located at the upper part of the Kolársky vrch deposit.

Analytical methods

The powder X-ray diffraction data of nesquehonite were collected on a Bruker D8 Advance diffractometer (National Museum, Prague, Czech Republic) with a solid-state 1D Lynx-Eye detector using CuK_α radiation and operating at 40 kV and 40 mA. The powder patterns were collected using Bragg-Brentano geometry in the range 3 - 70° 2θ, in 0.01° steps with a counting time of 8 s per step. Positions and intensities of reflections were found and refined using the PearsonVII profile-shape function with the ZDS program package (Ondruš 1993) and the unit-cell parameters were refined by the least-squares algorithm implemented by Burnham (1962). The experimental powder pattern was indexed in line with the calculated values of intensities obtained from the crystal structure of nesquehonite (Giester al. 2000), based on Lazy Pulverix program (Yvon et al. 1977).

Chemical composition of nesquehonite and associated minerals was analysed with a Cameca SX-100 electron microprobe (Masaryk University, Brno, Czech Republic) operating in the wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 5 nA, and a beam diameter of 10 μm. The following lines and standards were used: *K*α: albite (Na), andalusite (Al), andradite (Fe), Co (Co), fluorapatite (P), gahnite (Zn), lammerite (Cu), Mg_2SiO_4 (Mg), Ni_2SiO_4 (Ni), orthoclase (K), $ScVO_4$ (V), spessartine (Mn), $SrSO_4$ (S), vanadinite (Cl, V), wollastonite (Si, Ca); *L*α: lammerite (As), $SrSO_4$ (Sr); *L*β: Sb (Sb) and *M*β: Bi (Bi). Peak counting times (CT) were 20 s for the main elements and 60 s for the minor elements; CT for each

Fig. 1 *White pseudomorphs of nesquehonite after aggregates of lansfordite crystals. Photo J. Sejkora, field of view is 17 mm.*

Fig. 2 *White pseudomorphs of nesquehonite after flattened crystals of lansfordite. Photo J. Sejkora, field of view is 8 mm.*

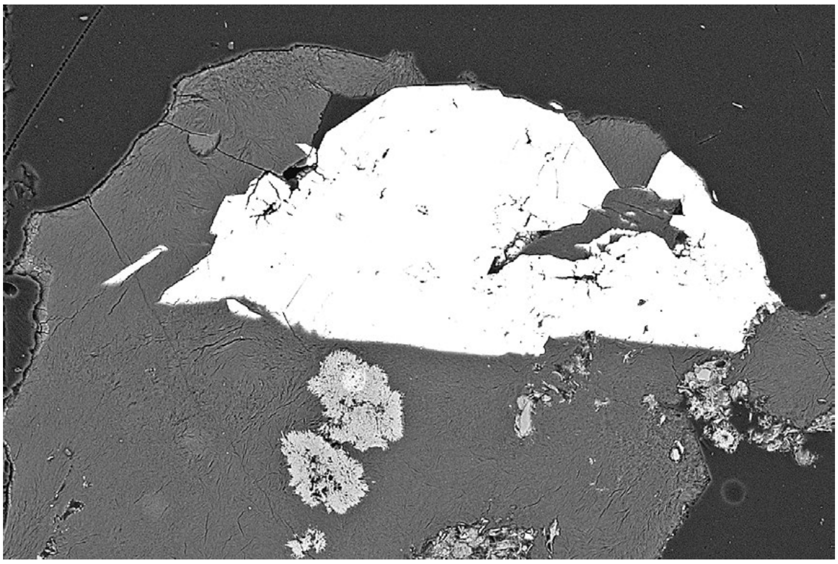

Fig. 3 *Nesquehonite (grey) associated with brandholzite (white) and hörnesite (light grey spheres). BSE photo by J. Sejkora, field of view is 0.8 mm.*

background was one-half of the peak time. The raw intensities were converted to the concentrations automatically the using *PAP* (Pouchou, Pichoir 1985) matrix-correction software.

Results

Nesquehonite occurs as white opaque pseudomorphs after pre-existing flattened crystals and crystalline aggregates of lansfordite up to 18 mm in size (Figs. 1, 2) growing on a surface of wall rock with minor stibnite and arsenopyrite impregnations and abundant dolomite veinlets. It is very rare and it is associated together with other post-mining supergene minerals like aragonite, gypsum, brandholzite and hörnesite (Fig. 3).

The experimental powder data set given in Table 1 agrees well with the X-ray pattern calculated from the single-crystal data of nesquehonite from Lavrion (Giester et al. 2000). The refined unit-cell parameters of nesquehonite from Pezinok are compared in Table 2 with published data.

Chemical composition of nesquehonite from Pezinok is very simple. In addition to 33.45 - 35.65 wt. % of MgO (slightly higher than the ideal content of 29.13 wt. %, probably due to the dehydration under EPMA conditions) only minor contents of SiO_2 in the range 0.25 - 0.31 wt. % were detected.

Brandholzite occurs as colourless, well developed, tabular pseudohexagonal crystals up to 3 mm in size, closely associated with nesquehonite. Its average chemical composition (mean of 4 points) is MgO 7.40, SrO 5.63, Sb_2O_5 73.10, As_2O_5 1.33 wt. % corresponding to the empirical formula $(Mg_{0.72}Sr_{0.21})_{\Sigma 0.93}(Sb_{1.95}As_{0.05})_{\Sigma 2.00}(OH)_{12}\cdot 6H_2O$ (on the basis Sb+As = 2 *apfu*). The unusual contents of Sr were determined in this mineral; previously studied brandholzite samples from Pezinok-Kolársky vrch (Majzlan et al. 2016) as well as from Pernek-Krížnica (Sejkora et al. 2010) or Brandholz-Goldkronach (Friedrich et al. 2000) do not contain this element even in minor amounts.

Hörnesite forms microscopic spherical aggregates up to 70 µm (Fig. 3) enclosed in nesquehonite. It has near end-member composition (mean of 2 points) MgO 27.40, FeO 0.25, As_2O_5 46.44, SiO_2 0.61, SO_3 0.32 wt. %, with empirical formula $(Mg_{3.24}Fe_{0.01})_{\Sigma 3.25}(AsO_4)_{1.93}(SiO_4)_{0.04}(SO_4)_{0.03}\cdot 8H_2O$ (based on As+Si+S = 2 *apfu*).

Conclusions

An uncommon post-mining mineral assemblage with supergene nesquehonite, Sr-rich brandholzite and hörnesite was recently discovered at the abandoned Kolársky vrch antimony deposit near Pezinok, Malé Karpaty Mts., Slovakia. Nesquehonite was formed as a dehydration product of pre-existing lansfordite crystals. The whole supergene assemblage is a product of post-mining weathering of ore minerals (stibnite, arsenopyrite) in carbonate (dolomite) rich environment under near-neutral pH conditions.

Table 1 *X-ray powder diffraction data of nesquehonite from Pezinok*

$d_{obs.}$	$I_{obs.}$	$d_{calc.}$	*h*	*k*	*l*
6.512	79.4	6.512	1	0	-1
6.477	54.7	6.478	1	0	1
6.060	2.4	6.059	0	0	2
4.909	52.5	4.905	0	1	1
4.144	2.4	4.141	1	1	-1
3.850	100.0	3.847	2	0	0
3.587	13.3	3.585	1	0	-3
3.570	1.9	3.568	1	0	3
3.238	4.6	3.239	2	0	2
3.225	13.9	3.227	0	1	3
3.029	35.8	3.030	2	1	-1
		3.029	0	0	4
		3.024	2	1	1
2.983	1.7	2.981	1	1	-3
2.971	2.9	2.971	1	1	3
2.783	9.2	2.783	2	1	-2
2.771	6.9	2.773	2	1	2
2.618	18.3	2.619	0	2	1
2.513	10.2	2.512	3	0	-1
2.507	10.7	2.506	3	0	1
2.498	7.8	2.499	1	1	-4
2.489	4.1	2.491	1	1	4
2.4665	6.2	2.4667	2	1	3
2.3380	3.3	2.3384	1	2	-2
		2.3352	1	2	2
2.1713	5.0	2.1707	3	0	-3
2.1658	2.2	2.1661	2	2	-1
2.1572	1.3	2.1578	3	1	2
2.1269	1.9	2.1259	1	1	-5
2.1206	1.9	2.1200	1	1	5
2.0194	5.5	2.0197	0	0	6
2.0077	1.8	2.0082	0	2	4
2.0018	1.4	2.0033	3	1	3
1.9245	15.7	1.9235	4	0	0
1.8434	2.4	1.8434	3	1	-4
1.8346	1.5	1.8342	3	1	4
1.7979	6.1	1.7982	0	2	5
1.7151	2.1	1.7150	0	3	2
1.6548	3.4	1.6555	4	1	-3
1.6479	3.7	1.6475	0	1	7
1.5500	2.7	1.5512	4	2	-1
		1.5493	4	2	1

Table 2 *Unit-cell parameters for nesquehonite (for the monoclinic space group $P2_1/n$)*

		a [Å]	*b* [Å]	*c* [Å]	*β* [°]	*V* [Å³]
Pezinok	this paper	7.694(1)	5.364(1)	12.118(2)	90.33(2)	500.2(1)
Lavrion	Giester et al. (2000)	7.701(1)	5.365(1)	12.126(2)	91.41(1)	501.0(1)
synth.	Stephan, MacGillavry (1972)	7.705(1)	5.3673(6)	12.121(1)	90.45(1)	501.2
Jáchymov	Sejkora, Gabašová (1995)	7.694(5)	5.369(6)	12.101(7)	90.37(4)	499.9

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