https://doi.org/10.46861/bmp.31.089 PŮVODNÍ PRÁCE/ORIGINAL PAPER

Retgersite from mine dump of the Lill shaft, Březové Hory ore district, Příbram (Czech Republic)

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Sejkora J, Škácha P, Vrtiška L, Dolníček Z, Jindra J (2023) Retgersite from mine dump of the Lill shaft, Březové Hory ore district, Příbram (Czech Republic). Bull Mineral Petrolog 31(1): 89-94 ISSN 2570-7337

Abstract

Rare sulphate of nickel, retgersite, was identified on the one specimen collected on the dump of the Lill shaft, Březové Hory ore district, Příbram (Czech Republic) in 1990s. The specimen consists of quartz gangue with dominant millerite and sphalerite. Retgersite forms light blue to blue-green curved fibrous microcrystalline aggregates up to 2 mm in size with vitreous lustre, growing on the surface and in small outer vugs of the supergene altered gangue. Retgersite was identified by PXRD and its refined unit-cell parameters (for the tetragonal space group $P4_12_12$) are: *a* 6.7838(2) Å, *c* 18.2951(8) Å and *V* 841.94(4) Å^3. Results of semiquantitative chemical analysis (EDS) as well as vibrational spectra (Raman, infrared) including their tentative assignments are also given. The studied retgersite was formed by (sub) recent weathering of primary nickel mineralisation (mostly millerite) in the mine dump conditions.

***Key words:** retgersite, sulphate, supergene mineralization, vibrational spectroscopy, Březové Hory base-metal district, Příbram ore area Czech Republic*

Received 10. 4. 2023; accepted 20. 6. 2023

Introduction

The Lill shaft is one of the economically less important base-metal mines being active between the years 1857 - 1902. Small occurrences of uraninite were explored during 1961 - 1965 there. The Lill shaft is localized in the Černojamské part of the Březové Hory ore district, the most important base-metal Ag-Pb-Sb-Zn district in the Czech Republic (Bambas 1990). The Lill shaft was very important mineralogical locality during the mining (Babánek et al. 1875 and others) and when the mine dump was processed during 1980´s to 1990´s. At that time also the specimen containing retgersite was discovered by Jaroslav Jindra.

Retgersite is rare hydrated tetragonal nickel sulphate, $NiSO_4·6H_2O$, usually originated by weathering of the primary Ni mineralisation in environment rich in nickel and low in arsenic. Its type locality is the Ragra mine (Minasragra) near Cerro de Pasco in Peru (Frondel, Palache 1949). It was described from several localities in the Czech Republic so far, usually from the deposits of the five-element formation: Smrkovec (Sejkora 1992), Jáchymov (Sejkora, Řídkošil 1993) and Horní Slavkov uranium deposit (Sejkora, Plášil 2009). Three localities of retgersite are known in Slovakia: Čierna Lehota (Mikuš, Chovan 2007), Dobšiná (Fehér at al. 2016) and Rudňany (Števko et al. 2019). The description of the specimen from the Lill shaft with retgersite and its properties is the aim of this paper.

Occurrence - geological setting and mineralogy

The Příbram ore area consists of two principal districts comprising uranium and base-metal vein mineralizations: the westward lying Březové Hory ore district, where base -metal mineralization prevails over uranium ores, and the eastward Příbram uranium and base-metal district, where uranium ores predominate. The late Variscan hydrothermal ore veins are situated in Teplá-Barrandian volcano-sedimentary Unit in the exocontact of the granitic rocks of the Central Bohemian Plutonic Complex. The Březové Hory ore district consists of three deposits: central Březové Hory, Černojamské and Bohutín deposit. The Březové Hory and Bohutín deposits are situated mostly in the Cambrian conglomerates, greywacke and sandstones or quartz diorite and tonalite in the case of the part of the Bohutín deposit. The Lill shaft was the most important mine within the Černojamské deposit. It is situated in the Upper Proterozoic varied volcano-sedimentary unit represented by metabasalts and vein basalts, lavas, tuffs and tuffites (in the form of irrecual bodies, sills and dyke). Graphitic shales, greywackes and siltstones are the most common sedimentary rocks. Also the thin layers of flint shales and limestones were found there. Alternation of various types of rocks within the whole area is typical with the increasing amount of the volcanic material with increasing depth (Bambas 1990).

Fourteen ore veins were found in the area of the Lill shaft with the most important Horní Černojamská and 2nd

Ležatá vein. Sphalerite, siderite-sulphidic, galena-baryte-ankerite, Mn-calcite-pyrite, uraninite and calcite-baryte mineralisation stages were observed there. Millerite was one of the relatively common Ni-minerals on the locality even though usually in the microscopic dimensions. It occurs in the dolomite-ankerite carbonate and associated with galena and sphalerite. The second type of millerite occurrence was found in vugs of quartz gangue with common nickeline (Mining Museum Příbram collections) (Škubal, Janout 1965). Siegenite in association with heazlewoodite and millerite was described by Plášil et al. (2009).

The Lill shaft or its mine dump is well known as locality of many primary and supergene minerals (e.g. Škácha, Plášil, 2002). The most interesting supergene minerals are serpierite, wulfenite, brianyoungite or munakataite (Sejkora et al. 2010) and two new minerals - znucalite (Ondruš et al. 1990) and bouškaite (Sejkora et al. 2019).

Specimen characterization

Specimen of the size 13 × 6 × 7 cm containing retgersite is formed by 6 cm thick sphalerite-millerite vein. The outer parts of the symmetric ore vein are formed by coarse-grained dark brown sphalerite. The middle 3 cm thick part contains large amount of quartz of grey and black colour forming non-distinct globular aggregates up to 1.5 cm in diameter heavily covered with millerite needles usually up to 1 mm in size, more rarely up to 25 mm. The external part of the specimen is strongly altered from the dump condition. It is covered by yellowish and greenish supergene phases of the amorphous look. Retgersite occurs on the surface and in small protected cavities of gangue as microcrystalline very brittle curved fibrous aggregates up to 2 mm in size (Fig. 1). It is light blue to blue-green with vitreous lustre.

Due to the very good solubility of retgersite in water, its chemical composition was studied only semi-quantitatively, using a Bruker energy-dispersive analyzer integrated in a Cameca SX100 electron microanalyzer (National Museum, Prague, Czech Republic). In addition to the dominant contents of Ni, S and O (Fig. 2), a minor contents of Zn and Co, which very probably isomorphically substitute for Ni, were also detected in the studied sample.

X-ray powder diffraction

Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer (National Museum, Prague) with a solid-state 1D LynxEye detector using CuK_{α} radiation and operating at 40 kV and 40 mA. The powder pattern was collected using Bragg-Brentano geometry in the range 2.5 - 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 Pearson VII 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 synthetic retgersite (Stadnicka et al. 1987), based on Lazy Pulverix program (Yvon et al. 1977).

The experimental X-ray powder pattern (Table 1) agrees very well with published data for retgersite as well as with those calculated from the crystal structure of this mineral (Stadnicka et al. 1987). The refined unit-cell parameters are compared in the Table 2 with published data.

Fig. 1 *Fibrous aggregates of retgersite with microcrystalline structure from the dump of the Lill shaft. Field of view 3.2 mm. Photo by J. Sejkora.*

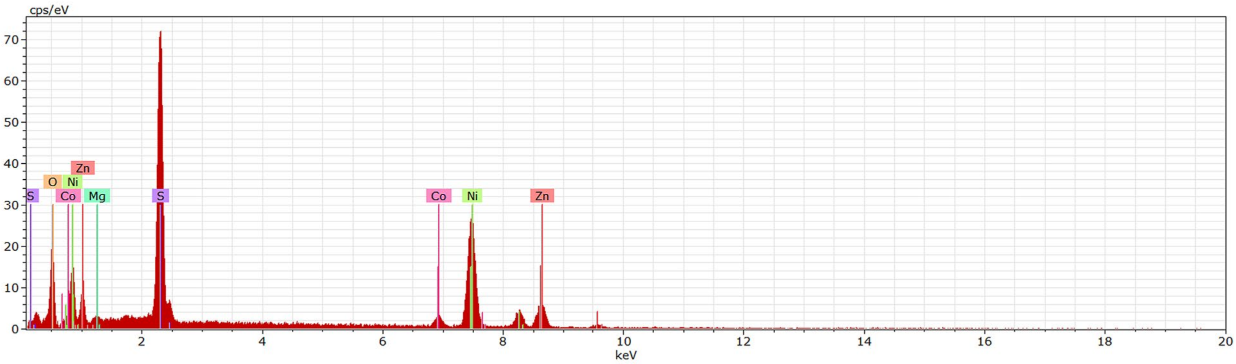

Fig. 2 *Energy dispersive X-ray spectrum of the retgersite from the Lill shaft dump, Březové Hory ore district, Příbram. Operator P. Škácha.*

Raman spectroscopy

The Raman spectra of studied sample were collected in the range 4000 - 40 cm^{-1} using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope. The Raman signal was excited by an unpolarized green 532 nm solid state, diode-pumped laser and detected by a CCD detector. The experimental parameters were: 100x objective, 10 s exposure time, 300 exposures, 50 μm slit spectrograph aperture and 6 mW laser power level. The spectra were repeatedly acquired from different grains in order to obtain a representative spectrum with the best signal-to-noise ratio. The eventual thermal damage of the measured point was excluded by visual inspection of excited surface after measurement, by observation of possible decay of spectral features in the start of excitation and checking for thermal downshift of Raman lines. The instrument was set up by a software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser-frequency calibration) and standardized white-light sources (intensity calibration). Spectral manipulations were performed using the Omnic 9 software (Thermo Scientific).

The Raman spectrum of retgersite from Příbram (Fig. 3) is close to the spectra of this mineral given in the RRUFF database (Lafuente et al. 2015) and agree very well with spectrum of well-defined sample of retgersite from Rudňany (Števko et al. 2019). The following interpretation of studied spectrum (Table 3) is based on papers of Ross (1974), Nakamoto (2009) and Števko et al. (2019).

A strong broad band with three components at 3416, 3261 and 3106 cm^{-1} is assigned to ν OH stretching vibrations of hydrogen-bonded water molecules. According to the empirical relation between energy of vibration and the corresponding bond length (Libowitzky 1999), O-H×××O hydrogen-bond lengths vary approximately in the range from 2.83 to 2.68 Å, which correspond to the lengths determined by crystal structure study (Stadnicka et al. 1987). A very weak band at 1645 cm^{-1} is attributed to the ν_2 bending vibrations of water molecules.

A medium-intensity bands at 1128 and 1087 cm^{-1} are assigned to the split triply degenerate ν_3 $(SO_4)^{2-}$ antisymmetric stretching vibrations. A strong band at 985 cm^{-1} with is attributed to the ν_1 $(SO_4)^{2-}$ symmetric stretching vibrations. Very weak and broad bands at 864 and 788 cm^{-1} may be connected with the libration modes of water molecules. A medium-intensity band at 606 cm^{-1} is assigned to the split triply degenerate ν_4 $(SO_4)^{2-}$ bending vibrations and those at 467 and 433 cm^{-1} to the split doubly degenerate ν_2 $(SO_4)^{2-}$ bending vibrations. Other observed bands at 374, 263, 242, 208, 162, 110, 73 and 56 cm^{-1} are related to vibrations of Me-O bonds (Me: Ni, Zn, Co) and external lattice vibration modes.

Infrared spectroscopy

The infrared vibrational spectrum of retgersite was recorded by the attenuated total reflection (ATR) method with a diamond cell on a Nicolet iS5 spectrometer. Spectra over the 4000 - 400 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.4747 cm/s. Spectra were co-added to improve the signal-to-noise ratio.

The experimental spectrum is very similar to those for sample from Rudňany (Števko et al. 2019) and agrees with retgersite spectra published by Chukanov (2014). The full-range spectrum is given in Figure 4 and its tentative assignment in Table 4. Strong and broad infrared band with components at 3400, 3267, 3182 and 3092 cm^{-1} are attributed to the ν O-H stretching vibration of hydrogen bonded water molecules. According to Libowitzky (1999) correlation function, O-H×××O hydrogen bond lengths vary approximately from 2.81 to 2.68 Å. A medium infra-

Table 1 *X-ray powder diffraction data of retgersite from the Lill shaft*

d_{obs}	I_{obs}	d_{calc}	h	k	l	d_{obs}	I_{obs}	d_{calc}	h	k	l	d_{obs}	I_{obs}	d_{calc}	h	k	l
6.357	3.7	6.361	1	0	1	2.781	1.0	2.781	1	0	6	1.9802	1.8	1.9801	2	1	7
4.638	5.8	4.640	1	1	1	2.724	10.2	2.724	2	0	4	1.9425	0.5	1.9422	3	1	4
4.574	36.4	4.574	0	0	4	2.573	7.0	2.573	1	1	6	1.8963	2.1	1.8962	2	0	8
4.247	100.0	4.248	1	1	2	2.528	3.7	2.528	2	1	4	1.8815	1.0	1.8815	3	2	0
3.770	3.4	3.770	1	1	3	2.3353	6.8	2.3355	2	1	5	1.8508	1.6	1.8506	3	1	5
3.392	5.3	3.392	2	0	0	2.2947	1.0	2.2950	1	1	7	1.8263	1.3	1.8262	2	1	8
3.335	3.4	3.335	2	0	1	2.1670	0.8	2.1671	1	0	8	1.7547	1.8	1.7545	3	1	6
3.180	1.3	3.180	2	0	2	2.1308	3.4	2.1306	3	1	1	1.7095	1.5	1.7094	1	1	10
3.033	1.6	3.034	2	1	0	2.1239	2.3	2.1241	2	2	4	1.6888	1.1	1.6887	4	0	1
2.964	10.8	2.964	2	0	3	2.1202	2.1	2.1202	3	0	3	1.6552	1.5	1.6551	2	2	8
2.909	2.0	2.909	1	1	5	2.0886	2.4	2.0886	3	1	2	1.6386	0.5	1.6387	4	1	1
2.879	1.5	2.880	2	1	2	2.0235	1.5	2.0237	3	1	3	1.6342	1.3	1.6339	4	0	3

Table 2 *Unit-cell parameters for retgersite (for tetragonal space group* $P4_12_12$*)*

		a [Å]	c [Å]	V [Å^3]
Lill shaft, Příbram	this paper	6.7838(2)	18.2951(8)	841.94(4)
Rudňany	Števko et al. (2019)	6.7820(5)	18.281(2)	840.8(1)
synth.	Rousseau et al. (2000)	6.782(1)	18.274(3)	840.5
Jáchymov	Sejkora, Řídkošil (1993)	6.772(1)	18.249(5)	836.9
synth.	Angel, Finger (1988)	6.780(1)	18.285(2)	840.5(3)
synth.	Stadnicka et al. (1987)	6.783(1)	18.288(2)	841.4(3)

red band at 1640 cm^{-1} is assigned to the ν_2 H_2O bending vibration of water molecules.

Very strong infrared bands at 1078 cm^{-1} is connected to the triply degenerate ν_3 $(SO_4)^{2-}$ antisymmetric stretching vibrations and its shoulder at 989 cm^{-1} probably with the ν_1 $(SO_4)^{2-}$ symmetric stretching vibration. Weak to medium-intensity bands at 847 and 784 cm^{-1} may be attributed to the libration modes of water molecules. Strong band at 605 cm^{-1} with shoulders at 665 and 623 cm^{-1} is assigned to the split triply degenerate ν_4 $(SO_4)^{2-}$ bending vibrations and band at 463 with shoulder at 436 cm^{-1} to the split doubly degenerate ν_2 $(SO_4)^{2-}$ bending vibrations.

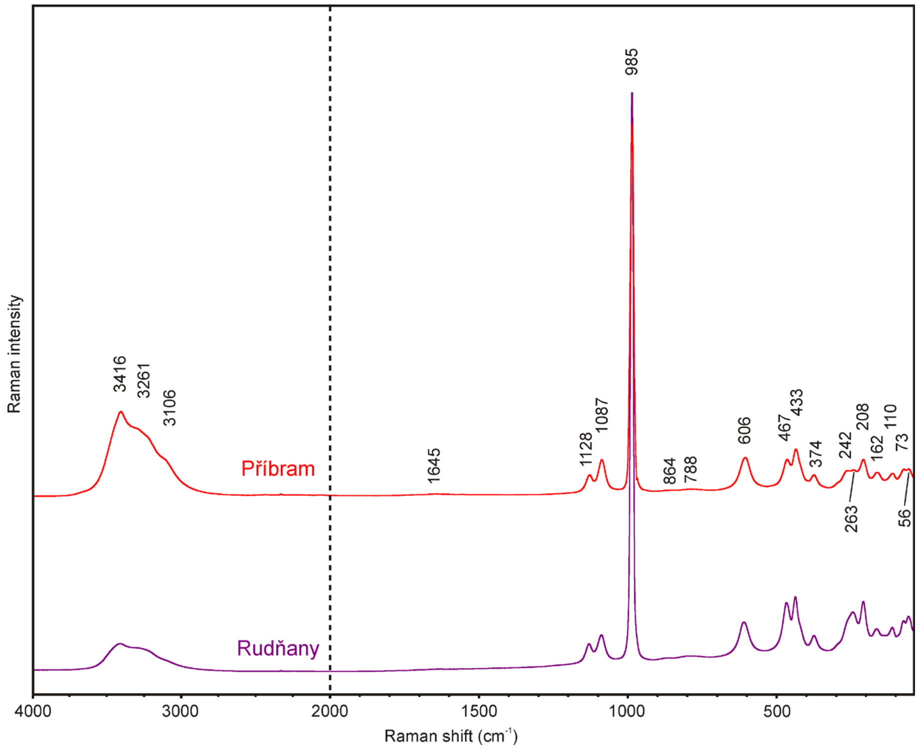

Fig. 3 *Raman spectrum for retgersite from Příbram (split at 2000 cm^{-1}) in comparison with sample from Rudňany (Števko et al. 2019).*

Table 3 *Tentative assignment of Raman spectrum of retgersite from Příbram*

Příbram	1*	2*	3*	4*	5*	tentative assignment
3416	3410					ν OH stretching vibrations of hydrogen-bonded water molecules
3261	3255					
3106						
1645	1651					ν_2 bending vibrations of water molecules
1128	1132	1125				ν_3 $(SO_4)^{2-}$ antisymmetric stretching vibrations
1087	1088	1088	1087		1091	
985	985	987	986	983	987	ν_1 $(SO_4)^{2-}$ symmetric stretching vibrations
864	877					libration modes of water molecules
788	795					
606	610	603	602	607	618	ν_4 $(SO_4)^{2-}$ bending vibrations
467	471	459	458	469	467	ν_2 $(SO_4)^{2-}$ bending vibrations
433	439	427	425		438	
374	375	373	374	388	370	vibrations of Me-O bonds and external lattice vibration modes
263		293	347			
242	245	267	273	243	246	
208	209	212	208		208	
			193			
162	166	161	158			
110	113					
73	78					
56	60					

1* - Rudňany, Slovak Republic (Števko et al. 2019)
2* - R100086 - synthetic retgersite, Fluka Chemie 72280, RRUFF (Lafuente et al. 2015)
3* - R130366 - Minas Ragra mine, Pasco, Peru, RRUFF (Lafuente et al. 2015)
4* - R130119 - Cerro de Pasco, Alcides Carrión Province, Pasco department, Peru, RRUFF (Lafuente et al. 2015)
5* - R70655 - Lovelock mine, Bolivia, Cottonwood Canyon, Table Mountain District, Churchill County, Nevada, USA, RRUFF (Lafuente et al. 2015)

Discussion and conclusions

In the dump material of the Lill shaft, base-metal district Březové Hory, Příbram, the occurrence of a relatively rare Ni sulfate, retgersite, which was previously unknown at this ore district, was identified by set of methods including powder X-ray diffraction, energy dispersive X-ray and Raman and infrared spectroscopy analysis. The studied retgersite was formed by (sub)recent weathering of primary nickel mineralisation (mostly millerite) in the mine dump conditions.

According to Petrova et al. (2012) retgersite directly crystallizes from an aqueous solution only at temperatures > 31.5 °C, and at lower temperatures formation of heptahydrate morenosite is preferred. Retgersite may represent the dehydration product of morenosite. The exception to the direct formation of retgersite at temperatures lower than 31.5 °C is the crystallization from acidic solutions containing free sulfuric acid. The morphological character of the retgersite aggregates (without distinct signs of dehydration processes) indicates that retgersite at the Lill mine dump crystallized directly from acidic solutions in a relatively dry environment and is not a product of dehydration of pre-existing morenosite.

Acknowledgements

This study was financially supported by the Ministry of Culture of the Czech Republic (long-term project DKRVO 2019-2023/1.II.e; National Museum, 00023272).

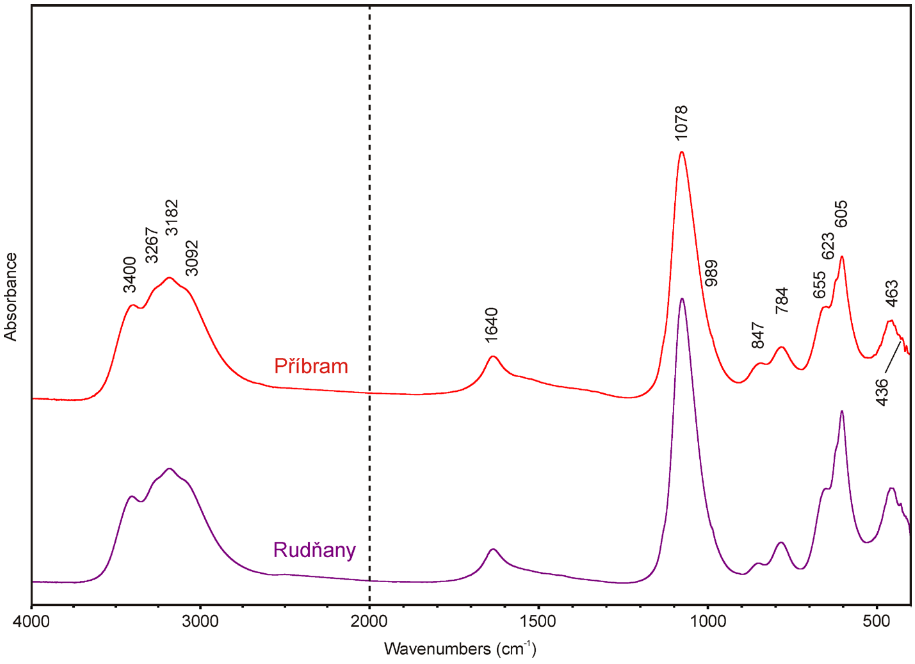

Fig. 4 *Infrared spectrum for retgersite from Příbram (split at 2000 cm^{-1}) in comparison with sample from Rudňany (Števko et al. 2019).*

Table 4 *Tentative assignment of infrared spectrum of retgersite from Příbram*

Příbram	1*	2*	3*	tentative assignment
3400	3411	3470	3440	ν OH stretching vibrations of hydrogen-bonded water molecules
3267	3269	3250	3248	
3182	3181			
3092	3090			
		2280	2250	
			2070	
1640	1635	1645	1645	ν_2 bending vibrations of water molecules
1078	1078	1094	1096	ν_3 $(SO_4)^{2-}$ antisymmetric stretching vibrations
989	980		986	ν_1 symetrická valenčná vibrácia $(SO_4)^{2-}$
847	853	840	845	I libration modes of water molecules
784	782	784	785	
655	657	663	665	ν_4 $(SO_4)^{2-}$ bending vibrations
623	625	623	617	
605	603			
		505		ν_2 $(SO_4)^{2-}$ bending vibrations
463	461	470	470	
436	430			

1*- Rudňany, Slovak Republic (Števko et al. 2019)
2* S112 - Jáchymov, Czech Republic (Chukanov 2014)
3* S238 - Pechenga Ni–Cu ore field, Russia (Chukanov 2014)

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