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Vymazalováite, $Pd_3Bi_2S_2$, a new mineral from the Noril'sk-Talnakh deposit, Krasnoyarskiy region, Russia

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ABSTRACT

Vymazalováite, $Pd_3Bi_2S_2$ is a new platinum-group mineral discovered in the Komsomolsky mine of the Talnakh deposit, Noril'sk district, Russia. It forms small (from a few μm to 20–35 μm) inclusions or euhedral grains in intergrowths of polarite, sobolevskite, acanthite and unnamed $(Pd,Ag)_5BiS_2$ in aggregates (up to ~200 μm) in galena and rarely in chalcopyrite. It occurs with telargpalite, cooperite, braggite, vysotskite, sopcheite, stibiopalladinite, sobolevskite, moncheite, kotulskite, malyshevite, insizwaite, Au-bearing silver and the newly described mineral kravtsovite ($PdAg_2S$) in association with pyrite, chalcopyrite and galena in vein-disseminated mineralization in skarn rocks. Synthetic vymazalováite is brittle; it has a metallic lustre and a grey streak. In plane-polarized reflected light, vymazalováite is creamy grey and appears slightly brownish against galena in the assemblage with chalcopyrite. It exhibits no internal reflections. Average reflectance values in air for natural and synthetic vymazalováite are (*R* natural, *R* synthetic in %) are: 46.35, 45.7 at 470 nm, 47.65, 47.45 at 546 nm, 48.5, 48.2 at 589 nm and 49.5, 49.0 at 650 nm. Seven electron probe micro-analyses of vymazalováite give an average composition: Pd 40.42, Bi 49.15, Ag 0.55, Pb 1.02, S 7.77 and Se 0.26, total 99.17 wt.%, corresponding to the empirical formula $Pd_{3.05}(Bi_{1.89}Ag_{0.04}Pb_{0.04})_{\Sigma 1.97}(S_{1.95}Se_{0.03})_{\Sigma 1.98}$ based on a total of 7 atoms per formula unit. The simplified formula is $Pd_3Bi_2S_2$. The mineral is cubic, space group $I2_13$, with $a = 8.3097(9)$ Å, $V = 573.79(1)$ Å^3 and $Z = 4$. The density calculated on the basis of the empirical formula and cell dimensions of synthetic vymazalováite is 9.25 g/cm^3. The strongest lines in the powder X-ray diffraction pattern of synthetic vymazalováite [*d* in Å (*I*) (*hkl*)] are: 4.15(32)(200), 2.93(78)(220), 2.40(100)(220), 2.08(53)(400), 1.695 (34)(422), 1.468(35)(440) and 1.252(31)(622). The structural identity of natural vymazalováite with synthetic $Pd_3Bi_2S_2$ was confirmed by electron back-scatter diffraction measurements on the natural sample. This new mineral honours Dr Anna Vymazalová of the Czech Geological Survey, Prague.

Keywords: vymazalováite, platinum-group mineral, $Pd_3Bi_2S_2$ phase, electron-microprobe data, reflectance data, X-ray-diffraction data, crystal structure, Komsomolsky mine, Talnakh deposit, Noril'sk district, Russia.

Introduction

Vymazalováite, $Pd_3Bi_2S_2$, was found in vein-disseminated pyrite-chalcopyrite-galena ores in the Talnakh deposit, Noril'sk, Russian Federation at 69°30'20"N and 88°27'17"E. The host rocks are diopside- hydrogrossular-serpentine metasomatites developed in diopside-monticellite skarns where monticellite is replaced by hydrogrossular and serpentine. These rocks lie ~30 m below the lower contact of the Talnakh intrusion (eastern part of the Komsomolsky mine). Mineralization

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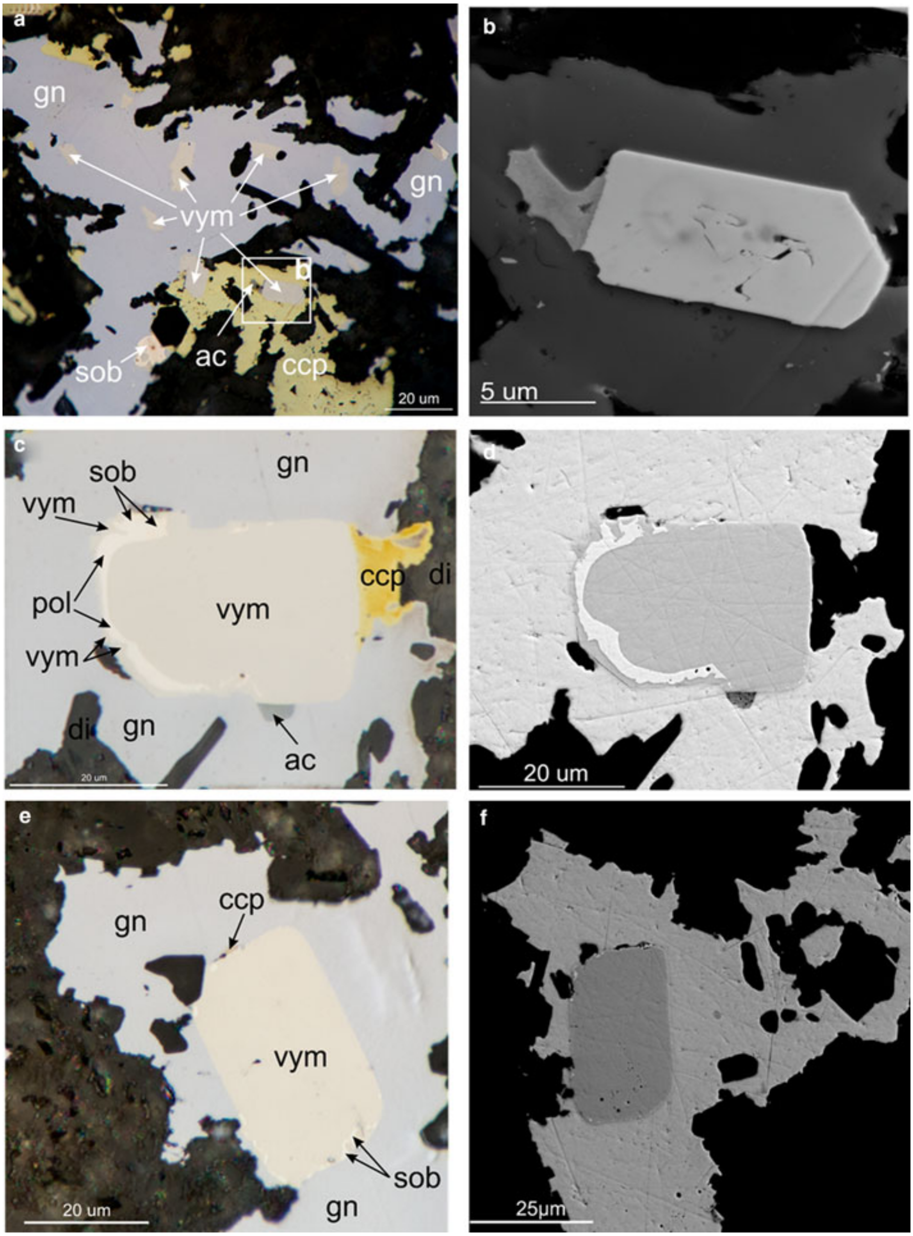

FIG. 1. (*a*) reflected light image of vymazalováite enclosed in galena and chalcopyrite; (*b*) back-scattered electron (BSE) images of an enlargement (marked as square) showing vymazalováite intergrown with acanthite in chalcopyrite; (*c*) reflected-light image of vymazalováite grain rimmed by polarite and sobolovskite, intergrown with acanthite and chalcopyrite in galena; (*d*) similar area to (*c*) in BSE; (*e*) reflected-light image illustrating euhedral grain of vymazalováite enclosed in galena; and (*f*) similar area to (*e*) in BSE. Key: vym – vymazalováite; gn – galena, ccp – chalcopyrite, sob – sobolevskite; pol – polarite; ac – acanthite; di - diopside.

represents the outermost part of the disseminated ores and is characterized by a lack of Ni minerals, also with no Ni content in the platinum-group minerals. The ores are known for their large galena content in an association of pyrite and chalcopyrite with abundant Pd-, Pt-, Ag- and Au-bearing minerals. Silver and gold not only form alloys but also are commonly incorporated in sulfides, selenides, sulfo-selenides and telluro-sulfoselenides (Sluzhenikin and Mohkov, 2015). These ores were formed during hydrothermal replacement of skarns.

Vymazalováite forms small (from a few μm to 35 μm) inclusions or euhedral grains, generally rectangular in polished section, in intergrowths of polarite, sobolevskite, acanthite and unnamed $(Pd, Ag)_5BiS_2$ in galena, rarely in chalcopyrite. Less commonly, the mineral occurs in aggregates (from a few μm to 35 μm) composed of intergrowths of telargpalite, braggite, vysotskite, sopcheite, stibiopalladinite, sobolevskite, moncheite, kotulskite, malyshevite ($PdCuBiS_3$), insizwaite, acanthite, Au-bearing silver and the newly described mineral kravtsovite ($PdAg_2S$) (Vymazalová *et al.* 2017) in association with pyrite, chalcopyrite and galena (Fig. 1).

Both the mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2016-105). The mineral name vymazalováite is chosen to honour Dr Anna Vymazalová (*b.* 1974) research scientist at the Czech Geological Survey for her contributions to the ore and experimental mineralogy of the platinum-group minerals and for her participation in the description of several new minerals. The holotype (polished section) is deposited at the Department of Earth Sciences of the Natural History Museum, London, UK, catalogue No BM 2016, 150. According to the chemical composition the mineral belongs to the 02.BC group (sulfides with Pd) of the Strunz & Nickel classification scheme (Strunz and Nickel, 2001).

Appearance, physical and optical properties

In plane-polarized reflected light, vymazalováite is creamy grey in the assemblage with galena and chalcopyrite (Fig. 1). It is isotropic and displays no internal reflections.

Vymazalováite is opaque with a metallic lustre. The powder of synthetic vymazalováite is grey in colour and has a grey streak. Synthetic vymazalováite is brittle. The density calculated on the basis of the empirical formula and cell dimensions of synthetic vymazalováite is 9.25 g/cm^3.

Reflectance measurements were made in air relative to a WTiC standard on both natural and synthetic vymazalováite using a J & M TIDAS diode array spectrometer attached to a Zeiss Axiotron microscope. The results are tabulated (Table 1) and illustrated in Fig. 2. The reflectance spectra for natural and synthetic vymazalováite are in good agreement bearing in mind the effect of the minor element substitutions in the natural grains and the fine grain size of the inclusions in galena and chalcopyrite.

Chemical composition

Electron probe micro-analysis (EPMA) on grains of natural vymazalováite were obtained using an Inca

TABLE 1. Reflectance data for natural and synthetic vymazalováite.*

	Natural		Synthetic[3]	
λ (nm)	*R* (%) Gal[1]	*R* (%) Chal[2]	*R* (%)	*R* (%)
400	44.9	45.2	44.2	44.0
420	45.3	45.5	44.7	44.3
440	45.7	45.8	45.1	44.7
460	46.1	46.2	45.6	45.2
470	**46.3**	**46.4**	**45.9**	**45.5**
480	46.4	46.5	46.2	46.8
500	46.7	46.9	46.8	46.3
520	47.1	47.2	47.2	46.8
540	47.5	47.6	47.5	47.2
546	**47.6**	**47.7**	**47.6**	**47.3**
560	47.8	48.0	47.8	47.6
580	48.2	48.4	48.1	47.9
589	**48.4**	**48.6**	**48.3**	**48.1**
600	48.6	48.8	48.5	48.2
620	48.9	49.1	48.8	48.5
640	49.2	49.4	49.0	48.8
650	**49.4**	**49.6**	**49.1**	**48.9**
660	49.5	49.7	49.2	49.0
680	49.8	50.0	49.5	49.3
700	50.1	50.2	49.8	49.7

*Wavelengths required by the Commission on Ore Mineralogy are given in bold. *R* is the reflectance at a given wavelength for a cubic mineral.
[1]Gal is for an inclusion in galena;
[2]Chal is for an inclusion in chalcopyrite.
[3]Two grains of the synthetic vymazalováite were measured.

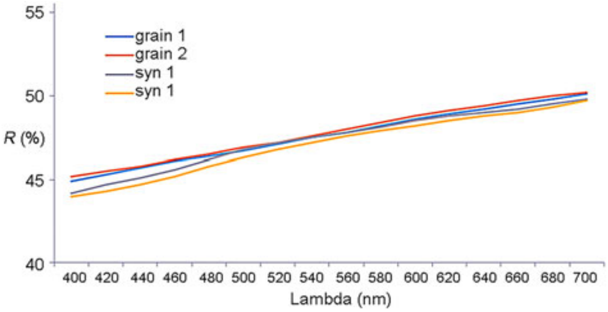

FIG. 2. Reflectance data for vymazalováite and synthetic grains of $Pd_3Bi_2S_2$. Grain 1 is of an inclusion in galena. Grain 2 an inclusion in chalcopyrite.

Wave 500 (WDS, Oxford Instruments) installed on an SEM Lyra 3GM (TESCAN), at the TESCAN demonstration laboratory in Moscow, Russia, with analytical conditions 20 kV, 10 nA and counting times 30 s (on peak positions)/2×15 s (background on left and right positions). The spectra were collected on Pb*M*α, Bi*M*α, Pd*L*α, Ag*L*α, S*K*α and Se*L*α lines with standards of pure Se, Pd, Ag, Bi, synthetic PbTe and natural FeS_2 (pyrite).

Synthetic vymazalováite was investigated using a CAMECA SX-100 electron probe microanalyser in wavelength-dispersive mode with an electron beam focused to 1–2 μm at the Institute of Geology of the Czech Academy of Sciences, Prague. Pure elements and FeS_2 were used as standards and the radiations measured were Bi*M*α Pd*L*α, S*K*α, with an accelerating voltage of 15 kV and a beam current of 10 nA measured on the Faraday cup.

Results of the EPMA are given in Table 2. The empirical formula calculated on the basis of 7 atoms per formula unit is $Pd_{3.05}(Bi_{1.89}Ag_{0.04}Pb_{0.04})_{\Sigma 1.97}(S_{1.95}Se_{0.03})_{\Sigma 1.98}$ for natural vymazalováite and $Pd_{3.04}Bi_{1.97}S_{1.99}$ for synthetic vymazalováite giving a simplified formula of $Pd_3Bi_2S_2$.

Synthetic analogue

The small size and nature of the intergrowths of vymazalováite with polarite, galena and chalcopyrite prevented its extraction and isolation in an amount sufficient for the relevant crystallographic and structural investigations. Therefore, these investigations were performed on the synthetic phase $Pd_3Bi_2S_2$, being equivalent to natural vymazalováite.

The synthetic $Pd_3Bi_2S_2$ phase was prepared using an evacuated silica glass tube method in the Laboratory of Experimental Mineralogy of the Czech Geological Survey in Prague. Palladium (99.95%), bismuth (99.999%) and sulfur (99.999%) were used as starting materials for synthesis. The evacuated tube with its charge was sealed and annealed. After cooling using a cold-water bath, the charge was ground into powder in acetone using an agate mortar and mixed thoroughly to homogenize. The pulverized charge was sealed in an evacuated silica-glass tube again and heated at 400°C for 70 days. The experimental product was quenched rapidly in cold water.

Crystallography

The crystal structure of synthetic $Pd_3Bi_2S_2$ was solved using single-crystal work by Weihrich *et al.* (2007) and Weihrich and Anusca (2006) (ICDS database card No. 417634) and also confirmed by experimental study and the powder X-ray diffraction (XRD) data obtained from the synthetic analogue (provided by A. Vymazalová). The data are as follows: the mineral is cubic, space group $I2_13$, with

TABLE 2. Electron probe micro-analyses (wt.%) for vymazalováite (mean of 7 analyses).

Element	Mean	Range	Stand. Dev.
S	7.77	7.52–7.92	0.14
Se	0.26	0.12–0.38	0.09
Pd	40.42	39.68–41.44	0.58
Pb	1.02	0.65–1.62	0.33
Bi	49.15	48.08–49.99	0.78
Ag	0.55	0.26–1.01	0.22
Total	99.17		

Stand. Dev: standard deviation.

TABLE 3. Powder XRD data (*d* in Å) for synthetic vymazalováite compared to data taken from ICDD-PDF2 01-077-5340 card ($I \geq 1$).

$Pd_3Bi_2S_2$ (synthetic powder XRD data)				ICDD-PDF2 01-077-5340 card	
[*hkl*]	I_{obs}	d_{obs}	d_{calc}	I_{calc}	d_{calc}
1 1 0	23	5.8600	5.8754	28	5.8759
2 0 0	**32**	**4.1473**	**4.1546**	**37**	**4.1549**
2 1 1	25	3.3877	3.3922	25	3.3924
2 2 0	**78**	**2.9342**	**2.9377**	**75**	**2.9379**
0 1 3	24	2.6248	2.6276	21	2.6278
2 2 2	**100**	**2.3963**	**2.3986**	**100**	**2.3988**
1 2 3	20	2.2188	2.2207	15	2.2209
4 0 0	**53**	**2.0757**	**2.0773**	**61**	**2.0774**
4 1 1	16	1.9570	1.9585	8	1.9586
0 2 4	**27**	**1.8568**	**1.8580**	**18**	**1.8581**
3 3 2	4	1.7705	1.7715	3	1.7716
4 2 2	**34**	**1.6952**	**1.6961**	**25**	**1.6962**
1 3 4	14	1.6287	1.6296	10	1.6297
5 2 1	4	1.5163	1.5170	3	1.5171
4 4 0	**35**	**1.4682**	**1.4689**	**28**	**1.4690**
0 3 5	7	1.4244	1.4250	5	1.4251
6 0 0	12	1.3843	1.3849	8	1.3850
2 3 5	5	1.3475	1.3479	4	1.3480
6 2 0	10	1.3133	1.3138	7	1.3139
1 4 5	2	1.2818	1.2821	1	1.2822
6 2 2	**31**	**1.2523**	**1.2526**	**23**	**1.2527**
6 3 1	4	1.2247	1.2251	2	1.2252
4 4 4	11	1.1990	1.1993	7	1.1994
0 1 7	6	1.1748	1.1751	4	1.1752
6 4 0	6	1.1520	1.1523	4	1.1524
6 3 3	3	1.1305	1.1307	2	1.1308
2 4 6	12	1.1101	1.1104	8	1.1104
0 3 7	1	1.0907	1.0910	1	1.0911
1 5 6	2	1.0551	1.0553	1	1.0553
8 0 0	3	1.0384	1.0386	3	1.0387
7 4 1	4	1.0226	1.0228	3	1.0229
0 2 8	7	1.0075	1.0076	5	1.0077
3 5 6	2	0.9930	0.9931	1	0.9932
8 2 2	6	0.9791	0.9792	4	0.9793
7 4 3	5	0.9659	0.9659	3	0.9656
6 6 2	11	0.9530	0.9531	7	0.9532
7 5 2	1	0.9407	0.9408	1	0.9409
8 4 0	10	0.9289	0.9290	7	0.9291
8 3 3	1	0.9175	0.9176	1	0.9177
8 4 2	4	0.9065	0.9066	3	0.9067
1 6 7	2	0.8959	0.8960	1	0.8961
6 6 4	3	0.8857	0.8858	2	0.8858
0 3 9	3	0.8758	0.8759	2	0.8759
2 3 9	2	0.8570	0.8570	1	0.8571
8 4 4	7	0.8480	0.8480	5	0.8481
8 5 3	2	0.8394	0.8394	1	0.8394
10 0 0	3	0.8309	0.8309	2	0.8310

The eight strongest lines are given in bold.

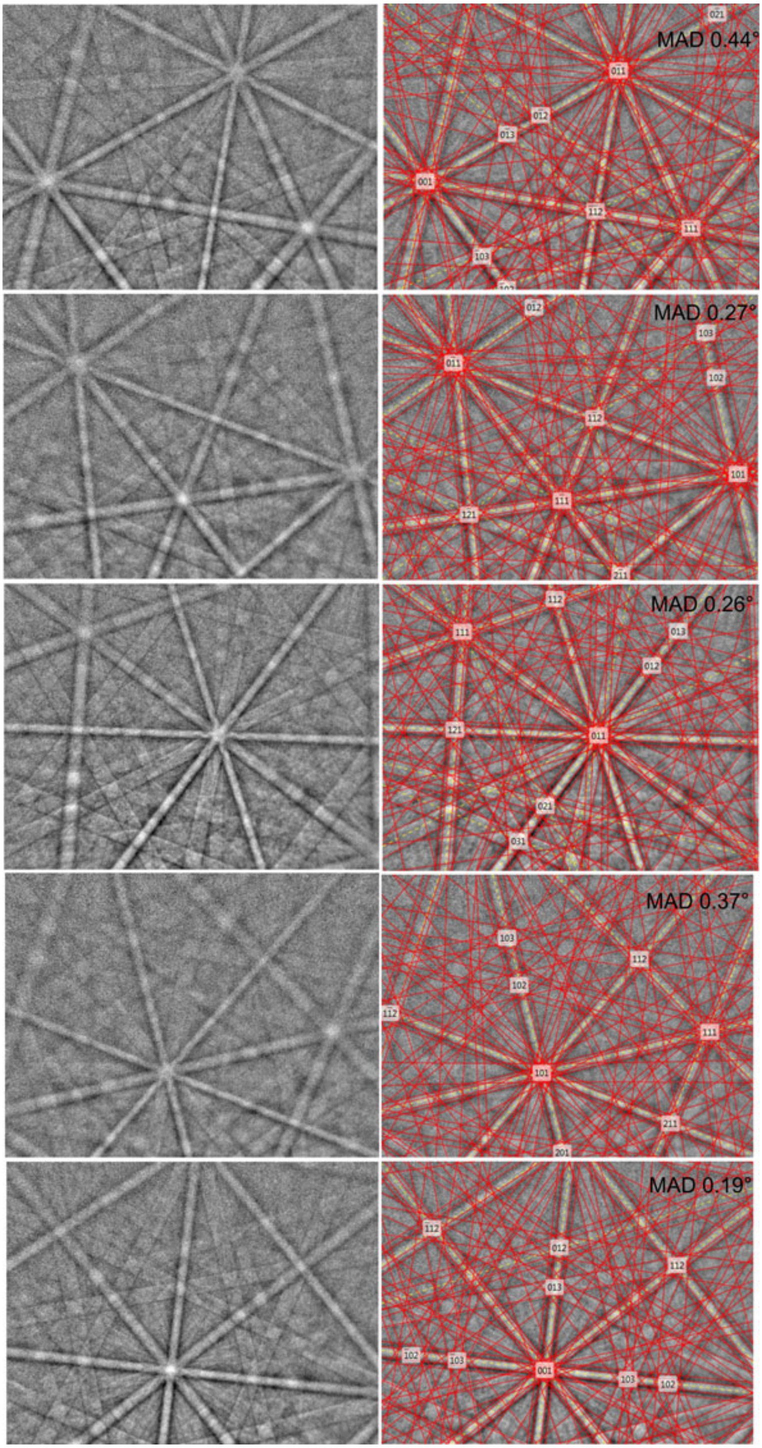

FIG. 3. EBSD images of vymazalováite obtained from grains with different orientations; in the right pane the Kikuchi bands are solved (indexed) using 92 reflector planes. Acquisition conditions: accelerating voltage = 30 kV, beam current = 0.3 nA, no binning (full EBSP resolution is 1344 x 1024). Indexing conditions: refined accuracy mode, 12 bands, 92 reflectors.

$a = 8.3097(9)$ Å, $V = 573.79(1)$ Å^3 and $Z = 4$. The strongest lines in the powder XRD pattern of synthetic vymazalováite [*d* in Å (*I*) (*hkl*)] are: 4.15 (32)(200), 2.93(78)(220), 2.40(100)(220), 2.08(53) (400), 1.695(34)(422), 1.468(35)(440) and 1.252 (31)(622). Complete X-ray data are listed in the International Centre for Diffraction Data database (ICDD-PDF2 01-077-5340 card). X-ray data for synthetic $Pd_3Bi_2S_2$ are given in Table 3.

The structural identity of the natural vymazalováite with the structural model proposed by Weihrich *et al*. (2007) for the synthetic $Pd_3Bi_2S_2$ phase was confirmed by electron back-scatter diffraction (EBSD) measurements on the natural sample.

TESCAN Lyra 3 GMH and Mira 3 scanning electron microscopes combined with Oxford Instruments X-Max80 (EDS), NordlysMax3 (EBSD) and Inca Wave500 (WDS) detectors were used for the measurements. The surface of the natural sample was prepared for investigation by polishing with colloidal silica and/or ion milling with a focused ion gun (FIB). EBSD patterns (EBSPs) were collected and processed using a proprietary computer program *AztecHKL* (Oxford Instruments). The centres of twelve Kikuchi bands were automatically detected using the Hough transform routine with a resolution of 60 (internal Hough space resolution parameter in the *AztecHKL* software). The solid angles calculated from the patterns were compared with a synthetic $Pd_3Bi_2S_2$ match [using Weihrich *et al*. (2007) crystal-structure data converted with *Twist* software (Oxford Instruments)] to index the patterns. The EBSD patterns (also known as Kikuchi patterns) obtained from the natural material (twenty-two measurements on different spots on natural vymazalováite) were found to match the patterns generated from the structural model described by Weihrich *et al*. (2007) for synthetic $Pd_3Bi_2S_2$. The values of the mean angular deviation (MAD, i.e. goodness of fit of the solution) between the calculated and measured Kikuchi bands range between 0.16° and 0.49°. These values reveal a very good match; as long as values of mean angular deviation are <1°, they are considered as indicators of an acceptable fit (see Fig. 3).

The crystal structure of vymazalováite is a structure type of corderoite ($Hg_3S_2Cl_2$). It belongs to the antiperovskite superstructure, and is structurally related to pašavaite ($Pd_3Pb_2Te_2$), shandite and parkerite and can be called a 'cubic parkerite'. It is related closely to the monoclinic parkerite, differing in the occupation of one Pd position only. The three structure types of shandites, monoclinic and cubic parkerites could be derived from a modelling scheme that uses a CsCl or perovskite superstructure (Weihrich *et al*. 2007). On the basis of its chemical composition the mineral is the Bi analogue of laflammeite ($Pd_3Pb_2S_2$).

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