

KUDRIAVITE, (Cd,Pb)Bi₂S₄, A NEW MINERAL SPECIES FROM KUDRIAVY VOLCANO, ITURUP ISLAND, KURILE ARC, RUSSIA

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ABSTRACT

Kudriavite, a new mineral species, occurs as a high-temperature (about 400°C) fumarole incrustation in the steep inner wall of the crater rim of Kudriavy volcano, on Iturup Island, in the Kurile arc, Russia. Associated minerals are cannizzarite, greenockite and pyrite. The mineral occurs as elongate slender platy opaque crystals up to $0.4 \times 0.2 \times 0.02$ mm, usually striated along the elongation. Box-shaped skeletal crystals also are common. The color is dark grey, with a slightly reddish hue and a metallic luster. The streak is black. Crystals of kudriavite have an uneven fracture and are very brittle. Reflectance values for the COM wavelengths [% (R_1 , R_2)] are: 470 nm (36.4, 29.6), 546 nm (38.8, 32.4), 589 nm (38.2, 31.8), and 650 nm (37.7, 31.4). The bireflectance is distinct; the anisotropy is rather strong, but without color effect. Its measured microhardness VHN_{10} is 129. The electron-microprobe analysis of holotype kudriavite gave Cd 8.25, Pb 13.10, Fe 0.17, Mn 0.26, Bi 55.37, In 2.80, Tl 0.02, S 17.70, Se 2.23, Cl 0.02, sum 99.92 wt.%. The empirical formula, based on seven atoms, is $(Cd_{0.51}Pb_{0.44}Fe_{0.02}Mn_{0.03})_{\Sigma 1.00}(Bi_{1.83}In_{0.17})_{\Sigma 2.00}(S_{3.81}Se_{0.19})_{\Sigma 4.00}$; the idealized formula is $(Cd,Pb)Bi_2S_4$. The ideal formula $CdBi_2S_4$ requires Cd 17.07, Bi 63.46, S 19.47, for a total of 100.00 wt.%. The strongest nine lines of the X-ray powder-diffraction pattern [d in Å (I)(hkl)] are: 3.715(m)(202), 3.632(m)(204), 3.520(s)(112), 3.274(s)(004,402), 3.169(m)(112), 2.948(s)(311), 2.809(s)(310), 2.346(m)(114,115), and 1.914(m)(511). The unit-cell parameters of kudriavite, determined on a single crystal, are: a 13.095(1), b 4.0032(3), c 14.711(1) Å, β 115.59(1)°, V 695.5(1) Å³, Z = 4, space group $C2/m$, D_{calc} = 6.578 g/cm³. According to the solution of the structure, kudriavite is the first natural homologue $N = 3$ of pavonite. The mineral (IMA No. 2003-011) is named after the discovery locality.

Keywords: kudriavite, Cd–Pb–Bi sulfosalt, pavonite homologue, fumarole, incrustation, Kudriavy, Iturup Island, Kurile arc, Russia.

SOMMAIRE

La kudriavite, nouvelle espèce minérale, a été découverte dans un encroûtement déposé à température élevée (environ 400°C) par une fumarole sur la paroi interne abrupte du cratère du volcan Kudriavy, sur l'île d'Iturup, arc des Kuriles, en Russie. Lui sont associés cannizzarite, greenockite et pyrite. Le minéral se présente en minces cristaux opaques allongés, atteignant $0.4 \times 0.2 \times 0.02$ mm, généralement avec des stries le long de l'allongement. Des cristaux squelettiques en forme de boîte sont aussi communs. Il s'agit de cristaux gris foncé, avec une teinte rougeâtre et un éclat métallique. La rayure est noire. Les cristaux de kudriavite ont une fracture inégale et sont très cassants. Les valeurs de réflectance aux longueurs d'onde COM [% (R_1 , R_2)] sont: 470 nm (36.4, 29.6), 546 nm (38.8, 32.4), 589 nm (38.2, 31.8), et 650 nm (37.7, 31.4). La biréflexance est distincte; l'anisotropie est plutôt forte, mais sans effets sur la couleur. La microdureté mesurée (VHN_{10}) est 129. Une analyse à la microsonde électronique de l'holotype a donné Cd 8.25, Pb 13.10, Fe 0.17, Mn 0.26, Bi 55.37, In 2.80, Tl 0.02, S 17.70, Se 2.23, Cl 0.02, pour un total de 99.92% (poids). La formule empirique, fondée sur un total de sept atomes, est $(Cd_{0.51}Pb_{0.44}Fe_{0.02}Mn_{0.03})_{\Sigma 1.00}(Bi_{1.83}In_{0.17})_{\Sigma 2.00}(S_{3.81}Se_{0.19})_{\Sigma 4.00}$; la formule idéalisée est $(Cd,Pb)Bi_2S_4$; le pôle $CdBi_2S_4$ requiert Cd 17.07, Bi 63.46, S 19.47, pour un total de 100.00% (poids). Les neuf raies les plus intenses du spectre de diffraction X, méthode des poudres [d en Å (I)(hkl)] sont: 3.715(m)(202), 3.632(m)(204),

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3.520(s)($\bar{1}12$), 3.274(s)(004, $\bar{4}02$), 3.169(m)(112), 2.948(s)($\bar{3}11$), 2.809(s)(310), 2.346(m)(114, $\bar{1}15$), et 1.914(m)(511). Les paramètres réticulaires de la kudriavite, déterminés sur monocristal, sont: a 13.095(1), b 4.0032(3), c 14.711(1) Å, β 115.59(1)°, V 695.5(1) Å³, $Z = 4$, groupe spatial $C2/m$, $D_{\text{calc}} = 6.578 \text{ g/cm}^3$. Selon la solution de la structure, la kudriavite serait le premier homologue naturel $N = 3$ de la pavonite. Le nom du minéral (IMA No. 2003–011) est inspiré de la localité de la découverte.

(Traduit par la Rédaction)

Keywords: kudriavite, sulfosel à Cd–Pb–Bi, homologue de la pavonite, fumarole, encroûtement, Kudriavy, île d'Iturup, arc des Kuriles, Russie.

INTRODUCTION

Kudriavite is the first cadmium–lead–bismuth sulfosalt to be found in nature. It occurs in fumaroles of the Kudriavy volcano, Iturup Island, Kuriles, Russia. Two other compounds, $\text{Cd}_3(\text{Pb}_{0.75}\text{Fe}_{0.25})\text{Bi}_{10}\text{S}_{18}\text{Se}$ and $\text{Cd}_2\text{Pb}_8\text{Bi}_{11}\text{S}_{24}\text{Se}_3$, were identified earlier on Mutnovsky volcano, in Kamchatka (Zelensky 2003). Insignificant amounts of Cd have been reported in solid solution in Pb–Bi sulfosalts from fumarolic exhalations on the island of Vulcano, in Italy: up to 0.28 wt.% in lillianite $\text{Pb}_3\text{Bi}_2(\text{S,Se})_6$ (Borodaev *et al.* 2001), up to 0.26 wt.% in mozgovaite $\text{PbBi}_4(\text{S,Se})_7$ (Vurro *et al.* 1999) and up to 0.4 wt.% in selenian heyrovskýite $\text{Pb}_6\text{Bi}_2(\text{S,Se})_9$ (Borodaev *et al.* 2003). On the other hand, several compounds have been synthesized in the system Cd–Bi–S, and their structures have been investigated (Choe *et al.* 1997).

The mineral is named for the locality, Kudriavy volcano (in Russian: Кудрявый). There are three versions of the name of this volcano in non-Russian publications: Kudriavy, Kudrjavy, and Kudryavy. We accepted the spelling “Kudriavy” following the book “Volcanoes of the World” (Simkin & Siebert 1994), and therefore the mineral name *kudriavite* seems most appropriate. Both the mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names of the IMA (No. 2003–011). Type material is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia (No. 3112/1).

GEOLOGICAL SETTING AND OCCURRENCE

Kudriavy volcano is located at the northern end of Iturup Island, in the southern portion of the Kurile volcanic arc (Fig. 1). It is stratovolcano (cone of 991 m elevation) of basaltic andesite composition that last erupted in 1883 (Gorshkov 1967). Together with several other cones, Kudriavy belongs to the eruptive complex of the Medvezhia caldera. Presently, volcanic activity is limited to fumarolic emissions at the top of the cone in an elongate crater (approximately 500×150 m). Since the last magmatic eruption, only episodic phreatic explosions have taken place (the last in October of 1999), and they can influence significantly the regime of degassing of the fumaroles. The maximum

temperature at the vent was 870°C in 2001; the highest-temperature vents have the strongest discharge.

Four high-temperature fumarolic fields have been recognized at the summit of Kudriavy volcano. They differ in temperature regime and mineral composition. One of them was named “Rhenium” fumarolic field (Fig. 2) and is famous for the first occurrence of natural rhenium disulfide, rheniite (Znamensky *et al.*, in prep.). Samples studied in the present work were collected from the southern part of this field in August 2001, at a sampling temperature of 400°C.

There are two layers of crusts of fumarolic products on the basaltic andesite: the upper layer (up to 20 cm) consists of secondary sulfates and oxides with relics of minerals of the original rock; the lower sulfide-rich layer (up to 0.5 m) contains pyrite, Pb–Bi sulfosalts, wurtzite, greenockite and rheniite. The kudriavite holotype was found in the lower zone at a depth of 0.5 m on the steep inner wall of crater rim. We consider the deposit a high-temperature fumarolic incrustation (about 400°C) formed during cooling of the gas on the surface of the altered basaltic andesite debris.

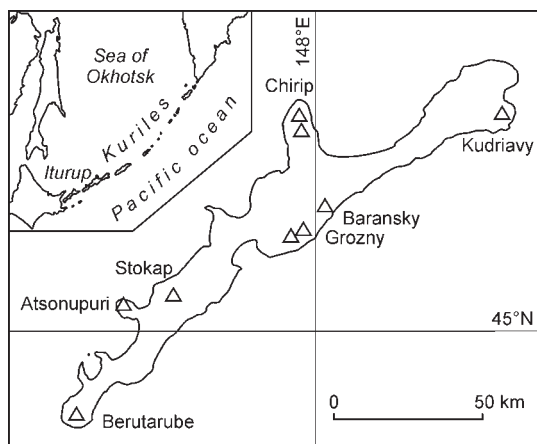


FIG. 1. Location of Kudriavy and other volcanoes on Iturup Island, Kurile volcanic arc.

APPEARANCE AND PHYSICAL PROPERTIES

The holotype of kudriavite consists of platy opaque crystals up to $0.4 \times 0.2 \times 0.02$ mm, which form chaotic aggregates of some mm in diameter in pores and fissures of the fumarolic crust. The mineral is dark-grey with a slight reddish tint and a metallic luster. The streak is black. The crystals are very brittle and have an uneven fracture. Associated minerals are brown hexagonal translucent plates of greenockite, thin sheets of cannizzarite, small crystals of pyrite, and native sulfur on the surface of the kudriavite crystals.

Individual crystals, aggregates and assemblages of kudriavite were studied with a scanning electron microscope (JEOL JSM 5610LV). The mineral forms slender platy crystals striated parallel to their elongation, alongside corroded crystals of greenockite and small crystals of pyrite (Fig. 3a). There are also spot-like grey efflorescences of an undetermined mineral on the faces of kudriavite crystals. The platy crystals commonly form parallel (Fig. 3b) as well as chaotic aggregates (Fig. 3c). In some cases, box-shaped skeletal crystals of kudriavite occur with small equant crystals of native sulfur on their tops and edges (Fig. 3d).

Under reflected light in polished sections, kudriavite is white with a slight yellow hue. Internal reflections are absent. The birefractance is weak to distinct. Under crossed nicols, the anisotropy is rather strong without color effect.

The reflectance of kudriavite was measured in air from 420 to 700 nm on randomly oriented grains using an automatic polarization microspectrophotometer MSFU-312 (LOMO, St. Petersburg), with Si as a standard. The results for the two extreme R_1 and R_2 values are shown in Table 1, with the spectral curves in Figure 4.

The microhardness VHN_{10} of kudriavite was measured on two pre-analyzed crystals with an indentation-hardness tester PMT-3M. We obtained 129 (123–135) kg/mm². The density could not be measured because of the small grain-size. The calculated density is 6.578 g/cm³.

CHEMICAL COMPOSITION

The holotype sample was analyzed with a CAMEBAX SX-50 electron microprobe (Moscow State University) under the following conditions: voltage 20 kV, beam current 30 nA; standards (emission lines): CdIn₂S₄ (CdL α , InL α), PbS (PbM α), FeS (FeK α), Mn (MnK α), Bi₂S₃ (BiM α , SK α), TlAsS₂ (TlM β), Bi₂Se₃ (SeL α), Pb₅(VO₄)₃Cl (ClK α). The beam was focused to 2 μ m.

Thirty electron-microprobe analyses of kudriavite were made. Results of a selection of nine analyses obtained on the part of the crystal used for the structure determination, given in Table 2, show the following ranges of major-element concentrations (in wt.%): Cd 7.33–9.26 (average 8.25), Pb 12.37–14.20 (average

13.10), Bi 54.55–56.46 (average 55.37) and S 17.26–18.04 (average 17.70). Indium and selenium are common but subordinate constituents, ranging from 2.49 to 3.15% (average 2.80) and from 1.14 to 2.54% (average 2.23), respectively. Common minor elements are Mn (0.20–0.33; average 0.26%) and Fe (0.09–0.32; average 0.17%); some analyses reveal a trace of Tl (up to 0.09 wt.%) and Cl (up to 0.07 wt.%).

All 30 analyses were used for correlation plots (Fig. 5), which reveal a negative correlation between Cd and (Pb + Mn + Fe), as well as between Bi and In, in addition to the expected correlation between S and Se. Taking into account these relationships, the analytical results were calculated on the basis of seven atoms, summing Cd with Pb, Mn and Fe, In with Bi and Se with S. The empirical chemical formula, calculated for the average result of nine selected electron-microprobe analyses, is $(Cd_{0.51}Pb_{0.44}Fe_{0.02}Mn_{0.03})_{\Sigma 1.00}(Bi_{1.83}In_{0.17})_{\Sigma 2.00}(S_{3.81}Se_{0.19})_{\Sigma 4.00}$, which is close to the idealized formula $(Cd,Pb)Bi_2S_4$. The ideal formula, $CdBi_2S_4$, requires Cd 17.07, Bi 63.46, S 19.47, total 100.00 wt.%.

X-RAY-DIFFRACTION STUDY

A fragment of the pre-analyzed crystal of kudriavite was used for an X-ray study. Single-crystal data show that kudriavite crystallizes in the space group $C2/m$ (No. 12), with unit-cell parameters a 13.095(1), b 4.0032(3), c 14.711(1) Å, β 115.59(1)°, V 695.5(1) Å³. These parameters are close to the cell constants of the synthetic phase $CdBi_2S_4$: a 13.095(2), b 3.9792(7), c 14.611(3) Å, β 116.30(1)° (Choe *et al.* 1997). The theoretical powder-diffraction data, calculated using the program LAZY PULVERIX (Yvon *et al.* 1977), agree with those obtained with a 114.6 mm Gandolfi camera and filtered CuK α radiation (Table 3).

The crystal structure was solved by direct methods (SHELXS97, Sheldrick 1997a) from X-ray diffraction on a tubular crystal ($\{001\}$) measured on a Bruker-AXS SMART 1000 CCD system (Balić-Zunić & Makovicky, in prep.). The least-squares refinement of the structure

TABLE 1. REFLECTANCE DATA FOR KUDRIAVITE

λ	R_1	R_2	λ	R_1	R_2
400 nm	30.3 %	21.0 %	560 nm	38.7 %	32.3 %
420	32.1	23.5	580	38.3	32.0
440	33.8	26.1	589 (COM)	38.2	31.8
460	35.6	28.5	600	38.2	31.7
470 (COM)	36.4	29.6	620	38.1	31.6
480	36.9	30.4	640	37.8	31.5
500	37.9	31.5	650 (COM)	37.7	31.4
520	38.4	32.1	660	37.6	31.4
540	38.7	32.3	680	37.5	31.3
546 (COM)	38.8	32.4	700	37.3	31.3

Standard: Si.



FIG. 2. Summit of Kudriavitskiy volcano. On the right side is the "Rhenium" fumarolic field (approximately 50 × 20 m in size) emitting clouds of volcanic gas. The phreatic crater of 1999 eruption occurs at the left. The site of the kudriavite sample is shown by an arrow. The photo was taken in 2001.

TABLE 2. CHEMICAL COMPOSITION OF KUDRIAVITE

N ^o	Cd	Pb	Fe	Mn	Bi	In	Tl	S	Se	Cl	Total
1	7.33	14.20	0.24	0.33	55.35	3.15	0.05	18.03	1.82	0.00	100.50
2	7.73	14.14	0.32	0.26	55.21	3.05	0.00	18.04	1.14	0.00	99.89
3	7.96	13.32	0.13	0.30	55.70	2.92	0.03	17.76	2.41	0.05	100.58
4	8.01	13.16	0.14	0.21	54.55	2.96	0.00	17.81	2.50	0.03	99.37
5	8.49	13.05	0.19	0.32	55.75	2.70	0.00	17.68	2.49	0.01	100.68
6	8.43	12.32	0.16	0.20	54.83	2.64	0.00	17.26	2.54	0.07	98.45
7	8.52	12.44	0.09	0.30	54.89	2.52	0.00	17.51	2.52	0.03	98.82
8	8.56	12.94	0.12	0.25	56.46	2.73	0.00	17.63	2.29	0.00	100.98
9	9.26	12.37	0.14	0.21	55.63	2.49	0.09	17.59	2.33	0.01	100.12
Ave.	8.25	13.10	0.17	0.26	55.37	2.80	0.02	17.70	2.23	0.02	99.92
1	(Cd _{0.45} Pb _{0.47} Fe _{0.03} Mn _{0.04}) ₂ 0.99 (Bi _{1.81} In _{0.16}) ₂ 2.00 (S _{3.85} Se _{0.16}) ₂ 4.01										
2	(Cd _{0.43} Pb _{0.47} Fe _{0.04} Mn _{0.03}) ₂ 1.01 (Bi _{1.82} In _{0.18}) ₂ 2.00 (S _{3.88} Se _{0.10}) ₂ 3.98										
3	(Cd _{0.40} Pb _{0.44} Fe _{0.02} Mn _{0.04}) ₂ 0.99 (Bi _{1.83} In _{0.17}) ₂ 2.00 (S _{3.80} Se _{0.21}) ₂ 4.01										
4	(Cd _{0.36} Pb _{0.44} Fe _{0.02} Mn _{0.03}) ₂ 0.98 (Bi _{1.80} In _{0.18}) ₂ 1.98 (S _{3.83} Se _{0.22}) ₂ 4.05										
5	(Cd _{0.35} Pb _{0.43} Fe _{0.02} Mn _{0.04}) ₂ 1.01 (Bi _{1.83} In _{0.16}) ₂ 1.99 (S _{3.78} Se _{0.22}) ₂ 4.00										
6	(Cd _{0.35} Pb _{0.42} Fe _{0.02} Mn _{0.04}) ₂ 1.00 (Bi _{1.84} In _{0.16}) ₂ 2.00 (S _{3.77} Se _{0.22}) ₂ 4.00										
7	(Cd _{0.31} Pb _{0.41} Fe _{0.01} Mn _{0.04}) ₂ 1.00 (Bi _{1.83} In _{0.15}) ₂ 1.98 (S _{3.80} Se _{0.22}) ₂ 4.02										
8	(Cd _{0.32} Pb _{0.43} Fe _{0.01} Mn _{0.03}) ₂ 0.99 (Bi _{1.86} In _{0.16}) ₂ 2.02 (S _{3.78} Se _{0.20}) ₂ 3.98										
9	(Cd _{0.37} Pb _{0.41} Fe _{0.02} Mn _{0.03}) ₂ 1.03 (Bi _{1.84} In _{0.15}) ₂ 1.99 (S _{3.78} Se _{0.20}) ₂ 3.98										
Ave.	(Cd _{0.35} Pb _{0.44} Fe _{0.02} Mn _{0.03}) ₂ 1.00 (Bi _{1.83} In _{0.17}) ₂ 2.00 (S _{3.81} Se _{0.19}) ₂ 4.00										

The chemical composition is reported in wt.%; the formula was calculated on the basis of seven atoms.

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR KUDRIAVITE

<i>I</i> _{est}	Gandolfi	<i>d</i> _{meas}	Theoretical		
			<i>I</i> _{theor}	<i>d</i> _{theor}	<i>h k l</i>
m		4.663	24	4.694	2 0 1
vw		3.818	11	3.791	1 1 0
m		3.715	97	3.690	2 0 2
m		3.632	95	3.640	2 0 4
s		3.520	83	3.508	1 1 2
s		3.274	16	3.317	0 0 4
"		"	32	3.273	4 0 2
w		3.211	9	3.167	4 0 3
m		3.169	38	3.111	1 1 2
s		2.948	83	2.935	3 1 1
s		2.809	100	2.807	3 1 0
vw		2.619	7	2.613	4 0 5
m		2.346	39	2.341	1 1 4
"		"	21	2.331	1 1 5
w		2.224	18	2.211	0 0 6
w		2.090	16	2.082	6 0 1
w		2.067	7	2.076	4 0 3
vw		2.041	31	2.037	1 1 6
vw		2.019	31	2.017	5 1 5
w		2.001	39	2.002	0 2 0
vw		1.977	14	1.968	6 0 0
vw		1.949	8	1.946	6 0 6
m		1.914	40	1.907	5 1 1
m		1.763	21	1.754	2 2 4
w		1.627	7	1.621	8 0 5
vw		1.315	2	1.311	6 0 11
vw		1.238	4	1.234	9 1 9

Gandolfi data were obtained with a 114.6 mm camera and filtered CuK α radiation. The theoretical powder-diffraction data were calculated with the program LAZY PULVERIX (Yvon *et al.* 1977). Intensities: s: strong, m: medium, w: weak, vw: very weak.

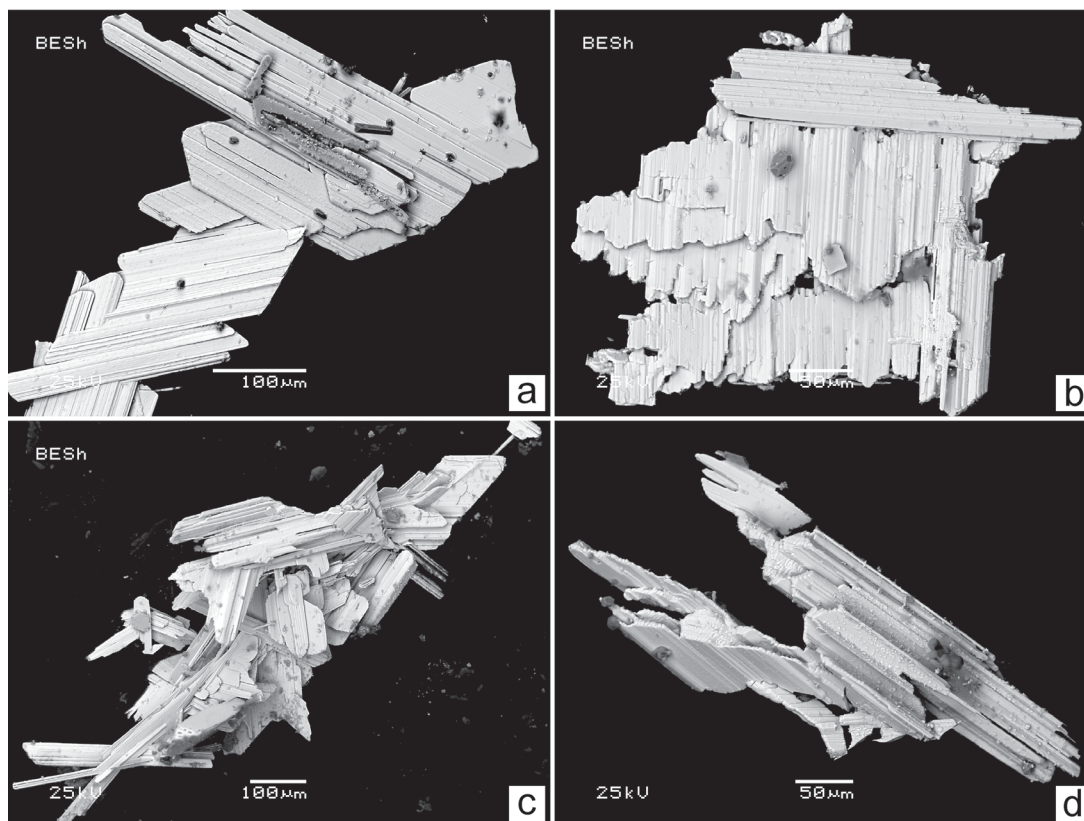


FIG. 3. Typical crystals, aggregates and assemblages of kudriavite. Scanning electron microscope JEOL JSM 5610LV. a. Platy crystals of kudriavite striated parallel to the elongation (light grey) with corroded crystals of greenockite (grey) and small crystals of pyrite (dark grey). b. Intergrowth of platy crystals of kudriavite parallel to each other with single small isometric crystal of pyrite. c. Chaotic aggregate of kudriavite crystals with rare hexagonal crystals of greenockite (gray); the small grey spots are not identified. d. Box-shaped skeletal crystals of kudriavite with small isometric crystals of native sulfur on their tops and along their edges.

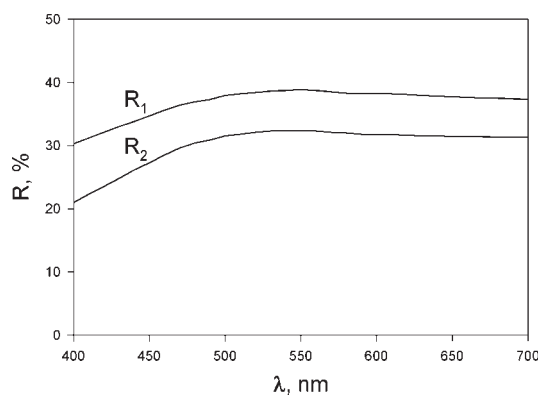


FIG. 4. Reflectance spectra of kudriavite in air.

(SHELXL97, Sheldrick 1997b) resulted in a final residual value R for observed reflections ($F > 4\sigma_F$) of 4.88%.

The crystal structure of kudriavite reveals that this mineral is a pavonite homologue, $N = 3$. It follows closely structural principles of the pavonite series. The “thin, non-accreting layers” (using the nomenclature used for the structures of the pavonite homologous series) are composed of paired columns of (predominantly) BiS_5 pyramids, which share edges with columns of slightly skewed octahedra. Cation–S distances and minor maxima connected with cation positions indicate mixing with Pb at the Bi2 sites. The Cd octahedra are almost identical to those observed in pure synthetic Cd–Bi sulfosalts (Choe *et al.* 1997). The refinement suggests the presence of 10–20 at.% of heavy cations, Bi or Pb, in the cadmium position.

The accreting layers (three octahedra wide along the layer diagonal, giving $N = 3$) have boundary Bi1 sites with bond lengths typical of those of Bi octahedra. The central octahedron of this layer was refined as 0.65 Bi and the rest as eccentric In, but some substitution of Cd in this site cannot be excluded.

As seen from the structure and from the example of CdBi_2S_4 (Choe *et al.* 1997), there is no structural reason for an exact Pb/Cd ratio. Cd contents can reach 100% relative, whereas the Pb contents (and, as a consequence, the minimum Cd contents) would be controlled by the steric limitations imposed on the skewed octahedral sites of the non-accreting layer.

DISCUSSION

Kudriavite, as well as cadmoindite, CdIn_2S_4 (Chaplygin *et al.* 2004), also from Kudriavy volcano, both contain significant quantities of both cadmium and indium. These elements belong to the group of rare metals and commonly occur in solid solution in minerals and ores, and are dispersed in rocks (Ivanov *et al.* 1989). The most common occurrence of these elements is in solid solutions in sulfides, especially in Zn sulfides. Minerals in which these elements are dominant are very rare, and they are always found in small amounts.

Conditions at the discovery site of kudriavite and cadmoindite prove their growth in a high-temperature flowing gas. Crystals of rare compounds like these new minerals seem due to the advantages of gas transport, which allowed mineral phases to crystallize from a medium rather depleted in ore metals (3 ppb of Cd and 1 ppb of In in a sample of gas condensate from the Rhenium fumarolic field). At the same time in a fumarolic environment, Cd minerals precipitate mostly at lower temperatures (350–550°C) than those of Zn (up to 750°C).

Both indium and cadmium can occur in sulfides either in octahedral or in tetrahedral coordination; in rare cases, both coordination states occur in the same compound. The chief minerals of tetrahedrally coordinated cadmium are greenockite (hexagonal CdS) and hawleyite (cubic CdS), and among rare minerals, we can quote černýite, $\text{Cu}_2\text{CdSnS}_4$ (Szymański 1978). Most minerals contain tetrahedrally coordinated cadmium, the exceptions being shadlunite (Pb,Cd) $(\text{Fe,Cu})_8\text{S}_8$ (Evstigneeva *et al.* 1973) and quadratite $\text{Ag}(\text{Cd,Pb})[\text{AsS}_3]$ (Berlepsch *et al.* 1999), which contain octahedrally coordinated Cd in solid solution with Pb. Kudriavite belongs to this group of minerals. Indium in minerals occurs in both coordinations: in sphalerite it is tetrahedral, as it is also in laforêtite AgInS_2 , a mineral of the chalcopyrite group (Meisser *et al.* 1999). Octahedrally coordinated In was found in synthetic Pb–In, Bi–In and Pb–Bi–In sulfides such as $\text{Pb}_4\text{In}_9\text{S}_{17}$ (Ginderow 1978). In rare instances, *e.g.*, in indite FeIn_2S_4 , both coordinations of In can occur (Hill *et al.* 1978).

Choe *et al.* (1997) synthesized Cd–Bi pavonite homologues $N = 3$ (CdBi_2S_4) and $N = 2$ (CdBi_4S_7) as well as their regular 1:1 intergrowth, $N = 2, 3$. Only the homologue $N = 3$ has so far been found at the Kudriavy volcano. In the pure Pb–Bi system, mozgovaite is a regular intergrowth of the pavonite and lillianite slabs (stoichiometric PbBi_4S_7 , a pure $N = 2$ pavonite homologue), whereas PbBi_2S_4 (galenobismutite) is a separate structure-type with parts of the structure showing affinities to the lillianite homologue, $N = 2$. Other parts of

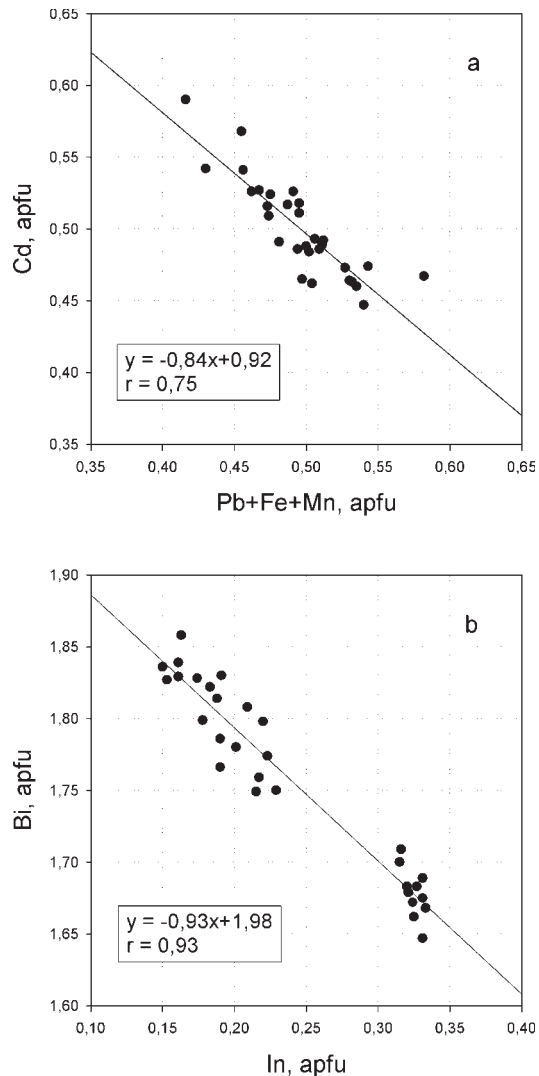


FIG. 5. Correlation relationships between elements in kudriavite. a. Negative correlation between Cd and (Pb + Fe + Mn). b. Negative correlation between Bi and In. Units: atoms per formula unit (apfu).

this structure deviate completely from the latter principle. These differences illustrate the limits imposed on the substitution of Cd for Pb, as observed in kudriavite and quadratite.

Besides grumiplucite HgBi_2S_4 (Orlandi *et al.* 1998), in which central octahedra in both layers are strongly deformed (flattened) because of the pronounced 2 + 4 coordination of mercury, kudriavite is the only natural $N = 3$ pavonite homologue. Octahedra and layers are very regular in this case. The regular copper–bismuth homologue of pavonite, $N = 3$, has not yet been found, despite the relative abundance of its $N = 4$ homologues (Žák *et al.* 1994, Topa *et al.* 2002).

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