The Canadian Mineralogist
Vol. 39, pp. 1115-1119 (2001)

BRADACZEKITE, $NaCu_4(AsO_4)_3$, A NEW MINERAL SPECIES FROM THE TOLBACHIK VOLCANO, KAMCHATKA PENINSULA, RUSSIA

STANISLAV K. FILATOV

Department of Crystallography, St. Petersburg University, University Emb. 7/9, St. Petersburg 199034, Russia

LIDIYA P. VERGASOVA

Institute of Volcanology of the Russian Academy of Sciences, Piyp Ave. 9, Petropavlovsk-Kamchatskii 683006, Russia

MARINA G. GORSKAYA AND SERGEY V. KRIVOVICHEV§

Department of Crystallography, St. Petersburg University, University Emb. 7/9, St. Petersburg 199034, Russia

PETER C. BURNS

Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, Indiana 46556-0767, U.S.A.

VLADIMIR V. ANANIEV

Institute of Volcanology of the Russian Academy of Sciences, Piyp Ave. 9, Petropavlovsk-Kamchatskii 683006, Russia

Abstract

Bradaczekite, $NaCu_4(AsO_4)_3$, was discovered in a fumarole in the North Breach of the Great fissure Tolbachik eruption (GFTE) in 1975–1976, Kamchatka Peninsula, Russia. Bradaczekite forms aggregates of dark blue plates elongate along [102]. The well-developed forms are {010}, {311}, {111} and {112}. The forms {301}, {001}, {321}, {101}, {100}, {021}, {110}, {131}, {111} and {341} are common. Associated minerals are hematite, tenorite, lammerite, urusovite, orthoclase and johillerite. The mineral has an adamantine luster and a light blue to white streak. No cleavage has been observed. The mineral is transparent, biaxial, optically negative, α 1.76(1), β 1.92(1), γ 1.96(1), $2V_{calc}$ 50.0°. The optical orientation is $Z = b$, $X \wedge c = 23°$ in the obtuse β angle. Bradaczekite shows strong pleochroism: *X* violet-red, *Y* green, *Z* greenish blue. The mineral is monoclinic, space group *C2/c*, *a* 12.051(1), *b* 12.434(1), *c* 7.2662(7) Å, β 117.942(1)°, *V* 961.8(2) Å^3, *Z* = 4, D_{calc} = 4.77(1) g/cm^3 (for the empirical formula). The strongest eight lines of the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 6.22(13)(020), 3.60(21)(202, 131), 3.43(100)(112, 310), 3.21(35)(002), 2.791(24)(402), 2.696(18)(330), 2.683(30)(240), and 2.665(17)(400). Electron-microprobe analyses yielded: Na_2O 5.17 (4.37–5.78), K_2O 0.35 (0.14–0.80), CuO 43.13 (41.31–45.22), ZnO 0.79 (0.19–1.18), Fe_2O_3 0.38 (0.03–1.05), As_2O_5 49.62 (48.61–50.66), V_2O_5 0.13 (0–0.90), total 99.55 (97.69–101.56) wt.%. The empirical formula, normalized to O = 12 *apfu* (atoms per formula unit), is $(Na_{1.16}K_{0.05})_{\Sigma 1.21}(Cu_{3.74}Zn_{0.07}Fe^{3+}_{0.03})_{\Sigma 3.84}(As_{3.00}V_{0.01})_{\Sigma 3.01}O_{12}$, close to the ideal $NaCu_4(AsO_4)_3$ confirmed by crystal-structure analysis. The mineral is named in honor of Hans Bradaczek, crystallographer at the Free University of Berlin.

Keywords: bradaczekite, new mineral species, arsenate, Tolbachik volcano, Kamchatka Peninsula, Russia.

Sommaire

Nous avons découvert la bradaczekite, $NaCu_4(AsO_4)_3$, dans une fumerole de la brèche du nord du volcan fissural de Tolbachik, en éruption en 1975–1976, dans la péninsule de Kamchatka, en Russie. La bradaczekite se présente en plaquettes bleu foncé allongées selon [102]. Les formes {010}, {311}, {111} et {112} sont bien développées. Les formes {301}, {001}, {321}, {101}, {100}, {021}, {110}, {131}, {111} et {341} sont courantes. Lui sont associées hématite, ténorite, lammerite, urusovite, orthoclase et johillerite. La nouvelle espèce possède un éclat adamantin et une rayure bleu pâle ou blanche. Aucun clivage n'est apparent. C'est un minéral transparent, biaxe négatif, α 1.76(1), β 1.92(1), γ 1.96(1), $2V_{calc.}$ 50.0°. L'orientation optique est $Z = b$, $X \wedge c = 23°$ dans l'angle β obtus. La bradaczekite fait preuve d'un fort pléochroïsme: *X* violette à rouge, *Y* vert, *Z* bleu verdâtre. Elle est

§ *E-mail address*: sergey@cryst.geol.pu.ru

monoclinique, groupe spatial *C*2/*c*, *a* 12.051(1), *b* 12.434(1), *c* 7.2662(7) Å, β 117.942(1)°, *V* 961.8(2) Å^3, *Z* = 4, $D_{calc.}$ = 4.77(1) g/cm^3 (pour la formule empirique). Les huit raies les plus intenses du spectre de diffraction X, méthode des poudres [*d* en Å(*I*)(*hkl*)] sont: 6.22(13)(020), 3.60(21)(202, 131), 3.43(100)(112, 310), 3.21(35)(002), 2.791(24)(402), 2.696(18)(330), 2.683(30)(240), et 2.665(17)(400). Les analyses à la microsonde électronique ont donné: Na_2O 5.17 (4.37–5.78), K_2O 0.35 (0.14–0.80), CuO 43.13 (41.31–45.22), ZnO 0.79 (0.19–1.18), Fe_2O_3 0.38 (0.03–1.05), As_2O_5 49.62 (48.61–50.66), V_2O_5 0.13 (0–0.90), pour un total de 99.55 (97.69–101.56)% (poids). La formule empirique, normalisée sur douze atomes d'oxygène par unité formulaire, est $(Na_{1.16}K_{0.05})_{\Sigma 1.21}(Cu_{3.74}Zn_{0.07}Fe^{3+}_{0.03})_{\Sigma 3.84}(As_{3.00}V_{0.01})_{\Sigma 3.01}O_{12}$, ce qui se rapproche de la formule idéale $NaCu_4(AsO_4)_3$, confirmée par une ébauche de la structure cristalline. Le nom honore Hans Bradaczek, cristallographe à l'Université Libre de Berlin.

(Traduit par la Rédaction)

Mots-clés: bradaczekite, nouvelle espèce minérale, arsenate, volcan Tolbachik, péninsule de Kamchatka, Russie.

Introduction

Bradaczekite is a sodium copper arsenate, $NaCu_4(AsO_4)_3$, recently discovered within a fumarole in the North Breach of the Great fissure Tolbachik eruption (GFTE) in the Kamchatka Peninsula, Russia. The mineral is named in honor of Hans Bradaczek (b. 1940), crystallographer at the Free University of Berlin. The type specimen is deposited in the Mining Museum, Mining Institute, St. Petersburg, Russia. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (case 2000–002). Bradaczekite has a synthetic analogue (Pertlik 1987). Our purpose is to document the physical and chemical attributes of this new species.

Locality and Occurrence

The GFTE is the largest basaltic eruption in more than 200 years (Fedotov 1984). It was active in 1975–1976 and consisted of two Breaches (North and South) and seven cones. Beginning in the late 1970s, fumarolic activity of the GFTE resulted in a unique assemblage of minerals, with two dozen new species discovered to date. Bradaczekite was found in 1980, 1983 and 1990 among the products of fumarolic activity on the second cinder cone of the North Breach. The mineral is found closely associated with hematite, tenorite, lammerite, urusovite, orthoclase and johillerite. Exhalative lammerite, $Cu_3(AsO_4)_2$, was detected in GFTE fumaroles by Filatov *et al.* (1984) and Popova & Popov

FIG. 1. SEM image of the aggregates of bradaczekite crystals. Magnification: ~ 600×.

TABLE 1. CHEMICAL COMPOSITION OF BRADACZEKITE

	Average from 37 analyses*	Range
Na_2O wt.%	5.17	4.37 – 5.78
K_2O	0.35	0.14 – 0.80
CuO	43.13	41.31 – 45.22
ZnO	0.79	0.19 – 1.18
Fe_2O_3	0.38	0.03 – 1.05
As_2O_5	49.62	48.61 – 50.66
V_2O_5	0.13	0.00 – 0.90
total	99.55	97.69 – 101.56

Structural formula: $(Na_{1.16}K_{0.05})_{\Sigma 1.21}(Cu_{3.74}Zn_{0.07}Fe^{3+}_{0.03})_{\Sigma 3.84}(As_{3.00}V_{0.01})_{\Sigma 3.01}O_{12}$ ($Z = 4$).
* Electron-microprobe data.

(1997). Glavatskikh & Bykova (1998) described johillerite, $Na(Mg,Zn)_3Cu(AsO_4)_3$, from the products of fumarolic activity of the second cinder cone of the North Breach. Bradaczekite forms aggregates of elongate plates (Fig. 1), and intergrowths with urusovite and johillerite are common. The size of individual grains is about 0.2 mm in length and about 0.1–0.2 mm across.

Chemical Composition

Chemical analytical data for bradaczekite were acquired with a Camebax electron microprobe utilizing an operating voltage of 15 kV and a beam current of 20 nA for all elements. The following standards were used: sanidine (Na, K), CuO (Cu), ZnO (Zn), shcherbinaite (V), lammerite (As) and Fe_2O_3 (Fe). No elements other than those mentioned above were detected. The results of the analyses are summarized in Table 1. The empirical formula of bradaczekite, $(Na_{1.16}K_{0.05})_{\Sigma 1.21}(Cu_{3.74}Zn_{0.07}Fe^{3+}_{0.03})_{\Sigma 3.84}(As_{3.00}V_{0.01})_{\Sigma 3.01}O_{12}$, calculated on the basis of O = 12 atoms per formula units (*apfu*), is close to the ideal $NaCu_4(AsO_4)_3$. The chemical formula of bradaczekite is confirmed by a crystal-structure analysis.

Crystal Morphology and Physical Properties

Crystals of bradaczekite are elongate along $[\bar{1}02]$. The morphology of bradaczekite crystals is rather complex (Fig. 2). The well-developed forms are {010}, {311}, {111} and {112}. The forms {301}, {001}, {321}, {101}, {100}, {021}, {110}, {131}, {111} and {341} are common. The $a : b : c$ proportions calculated from morphological data (0.960 : 1 : 0.593) are in good agreement with the proportions based on unit-cell parameters (0.969 : 1 : 0.585). The mineral is dark blue in color with an adamantine luster and a light blue to white streak. No cleavage was observed. The density calculated on the basis of the empirical formula is 4.77(1) g/cm^3. Bradaczekite is stable at room temperature and pressure, and is practically insoluble in water and alcohol. The mineral does not fluoresce in either short- or long-wave ultraviolet radiation.

Optical Properties

The mineral is transparent in transmitted light. Bradaczekite is biaxial and optically negative. The indices of refraction were measured in immersion liquids: α 1.76(1), β 1.92(1), γ 1.96(1), $2V_{calc}$ 50.0°. Optical orientation is Z = *b*, X $\wedge$ *c* = 23° in obtuse β angle. Bradaczekite shows strong pleochroism: *X* violet-red, *Y* green, *Z* greenish blue.

X-Ray Crystallography

Unit-cell parameters of bradaczekite were initially determined using a Weissenberg camera and were further refined by crystal-structure analysis. The mineral is monoclinic, space group *C2/c*, *a* 12.051(1), *b* 12.434(1), *c* 7.2662(7) Å, β 117.942(1)°, *V* 961.8(2) Å^3, and *Z* = 4. X-ray powder-diffraction data were obtained using Cu*K*α radiation (DRON–2 diffractometer, Ge internal standard). The powder pattern, together with intensities calculated from the crystal structure, are given in Table 2. The crystal-structure refinement of bradaczekite and its detailed description will be given elsewhere.

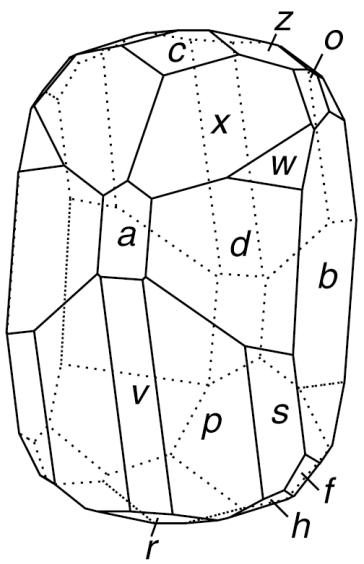

FIG. 2. Habit and crystal forms of bradaczekite. Legend: *a* {100}, *b* {010}, *c* {001}, *d* {110}, *f* {131}, *h* {111}, *o* {021}, *p* {311}, *r* {101}, *s* {321}, *v* {301}, *w* {341}, *x* {111}, *z* {112}.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR BRADACZEKITE

I_{meas}	d_{meas}	I_{calc}	d_{calc}	*hkl*	I_{meas}	d_{meas}	I_{calc}	d_{calc}	*hkl*
4	8.08	9	8.09	110	5	2.312	4	2.313	$\bar{3}12$
13+	6.22*	28	6.22	020			9	2.311	202
6	5.33	3	5.32	200	3	2.284*	4	2.285	132
4	4.14	0.1	4.15	$\bar{2}21$	2	2.096*	5	2.099	510
7	3.79	1	3.81	$\bar{3}11$	4	2.073	3	2.073	$\bar{3}33$
21+	3.60	12	3.59	$\bar{2}02$			4	2.072	060
		4	3.59	$\bar{1}31$	4	2.020	2	2.022	440
100+	3.43	100	3.43	$\bar{1}12$	5	1.972	13	1.977	$\bar{3}52$
		32	3.41	310	4	1.938	9	1.942	312
35+	3.21*	42	3.21	002			3	1.931	260
8	3.16*	5	3.15	$\bar{3}12$	2	1.893*	8	1.894	530
24+	2.791*	48	2.789	$\bar{4}02$	1	1.853	7	1.855	242
18+	2.696	4	2.696	330	5	1.838	9	1.841	152
30+	2.683*	95	2.684	240			1	1.830	$\bar{4}43$
17+	2.665*	40	2.662	400	10	1.786*	24	1.785	$\bar{2}04$
4	2.563*	11	2.561	$\bar{3}32$	6	1.774	7	1.776	332
3	2.446*	5	2.447	420			1	1.774	600
7	2.344	1	2.339	$\bar{3}11$	2	1.707	0.4	1.706	$\bar{4}61$
					8	1.681*	29	1.682	$\bar{6}42$

* Used for calculation of unit-cell parameters. The strongest eight lines are noted by a +.

Relationships to Other Minerals and Inorganic Compounds

It is apparent that bradaczekite belongs to the alluaudite group of phosphate and arsenate minerals. Minerals of this group are monoclinic, space group *C*2/*c* (Moore 1971, Moore & Ito 1979, Hatert *et al.* 2000). The alluaudite structure-type is based upon a framework of octahedra and tetrahedra with several interstitial cation sites. Among arsenate minerals that belong to the alluaudite group, johillerite (Keller & Hess 1988) is the closest to bradaczekite, as it contains the same set of interstitial cation positions.

As was mentioned above, bradaczekite is a natural analogue of $NaCu_4(AsO_4)_3$, a synthetic compound that was synthesized by Pertlik (1987) using hydrothermal methods at 490(5) K. There is only one another known sodium copper arsenate, $Na_4Cu(AsO_4)_2$, reported by Effenberger (1988). The copper sodium hydrogen arsenate, $Na_5Cu_3H(AsO_4)_4$, was described by Effenberger (1987). Neither of these two compounds belong to the alluaudite structure-type. However, $KCu_4(AsO_4)_3$ (Effenberger 1988) is isostructural with respect to bradaczekite.

After alarsite, $AlAsO_4$ (Semenova *et al.* 1994), coparsite, $Cu_4O_2[(As,V)O_4]Cl$ (Vergasova *et al.* 1999), and urusovite, $Cu[AlAsO_5]$ (Vergasova *et al.* 2000), bradaczekite is the fourth new As-bearing mineral species discovered in the Tolbachik fumaroles. It should be noted that several Tolbachik arsenates demonstrate a broad range of the As^{5+}-for-V^{5+} substitution (*e.g.*, coparsite), and there are many copper vanadate minerals of fumarolic origin (Birnie & Hughes 1979, Hughes & Birnie 1980, Hughes & Hadidiacos 1985, Robinson *et al.* 1987, Hughes *et al.* 1987a, b, 1988, Vergasova *et al.* 1990, 1998, 1999). However, none of these minerals belongs to the alluaudite structure-type.

Acknowledgements

The manuscript was materially improved following the comments of A. Eggers, J.M. Hughes, J.A. Mandarino and editorial comments of R.F. Martin. This work was supported by grant 99–05–65197 for S.K.F. and S.V.K. by the Russian Foundation of Basic Research.

References

Birnie, R.W. & Hughes, J.M. (1979): Stoiberite, $Cu_5V_2O_{10}$, a new copper vanadate from Izalco volcano, El Salvador, central America. *Am. Mineral.* **64**, 941-944.

Effenberger, H. (1987): The structure of pentasodium tricopper(II) hydrogentetraarsenate(V). *Acta Crystallogr.* **C43**, 399-402.

_____ (1988): On the crystal chemistry of three copper(II)-arsenates: $Cu_3(AsO_4)_2$-III, $Na_4Cu(AsO_4)_2$, and $KCu_4(AsO_4)_3$. *Monatsch. Chem.* **119**, 1103-1112.

Fedotov, S.A., ed. (1984): *Great Fissure Tolbachik Eruption.* Nauka, Moscow, Russia (in Russ.).

Filatov, S.K., Gaidamako, I.M., Glavatskikh, S.F., Starova, G.L. & Sorokin, N.D. (1984): Lammerite, $Cu_3[(As,P)O_4]_2$, from Kamchatka volcanic exhalations. *Dokl. Acad. Sci. USSR* **279**, 197-200.

Glavatskikh, S.F. & Bykova, E.Yu. (1998): First finding of exhalative johillerite (Kamchatka). *Dokl. Akad. Nauk* **361**, 795-798 (in Russ.).

HATERT, F., KELLER, P., LISSNER, F., ANTENUCCI, D. & FRANSOLET, A.M. (2000): First experimental evidence of alluaudite-like phosphates with high Li-content: the $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ series (x = 0 to 1). *Eur. J. Mineral.* **12**, 847-857.

HUGHES, J.M. & BIRNIE, R.W. (1980): Ziesite, β-$Cu_2V_2O_7$, a new copper vanadate and fumarole temperature indicator. *Am. Mineral.* **65**, 1146-1149.

_____, CHRISTIAN, B.S., FINGER, L.W. & MALINCONICO, L.L. (1987b): Mcbirneyite, $Cu_3(VO_4)_2$, a new sublimate mineral from the fumaroles of Izalco volcano, El Salvador. *J. Volcanol. Geotherm. Res.* **33**, 183-190.

_____, DREXLER, J.W., CAMPANA, C.F. & MALINCONICO, M.A.L. (1988): Howardevansite, $NaCu^{2+}Fe^{3+}{}_2(VO_4)_3$, a new fumarolic sublimate from Izalco Volcano, El Salvador: descriptive mineralogy and crystal structure. *Am. Mineral.* **73**, 181-186.

_____ & HADIDIACOS, C.G. (1985): Fingerite, $Cu_{11}O_2(VO_4)_6$, a new vanadium sublimate from Izalco volcano, El Salvador: descriptive mineralogy. *Am. Mineral.* **70**, 193-196.

_____, STARKEY, S.J., MALINCONICO, M.A.L. & MALINCONICO, L.L. (1987a): Lyonsite, $Cu^{2+}{}_3Fe^{3+}{}_4(VO_4)_6$, a new fumarolic sublimate from Izalco volcano, El Salvador: descriptive mineralogy and crystal structure. *Am. Mineral.* **72**, 1000-1005.

KELLER, P. & HESS, H. (1988): Die Kristallstrukturen von O'Danielite, $Na(Zn,Mg)_3H_2(AsO_4)_3$, und Johillerit, $Na(Zn,Mg)_3Cu(AsO_4)_3$. *Neues Jahrb. Mineral., Monatsh.*, 395-404.

MOORE, P.B. (1971): Crystal chemistry of the alluaudite structure type: contribution to the paragenesis of pegmatite phosphate giant crystals. *Am. Mineral.* **56**, 1955-1975.

_____ & ITO, J. (1979): Alluaudites, wyllieites, arrojadites: crystal chemistry and nomenclature. *Mineral. Mag.* **43**, 227-235.

PERTLIK, F. (1987): Hydrothermal synthesis and structure of sodium tetracopper (II) triarsenate(V). *Acta Crystallogr.* **C43**, 381-383.

POPOVA, V.I. & POPOV, V.A. (1997): New data on lammerite from Kamchatka. *Dokl. Akad. Nauk* **352**, 374-375 (in Russ.).

ROBINSON, P.D., HUGHES, J.M., MALINCONICO, M.A.L. (1987): Blossite, α-$Cu^{2+}{}_2V^{5+}{}_2O_7$, a new fumarolic sublimate from Izalco volcano, El Salvador. *Am. Mineral.* **72**, 397-400.

SEMENOVA, T.F., VERGASOVA, L.P., FILATOV, S.K. & ANAN'EV, V.V. (1994): Alarsite, $AlAsO_4$, a new mineral from volcanic exhalations. *Dokl. Russ. Acad. Sci.* **338**, 125-130.

VERGASOVA, L.P., FILATOV, S.K., GORSKAYA, M.G., MOLCHANOV, A.A., KRIVOVICHEV, S.V. & ANANIEV, V.V. (2000): Urusovite, $Cu[AlAsO_5]$, a new mineral from the Tolbachik volcano, Kamchatka, Russia. *Eur. J. Mineral.* **12**, 1041-1044.

_____, _____, SEMENOVA, T.F. & ANAN'EV, V.V. (1990): Leningradite $PbCu_3(VO_4)_2Cl_2$ – a new mineral from volcanic sublimates. *Dokl. Akad. Nauk SSSR* **310**, 1434-1437 (in Russ.).

_____, STAROVA, G.L., FILATOV, S.K., ANAN'EV, V.V. (1998): Averievite $Cu_5(VO_4)_2O_2$•nMX – a new mineral of volcanic exhalations. *Dokl. Ross. Akad. Nauk* **359**, 804-807 (in Russ.).

_____, _____, KRIVOVICHEV, S.V., FILATOV, S.K. & ANANIEV, V.V. (1999): Coparsite, $Cu_4O_2[(As,V)O_4]Cl$, a new mineral species from the Tolbachik volcano, Kamchatka Peninsula, Russia. *Can. Mineral.* **37**, 911-914.

Received October 22, 2000, revised manuscript accepted May 10, 2001.