

Joëlbruggerite, $\text{Pb}_3\text{Zn}_3(\text{Sb}^{5+}, \text{Te}^{6+})\text{As}_2\text{O}_{13}(\text{OH}, \text{O})$, the Sb^{5+} analog of dugganite, from the Black Pine mine, Montana

STUART J. MILLS,^{1,*} UWE KOLITSCH,² RITSURO MIYAWAKI,³ LEE A. GROAT,¹ AND GLENN POIRIER⁴

¹Department of Earth and Ocean Sciences, University of British Columbia, 6339 Stores Road, Vancouver, British Columbia V6T 1Z4, Canada

²Mineralogisch-Petrographische Abteilung, Naturhistorisches Museum Wien, Burgring 7, A-1010 Wien, Austria

³Department of Geology, National Museum of Nature and Science, 3-23-1, Hyakunin-cho, Shinjuku, Tokyo 169-0073, Japan

⁴Mineral Sciences Division, Canadian Museum of Nature, P.O. Box 3443, Station D, Ottawa, Ontario K1P 6P4, Canada

ABSTRACT

Joëlbruggerite, ideally $\text{Pb}_3\text{Zn}_3(\text{Sb}^{5+}, \text{Te}^{6+})\text{As}_2\text{O}_{13}(\text{OH}, \text{O})$, is a new arsenate mineral (IMA 2008-034) and the Sb^{5+} analog of dugganite, from the Black Pine mine, 14.5 km northwest of Philipsburg, Granite County, Montana. It is usually found perched on mimetite; other species that may be present include malachite, azurite, pseudomalachite, chalcocite, beudantite-corkite, duftite, dugganite, and kuksite, in milky quartz veins. Joëlbruggerite occurs as barrel-shaped or prismatic crystals up to about 50 μm across in various shades of purple. The crystals have an adamantine luster and a white streak. Mohs hardness is about 3. The fracture is irregular, and the tenacity is brittle. Joëlbruggerite crystals are uniaxial (–), with a calculated refractive index of $n = 1.993$, and weakly pleochroic: $X = Y = \text{gray}$, $Z = \text{purple}$; absorption: $Z > X = Y$. Crystals show straight extinction and are length-fast. The empirical chemical formula (mean of 5 electron microprobe analyses) calculated on the basis of 14 [O + OH] anions is $\text{Pb}_{3.112}(\text{Zn}_{2.689}\text{Fe}_{0.185}^{2+})\Sigma_{2.874}(\text{Sb}_{0.650}^{5+}\text{Te}_{0.451}^{6+})\Sigma_{1.101}(\text{As}_{1.551}\text{P}_{0.203}\text{Si}_{0.160})\Sigma_{1.914}\text{O}_{13.335}(\text{OH})_{0.665}$. Joëlbruggerite is trigonal, space group $P321$, $a = 8.4803(17)$, $c = 5.2334(12)$ Å, $V = 325.94(12)$ Å³, $Z = 1$. The five strongest lines in the powder X-ray diffraction pattern are [d_{obs} in Å (hkl)]: 3.298 (100) (111), 3.008 (89) (021), 1.905 (39) (122, 131), 2.456 (36) (012, 121, 030), and 1.609 (30) (112, 132, 231, 140). The crystal structure was solved from single-crystal X-ray diffraction data and refined to $R_1 = 0.038$ on the basis of 604 unique reflections with $F > 4\sigma(F)$. It is composed of heteropolyhedral sheets of edge-sharing (Sb,Te)O₆ octahedra and PbO₈ disphenoids, oriented parallel to (001). The sheets are cross-linked by AsO₄ and ZnO₄ tetrahedra, which share corners to form an interlinked, two- and three-connected two-dimensional net parallel to (001). The mineral is named for Joël Brugger (born 1967), Swiss-Australian mineralogist, for his contributions to mineralogy.

Keywords: Joëlbruggerite, new mineral, Sb^{5+} , arsenate, Black Pine mine, dugganite, crystal structure, bond valence

INTRODUCTION

The semi-metals antimony (Sb) and tellurium (Te) have relatively low crustal abundances (200 and 1 ppb, respectively), however high levels of both metals can be found in various ore deposits worldwide (e.g., for Sb, Consolidated Murchison mine near Gravelotte, South Africa—Yager 2007; for Te, Cripple Creek, Colorado—Kelley et al. 1998). Their mineralogy and crystal chemistry tend to be complex, owing to the various oxidation states for both elements (Sb^{3+} , Sb^{3+} and Te^{6+} , Te^{4+} , Te^0 , and Te^{2-}). Some 230 Sb and 140 Te minerals have so far been described, but only 10 contain both Sb and Te, and all these are sulfides or sulfosalts. The new mineral species joëlbruggerite, described here, appears to be the first mineral described where Sb^{5+} substitutes for Te^{6+} in the same site. The synthetic compound $(\text{H}_3\text{O})\text{SbTeO}_6$ (Turrillas et al. 1985; Alonso and Turrillas 2005) appears to be the only known example of Sb^{5+} replacing Te^{6+} in octahedral coordination, although some synthetic phases are

known with Sb^{3+} replacing Te^{4+} , e.g., $\text{Sb}_3\text{TeO}_6\text{Cl}$ (Alonso et al. 1985).

The type specimen of joëlbruggerite and associated material was collected in Spring 1993 by John Dagenais of Vancouver, British Columbia, Canada, at the Black Pine mine, 14.5 km NW of Philipsburg, Granite County, Montana (46°26'52"N, 113°21'56"W). The mineral is named for Joël Brugger (born 1967), Swiss-Australian mineralogist, for his contributions to mineralogy, in particular the description of new minerals (e.g., spriggite; Brugger et al. 2004), metamorphosed manganese deposits (e.g., Brugger and Meisser 2006), hydrothermal geochemistry (e.g., Brugger et al. 2007), and for his work on Te mineralogy (e.g., Grundler et al. 2008). The mineral and name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification prior to publication (IMA 2008-034). The type specimen is preserved in the Department of Mineralogy, South Australian Museum (G32400), with the co-type specimen (probe mount) preserved in the Mineral Sciences Division, Canadian Museum of Nature (CMNMC 86061).

* E-mail: smills@eos.ubc.ca

OCCURRENCE AND PARAGENESIS

Joëlbruggerite is usually found perched on mimetite; other species that may be present include malachite, azurite, pseudomalachite, chalcocite, beudantite-corkite, duftite, and the two joëlbruggerite-related species dugganite, $\text{Pb}_3\text{Zn}_3\text{TeAs}_2\text{O}_{14}$ (which is isostructural: Williams 1978; Lam et al. 1998) and kuskite, $\text{Pb}_3\text{Zn}_3\text{Te}^{6+}\text{O}_6(\text{PO}_4)_2$ (which is presumed isostructural but not yet confirmed: Kim et al. 1990; Mills et al. 2008) in milky quartz veins. The Black Pine mine is also the type locality for philipsburgite (Peacor et al. 1985) and is noted for its exceptional crystals of veszelyite (Waisman 1992). Tetrahedrite, bindheimite, and stibiconite are the only reported Sb minerals from the Black Pine mine (Waisman 1992), whereas no Te species have been reported prior to this study. Several other potentially new Sb-, W-, and/or Te-bearing secondary mineral species from this mine are currently under investigation by the first author.

Joëlbruggerite has crystallized from solutions rich in Pb, Zn, Sb, As, and Te derived from the breakdown of the primary ore body within the Mount Shields Formation (Peacor et al. 1985), which is part of the of the Middle Proterozoic Missoula Group (Wallace et al. 1986). Recently, the area has been remapped by Lonn et al. (2003), however the main units remain the same. The primary ore is hosted by veins of comb quartz, which is commonly vuggy, with the principal primary minerals being silver-bearing tetrahedrite, hübnerite, and pyrite. Galena, sphalerite, chalcopyrite, and native elements (Au, Ag, and Cu) are minor constituents within the veins. Tellurium is probably included in trace amounts within the tetrahedrite (e.g., Fadda et al. 2005) or possibly as Au/Ag tellurides.

As shown by available thermodynamic stability data (McPhail 1995; Filella and May 2003; Accornero et al. 2008), the formation of joëlbruggerite (as a tellurate) is likely to have occurred in a highly oxidizing environment, in water near equilibrium with atmospheric oxygen [$\log a_{\text{O}_2(\text{aq})} = -3.58$], similar to other secondary Te minerals such as xocolatlite (Grundler et al. 2008) (Fig. 1). In contrast, antimonates require only mildly oxidizing [$\log a_{\text{O}_2(\text{aq})} > -41$] and acidic conditions ($\text{pH} < 3$; Filella and May 2003). As joëlbruggerite contains substantial Te, the formation conditions are likely to be more oxidizing than required to produce antimonates. Tellurates are rare because such oxidizing conditions are rarely achieved and preserved—only at the surface, where leaching and erosion are important processes.

PHYSICAL AND OPTICAL PROPERTIES

Joëlbruggerite occurs as barrel-shaped or stout hexagonal prismatic $[0001]$ crystals up to about $50 \mu\text{m}$ across (Fig. 2). Forms observed are $\{0001\}$, $\{11\bar{2}0\}$, and $\{11\bar{2}1\}$. Crystals occur in various shades of purple (light purple, bluish purple, and grayish purple) and can be color-zoned, with light purple and grayish purple most prominent. Joëlbruggerite crystals are transparent, have a white streak, adamantine luster, and are non-fluorescent. Mohs hardness is about 3, estimated on the basis of dugganite group minerals, the fracture is irregular, and the tenacity is brittle. No macroscopic or microscopic twinning or cleavage was observed. The calculated density is 6.73 g/cm^3 (with empirical formula and single-crystal data), and crystals

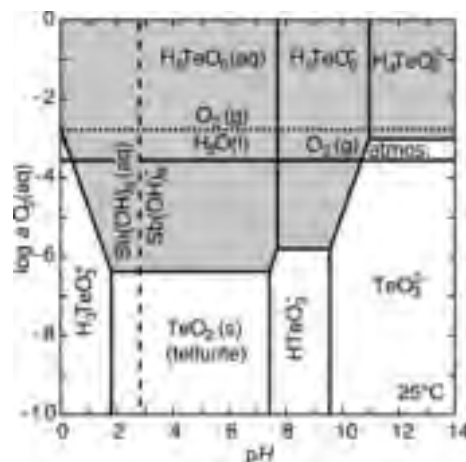


FIGURE 1. Speciation of tellurium and antimony in oxidized groundwaters (25 °C, 1.013 bar). The following thermodynamic data were used for constructing this diagram: tellurium species from McPhail (1995); $\text{Sb}(\text{OH})_3(\text{aq})/\text{Sb}(\text{OH})_6^-$ from Accornero et al. (2008); and $\text{O}_2(\text{g})/\text{O}_2(\text{aq})$ from the SUPCRT92 database (Johnson et al. 1992). The properties for antimony listed in Filella and May (2003) show that the Sb^{5+} species become predominant already at relatively reducing conditions [$\log a_{\text{O}_2(\text{aq})} > -41.35$]. Two $\text{O}_2(\text{aq})/\text{O}_2(\text{g})$ are plotted: $\text{O}_2(\text{g}) = 1.013 \text{ bar}$ (water stability) at $\log a_{\text{O}_2(\text{aq})} = -2.9$ and $\text{O}_2(\text{g}) = 0.21$ (atmospheric) at $\log a_{\text{O}_2(\text{aq})} = -3.6$.

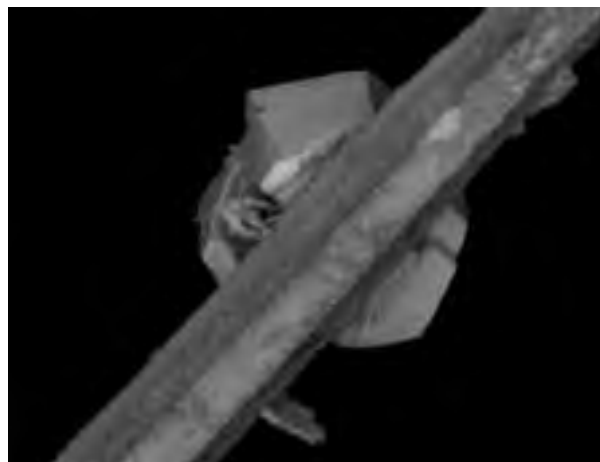


FIGURE 2. SEM image of a barrel-shaped joëlbruggerite crystal lanced by mimetite. The joëlbruggerite crystal is $30 \mu\text{m}$ across.

sink in Clerici solution (4.2 g/cm^3).

Crystals are confirmed uniaxial (–), however, the ω and ϵ values for joëlbruggerite were not measured due to the toxic oils needed to accurately characterize them. The calculated refractive index for white light based on the Gladstone-Dale compatibility (Mandarino 1981) is $n = 1.993$, which is slightly higher than the values obtained for dugganite ($\omega = 1.977$ and $\epsilon = 1.967$; Williams 1978). In transmitted light, joëlbruggerite is pale purple, with weak pleochroism: $X = Y = \text{gray}$, $Z = \text{purple}$, and absorption: $Z > X = Y$.

CHEMICAL COMPOSITION

Quantitative wavelength-dispersive electron-microprobe analyses (5 points) were carried out on joëlbruggerite with a JEOL 733 electron microprobe at the Mineral Sciences Division, Canadian Museum of Nature. Operating conditions were 20 kV, with beam current of 20 nA and a 2 µm beam diameter. Raw intensity data were corrected using a PAP matrix correction (Pouchou and Pichoir 1984). Sulfur, Se, V, Cu, and Ag were analyzed by WDS but not detected. No other elements were detected by energy dispersive spectroscopy. H₂O was calculated by normalizing the formula to 9 cations (excluding H), then OH was apportioned from 14 O atoms for charge balance. Structure analyses (see below) show that all sites are fully occupied (except H). The presence of hydroxyl ions was confirmed by Raman spectroscopy and crystal structure analyses (see below). The results, as well as the standards used, are shown in Table 1. The analytical totals for the microprobe data are slightly low. Possible reasons for the low totals include use of sulfide and telluride standards for an oxide mineral and the difficulty of preparing well-polished surfaces for the small, relatively soft crystals.

The mean composition of joëlbruggerite corresponds to the empirical formula (calculated on the basis of 14 [O + OH] apfu): Pb_{3.112}(Zn_{2.689}Fe_{0.185})_{Σ2.874}(Sb_{0.650}Te_{0.451})_{Σ1.101}(As_{1.551}P_{0.203}Si_{0.160})_{Σ1.914}O_{13.335}(OH)_{0.665}. The simplified end-member formula is Pb₃Zn₃Sb⁵⁺As₂O₁₃(OH), which requires: PbO 50.95, ZnO 18.57, Sb₂O₃ 12.31, As₂O₃ 17.49, H₂O 0.69, total 100.00 wt%, but the formula should be expressed as Pb₃Zn₃(Sb⁵⁺, Te⁶⁺)As₂O₁₃(OH, O), to reflect the significant Te⁶⁺ component in the structure.

Although there is potential for complete solid solution to exist between joëlbruggerite and dugganite at the Black Pine mine, the substitution of Sb⁵⁺ for Te⁶⁺ in the type specimen ranges only between 56 and 63% following the substitution mechanism (Sb⁵⁺OH)(Te⁶⁺O)₋₁. The presence of Sb in dugganite from the Kawazu mine, Shizuoka Prefecture, Japan (Sb₂O₃ ~5 wt%; Te⁶⁺:Sb⁵⁺ 0.72:0.30 based on 9 cations), was reported by Matsubara et al. (2004) and extends the solid-solution field (Fig. 3). The Sb-bearing dugganite from the Kawazu mine is pale blue and has slightly smaller unit-cell parameters of *a* = 8.490 and *c* = 5.216 Å (from Gandolfi powder data).

TABLE 1. Electron microprobe analyses of joëlbruggerite*

Constituent	wt%	Range	Std. dev.	Probe standard
ZnO	15.98	14.1–16.94	1.11	Sphalerite
PbO	50.72	49.45–53.47	1.60	Galena
FeO	0.97	0.28–2.71	1.01	Hematite
SiO ₂	0.70	0.5–1.02	0.19	Albite
TeO ₃	5.78	5.19–6.09	0.36	Sb ₂ Te ₃
Sb ₂ O ₃	7.68	7.12–8.44	0.55	Sb ₂ Te ₃
P ₂ O ₅	1.05	0.35–1.81	0.52	VP ₂ O ₇
As ₂ O ₃	13.02	11.51–13.68	0.88	GaAs
H ₂ O _{calc} †	0.44			
Total	96.34			

* S, Se, V, Cu, and Ag all analyzed for but not detected. No other elements detected by EDS.

† See text.

RAMAN SPECTROSCOPY

Near-infrared Raman analysis was performed using a Renishaw Imaging Microscope System 1000 (Department of Biochemistry, UBC), with a RL785 diode laser at a wavelength of 785 nm, a RenCam CCD detector and Renishaw WiRE Version 1.3.30 instrument control software. The data were analyzed using Galatic Grams/32 Version 4.14 software. Prior to data acquisition, a spectral calibration was carried out using the Raman spectrum obtained from a silicon wafer. Spectra were recorded in backscatter mode between 150 and 3500 cm⁻¹ with a spectral resolution of ±2 cm⁻¹ and a minimum lateral resolution of ~2 µm on the sample.

The Raman spectrum for joëlbruggerite shows several AsO₄ vibrational modes including the ν₃(AsO₄) vibrational mode at 818 cm⁻¹ and ν₁(AsO₄) stretching mode at 680 cm⁻¹. Additional bands were observed at 506, 475, 427, 383, 235, 200, 183, 168, and 150 cm⁻¹. The presence of hydroxyl ions was confirmed by OH-stretching bands at 3015 and 3030 cm⁻¹, although these bands are extremely weak.

CRYSTAL STRUCTURE

Experimental methods

The single-crystal study was carried out using a Bruker X8 ApexII single-crystal diffractometer at the Department of Chemistry, University of British Columbia. A barrel-shaped crystal with dimensions 0.03 × 0.03 × 0.02 mm was used for collection of intensity data at 293 K (Table 2). The intensity data were processed with the Bruker Apex program suite, with data reduction using the SAINT program (Bruker 2003) and absorption correction by the multi-scan method using SADABS (Bruker 2003).

The crystal structure of joëlbruggerite was solved in *P*321 (no. 150), by direct methods using SHELXS-97 (Sheldrick 1997a) and subsequent Fourier and difference Fourier syntheses, followed by anisotropic full-matrix least-squares refine-

TABLE 2. Summary of data collection conditions and refinement parameters for joëlbruggerite

Crystal data	
Cell parameters	<i>a</i> = 8.4803(17) Å <i>c</i> = 5.2334(12) Å <i>V</i> = 325.94(12) Å ³ <i>Z</i> = 1
Space group	<i>P</i> 321
Data collection	
Temperature	293(2) K
λ (MoKα)	0.71073 Å
Crystal shape, size	barrel-shaped, 0.03 × 0.03 × 0.02 mm
2θ _{max}	59.84°
Reflection range	-11 ≤ <i>h</i> ≤ 11; -11 ≤ <i>k</i> ≤ 10; -4 ≤ <i>l</i> ≤ 7
Total no. reflections	1785
No. unique reflections	604
No. reflections, <i>F</i> > 4σ(<i>F</i>)	497
Absorption coefficient μ	51.2 mm ⁻¹
<i>R</i> _{merge} on <i>F</i> ²	0.048
Refinement	
No. parameters refined	38
<i>R</i> ₁ , <i>F</i> > 4σ(<i>F</i>)	0.0389
<i>R</i> ₁ , all data	0.0510
w <i>R</i> ₂ (<i>F</i> ²)*, all data	0.0948
GO F	0.701
Δσ _{min} , Δσ _{max} (e/Å ³)	-1.6, 2.2

* *w* = 1/[σ²(*F*_o²) + (0.024*P*² + 50.1*P*)], *P* = [2*F*_o² + Max(*F*_o, 0)]/3.



FIGURE 3. Extent of the solid solution between joëlbruggerite and dugganite. Diamonds = Black Pine, square = Kawazu.

TABLE 3. Atomic coordinates, site occupancies, and displacement parameters (Å) for joëlbruggerite

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb	0.40396(12)	0.0	0.0	0.0261(3)	0.0309(4)	0.0270(5)	0.0191(4)	-0.0024(3)	-0.00121(17)	0.0135(2)
Sb*	0.0	0.0	1.0	0.0182(5)	0.0226(7)	0.0226(7)	0.0093(9)	0.0	0.0	0.0113(4)
Zn	0.0	-0.2450(3)	1/2	0.0248(6)	0.0215(12)	0.0333(12)	0.0158(11)	-0.0001(5)	-0.0003(11)	0.0107(6)
As	1/3	-1/3	0.4738(5)	0.0215(6)	0.0188(8)	0.0188(8)	0.0270(14)	0.0	0.0	0.0094(4)
O1	-0.127(2)	-0.2180(19)	0.212(2)	0.040(4)	0.043(8)	0.043(8)	0.030(6)	0.012(6)	-0.001(6)	0.018(7)
O2	-0.202(2)	-0.460(3)	0.669(3)	0.055(5)	0.056(11)	0.055(10)	0.038(8)	0.000(7)	0.007(7)	0.015(9)
O3	1/3	-1/3	-0.204(4)	0.023(4)	0.024(6)	0.024(6)	0.021(8)	0.0	0.0	0.012(3)

* Sb:Te 0.57:0.43.

ments on F^2 using SHELXL-97 (Sheldrick 1997b). The position of the H atom could not be determined (but see below for possible positions). The final model converged to $R_1 = 3.89\%$ for 497 reflections [$F_o > 4\sigma(F_o)$] and 5.10% for all 604 reflections. The refined atomic coordinates, site occupancies, and displacement parameters are given in Table 3; polyhedral bond distances in Table 4; and a bond-valence analysis in Table 5.

The quantitative coordination parameters calculated for joëlbruggerite and dugganite (Table 6) are: bond distance, the average bond distance, polyhedron volume (V_p), the volume of the sphere fitted to the positions of the coordinating atoms (V_s), volume distortion of the polyhedron (v), and the volume eccentricity (Δ). The calculations for V_s , v , and Δ are based on the determination of the centroid of coordination (Balić-Žunić and Makovicky 1996) and the measure of distortion for coordination polyhedra (Makovicky and Balić-Žunić 1998) and are calculated using the program IVTON (Balić-Žunić and Vicković 1996).

Description of the structure

The crystal structure determination shows that joëlbruggerite is the Sb^{5+} -dominant analog of dugganite, $Pb_3Zn_3Te^{6+}As_2O_{14}$ (Lam et al. 1998), with charge balance achieved by OH-for-O substitution. A similar charge balance mechanism was suggested by Kim et al. (1988) for vanadian, silician dugganite from Aldan, Russia, where heterovalent $(As, V)^{5+} \leftrightarrow Si^{4+}$ isomorphism is accomplished by $O^{2-} \leftrightarrow OH^-$ replacement. The joëlbruggerite structure is composed of heteropolyhedral sheets of edge-sharing $(Sb, Te)O_6$ octahedra and PbO_4 disphenoids, oriented parallel to (001). The sheets are cross-linked by AsO_4 and ZnO_4 tetrahedra, which share corners to form an interlinked, two- and three-connected two-dimensional net parallel to (001) (Figs. 4 and 5).

The average bond length for the Pb polyhedron, $\langle Pb-O \rangle$, is 2.707 Å, whereas $\langle Zn-O \rangle$ and $\langle (Sb, Te)-O \rangle$ are both 1.954 Å and $\langle As-O \rangle$ is 1.703 Å. The average bond lengths for Pb and Zn are in accord with literature values and those obtained by Lam et al. (1998) for dugganite ($\langle Pb-O \rangle$ of 2.74 and $\langle Zn-O \rangle$ of 1.94 Å) and give bond-valence sums (BVSs) of 1.96 (calculated using the values of Krivovichev and Brown 2001) and 2.10 valence units (v.u.), respectively (Table 5). The $\langle As-O \rangle$ is slightly longer than the expected value of 1.682 Å as determined by Baur (1981), and is more typical of protonated acid arsenates, where the tetrahedra are distorted due to hydrogen bonding, such as those described by Schwendtner and Kolitsch (2007) and more recently by Cooper and Hawthorne (2009). Inspection of the BVS (Table 5) shows that the O3 is undersaturated, and has a formal valence of 1.45 v.u. Considering the empirical formula

TABLE 4. Polyhedral bond distances (Å) in joëlbruggerite

Pb-O1	2.352(15)	×2
Pb-O2	2.642(19)	×2
Pb-O2	3.04(2)	×2
Pb-O3	2.793(7)	×2
$\langle Pb-O \rangle$	2.707	
Sb-O1	1.954(13)	×6
Zn-O1	1.932(14)	×2
Zn-O2	1.976(16)	×2
$\langle Zn-O \rangle$	1.954	
As-O3	1.685(19)	
As-O2	1.710(17)	×3
$\langle As-O \rangle$	1.704	

TABLE 5. Bond-valence analysis for joëlbruggerite

	Pb		Sb/Te*		Zn		As		Σ
O1	0.45	↓×2	0.895	↓×6	0.56	↓×2			1.90
O2	0.24	↓×2			0.49	↓×2	1.19	↓×3	2.03
	0.11	↓×2							
O3	0.18	↓×2					1.27		1.45
Σ	1.96		5.37		2.10		4.83		

* Calculated from the weighted Sb/Te contributions.

$Pb_{3.112}(Zn_{2.689}Fe_{0.185}^{2+})_{\Sigma 2.874}(Sb_{0.650}^{5+}Te_{0.451}^{6+})_{\Sigma 1.101}(As_{1.551}P_{0.203}Si_{0.160})_{\Sigma 1.914}O_{13.335}(OH)_{0.665}$, the O3 site is assumed to represent an OH group (part of which is substituted by O). The hydrogen bond donated by the OH group is assumed to be accepted by the O1 atom (1.90 v.u.), with an $O3 \cdots O1$ hydrogen-bond distance of ~ 2.6 Å. We were unable to refine the position for the hydrogen atom within the joëlbruggerite structure, however the most likely position is about $(1/3, -1/3, 0.5943)$ based on the second largest peak in the difference Fourier map ($1.95 e/\text{Å}^{-3}$) and its distance from O3 of 1.05 Å, both reasonable values for a site partially occupied by hydrogen. The only other possibility is at (0.4142, -0.2054, -0.1039), with an electron density of $1.03 e/\text{Å}^{-3}$ and distance to the O3 of 1.09 Å.

An alternative possibility of protonation and H-bonding would be that both O3 and, to a lesser extent, O1 are partially protonated, i.e., the presence of As-OH bonds and (Sb, Te)-OH-Zn linkages. This would be in accordance with a substitution scheme $Sb^{5+}OH \leftrightarrow Te^{6+}O$.

Analysis of the $^{61}(Sb^{5+}, Te^{6+})-O$ bond length using values of $\langle Sb-O \rangle$ of 1.98 Å (Effenberger 1985) and $\langle Te-O \rangle$ of 1.92 Å (e.g., Untenecker and Hoppe 1987; Loub 1993; Levason 1997; Vanek et al. 2000—54% of all Te-O bonds are between 1.91

TABLE 6. Quantitative coordination parameters for joëlbruggerite and dugganite

	Volume distortion parameter (v) %		Polyhedron volume (V_p) Å ³		Sphere volume (V_s) Å ³		Volume eccentricity (Δ)	
	joëlbruggerite	dugganite	joëlbruggerite	dugganite	joëlbruggerite	dugganite	joëlbruggerite	dugganite
Pb	12.43	11.82	32.83	36.26	86.54	94.86	0.4127	0.3956
Sb/Te	0.94	0.79	9.85	9.44	31.24	29.90	0.00	0.00
Zn	10.58	9.88	13.26	12.62	46.60	43.98	0.6965	0.6995
As	1.66	0.14	2.49	1.96	20.64	16.04	0.0270	0.0974

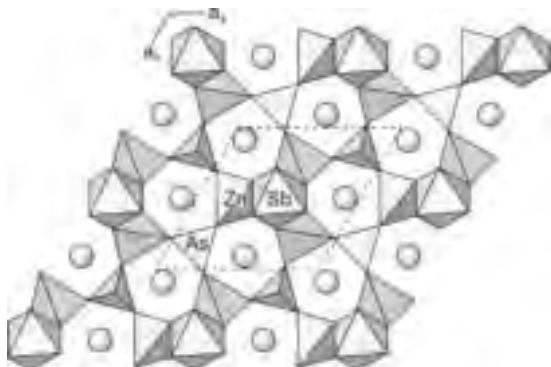


FIGURE 4. Crystal structure of joëlbruggerite projected onto (001); Pb atoms are indicated as spheres.

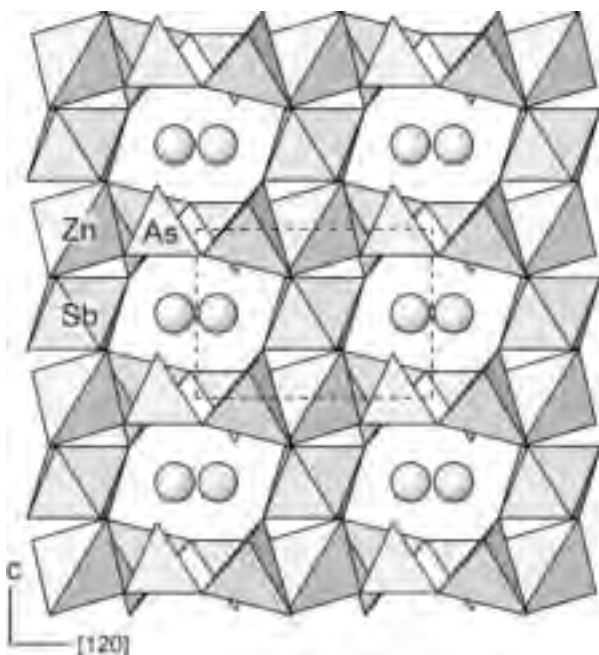


FIGURE 5. Crystal structure of joëlbruggerite projected down [100]; Pb atoms are indicated as spheres.

and 1.93 Å) suggests an Sb:Te ratio of 0.57:0.43, which is in good agreement with the range of EMPA data (see above; Fig. 3). However, determination of the BVS was more problematic. The b value of 0.37 Å (Brown and Altermatt 1985), which is used as an almost “universal constant” when undertaking BVS calculations, does not adequately describe some polarized ions. Recently, several authors have noted this and have derived new bond-valence parameters [e.g., Pb(II) $b = 0.49$ Å; $r_0 = 1.963$ Å; Krivovichev and Brown 2001]. Using $b = 0.37$ Å and $r_0 = 1.942$ Å for Sb^{5+} incorrectly overestimates the valence state of the Sb by 0.3 v.u. This led to a redetermination of the Sb-O bond-valence parameters r_0 and b (S.J. Mills, unpublished manuscript) and to a more reasonable BVS of 5.37 v.u. in joëlbruggerite.

The distortion parameters calculated for joëlbruggerite and dugganite are shown in Table 6. The degree of distortion (v) exhibited in all the polyhedra is greater in the structure of joëlbruggerite than in that of dugganite. The AsO_4 tetrahedra show the largest change (1.66% vs. 0.14%), due to the influence of the hydrogen atom on the undersaturated O3 atom, a feature not seen in the dugganite structure. The incorporation of Sb^{5+} into the Te^{6+} -centered octahedra did not significantly distort them (0.94% vs. 0.79%), as all six bonds are to O1.

X-RAY POWDER DIFFRACTION DATA

X-ray powder-diffraction data (Table 7) were collected with the same crystal used for the single-crystal study on a 114.6 mm diameter Gandolfi camera with Ni-filtered $\text{CuK}\alpha$ radiation at the Department of Geology, National Museum of Nature and Science, Japan. The data were recorded on an imaging plate and processed with a Fuji BAS-2500 bio-image analyzer using the computer program written by Nakamuta (1999). Data were calibrated with a quartz-standard (reference material NIST SRM no. 1878a) on the crystal of joëlbruggerite. Unit-cell parameters refined from the powder data using Chekcell (Laugier and Bochu 2004) are $a = 8.506(6)$ and $c = 5.2350(6)$ Å, $V = 327.996(3)$

TABLE 7. X-ray powder diffraction data for joëlbruggerite

hkl^*	I_{obs}	d_{obs}	I_{calc}^*	d_{calc}^*
010			1	7.344
001	6	5.236	32	5.233
011 } 110 }	22	4.244	{ 1 19	4.262 4.240
020	14	3.674	22	3.672
111	100	3.298	100	3.295
021	89	3.008	85	3.006
120	20	2.783	26	2.776
002	5	2.619	40	2.617
012 } 121 } 030 }	36	2.456	{ 2 5 37	2.465 2.452 2.448
112 } 031 }	11	2.224	{ 7 28	2.227 2.217
022 } 220 }	12	2.131	{ 10 4	2.131 2.120
130	13	2.041	16	2.037
221			2	1.965
122 } 131 }	39	1.905	{ 18 20	1.904 1.898
400 } 032 }	17	1.824	{ 1 16	1.834 1.787
013 } 230 }	2	1.689	{ 1 3	1.697 1.684
113 } 132 } 231 }	30	1.609	{ 8 5 4	1.613 1.607 1.604
140			8	1.603
023	1	1.576	7	1.575
123 } 050 }	1	1.472	{ 3 8	1.477 1.467
033 } 232 }			{ 1 2	1.420 1.416
051 } 330 }	12	1.419	{ 6 7	1.414 1.414
240	3	1.392	2	1.388
223	4	1.345	3	1.347
133	5	1.328	3	1.325
014 } 052 }	7	1.283	{ 1 5	1.288 1.281
151			4	1.279

Note: Strongest lines are denoted in bold.

* Calculated from the crystal structure using PowderCell.

Å³, which are in good agreement with those obtained from the single-crystal study.

ACKNOWLEDGMENTS

The Associate Editor, Ed Grew, reviewers Tony Kampf, Frédéric Hatert, and Bill Birch provided helpful comments on the manuscript that are greatly appreciated. Joël Brugger, Pascal Grundler, and Pete Williams are thanked for their insight into Sb and Te thermodynamics. Jim Ferraiolo and David Von Bargen are thanked for assistance with references. NSERC Canada is thanked for a Discovery Grant to L.A.G.

REFERENCES CITED

- Accornero, M., Marini, L., and Lelli, M. (2008) The dissociation constant of anti-monic acid at 10–40 °C. *Journal of Solution Chemistry*, 37, 785–800.
- Alonso, J.A. and Turrillas, X. (2005) Location of H⁺ sites in the fast proton-conductor (H₃O)SbTeO₆ pyrochlore. *Dalton Transactions*, 865–867.
- Alonso, J.A., Gutierrez-Puebla, E., Monge, A., and Ruiz-Valero, C. (1985) Synthesis and crystal structure of the layer compound Sb₃Te₆Cl. *Dalton Transactions*, 1633–1635.
- Balić-Zunić, T. and Makovicky, E. (1996) Determination of the centroid or “the best centre” of a coordination polyhedron. *Acta Crystallographica*, B52, 78–81.
- Balić-Zunić, T. and Vicković, I. (1996) IVTON—program for the calculation of geometrical aspects of crystal structures and some crystal chemical applications. *Journal of Applied Crystallography*, 29, 305–306.
- Baur, W.H. (1981) Interatomic distance predictions for computer simulation of crystal structures. In M. O’Keeffe and A. Navrotsky, Eds., *Structure and Bonding in Crystals*, Vol. II, p. 31–52. Academic Press, New York.
- Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallographica*, B41, 244–247.
- Brugger, J. and Meisser, N. (2006) Manganese-rich assemblages in the Barrhorn Unit, Turtmanntal, Central Alps, Switzerland. *Canadian Mineralogist*, 44, 229–248.
- Brugger, J., Krivovichev, S., Berlepsch, P., Meisser, N., Ansermet, S., and Armbruster, T. (2004) Spriggite, Pb₃[(UO₂)₆O₈(OH)₂](H₂O)₃, a new mineral with β-U₃O₈-type sheets: Description and crystal structure. *American Mineralogist*, 89, 339–347.
- Brugger, J., Etschmann, B., Liu, W., Testemale, D., Hazemann, J.-L., van Beek, W., and Proux, O. (2007) An XAS study of the chloride complexing of Cu(I) in brines. *Geochimica et Cosmochimica Acta*, 71, 4920–4941.
- Bruker (2003) SAINT, SADABS, and SHELXTL. Bruker AXS Inc., Madison, Wisconsin.
- Cooper, M.A. and Hawthorne, F.C. (2009) The crystal structure of burgessite, Co₂(H₂O)₄[AsO₃(OH)]₂(H₂O), and its relation to erythrite. *Canadian Mineralogist*, 47, 165–172.
- Effenberg, H. (1985) The crystal structure of mammothite, Pb₂Cu₄AlSbO₂(OH)₁₆Cl₄(SO₄)₂. *Tschermak’s Mineralogische und Petrographische Mitteilungen*, 34, 279–288.
- Fadda, S., Fiori, M., and Grillo, S.M. (2005) Chemical variations in tetrahedrite-tennantite minerals from the Furtei epithermal Au deposit, Sardinia, Italy: Mineral zoning and ore fluids evolution. Au-Ag-Te-Se deposits. IGCP Project 486, 2005 Field Workshop, Kiten, Bulgaria, 79–84.
- Filella, M. and May, P.M. (2003) Computer simulation of the low-molecular-weight inorganic species distribution of antimony(III) and antimony(V) in natural waters. *Geochimica et Cosmochimica Acta*, 67, 4013–4031.
- Grundler, P., Brugger, J., Meisser, N., Ansermet, S., Borg, S., Etschmann, B., Testemale, D., and Bolin, T. (2008) Xocolatlite, Ca₂Mn²⁺Te₂O₁₂·H₂O, a new tellurate related to kuranakhite: Description and measurement of Te oxidation state by XANES spectroscopy. *American Mineralogist*, 93, 1911–1920.
- Johnson, J.W., Oelkers, E.H., and Helgeson, H.C. (1992) SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species and reactions from 1 to 5000 bars and 0 to 1000 °C. *Computers and Geosciences*, 18, 899–920.
- Kelley, K.D., Romberger, S.B., Beaty, D.W., Pontius, J.A., Snee, L.W., Stein, H.J., and Thompson, T.B. (1998) Geochemical and geochronological constraints on the genesis of Au-Te deposits at Cripple Creek, Colorado. *Economic Geology*, 93, 981–1012.
- Kim, A.A., Zayakina, N.V., Lavrent’ev, Yu.G., and Makhotko, V.F. (1988) Vanadate silicic variety of dugganite: First find in the USSR. *Mineralogicheskii Zhurnal*, 10, 85–89 (in Russian).
- Kim, A.A., Zayakina, N.V., and Makhotko, V.F. (1990) Kuskite Pb₂Zn₃Te⁶⁺O₆(PO₄)₂ and chermnykhite Pb₂Zn₃Te⁶⁺O₆(VO₄)₂—new tellurates from the Kuranakh gold deposit (Central Aldan, southern Yakutia). *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, 119, 50–57 (in Russian).
- Krivovichev, S.V. and Brown, I.D. (2001) Are the compressive effects of encapsulation an artifact of the bond valence parameters? *Zeitschrift für Kristallographie*, 216, 245–247.
- Lam, A.E., Groat, L.A., and Ercit, T.S. (1998) The crystal structure of dugganite, Pb₂Zn₃TeAs₂O₁₄. *Canadian Mineralogist*, 36, 823–830.
- Laugier, J. and Bochu, B. (2004) Chekcell: Graphical powder indexing cell and space group assignment software, <http://www.ccp14.ac.uk/tutorial/lmgp/>.
- Levason, W. (1997) The coordination chemistry of periodate and tellurate ligands. *Coordination Chemistry Reviews*, 161, 33–79.
- Lonn, J.D., McDonald, C., Lewis, R.S., Kalakay, T.J., O’Neill, J.M., Berg, R.B., and Hargrave, P. (2003) Preliminary geologic map of the Philipsburg 30’ × 60’ quadrangle, Montana. Montana Bureau of Mines and Geology Open File Report, MBMG 483, scale 1:100 000.
- Loub, J. (1993) The oxides and oxyacids of tellurium. *Collection of Czechoslovak Chemical Communications*, 58, 1717–1738.
- Makovicky, E. and Balić-Zunić, T. (1998) New measure of distortion for coordination polyhedra. *Acta Crystallographica*, B54, 766–773.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship. IV. The compatibility concept and its application. *Canadian Mineralogist*, 19, 441–450.
- Matsubara, S., Miyawaki, R., Yokoyama, K., Harada, A., and Sakamoto, M. (2004) Dugganite from the Kawazu mine, Shizuoka Prefecture, Japan. *Mineralogical Society of Japan, Annual Meeting Abstracts*, vol. 2004, k08–02 (in Japanese).
- McPhail, D.C. (1995) Thermodynamic properties of aqueous tellurium species between 25, 382, and 350 °C. *Geochimica et Cosmochimica Acta*, 59, 851–866.
- Mills, S.J., Groat, L.A., and Kolitsch, U. (2008) Te, Sb, and W mineralization at the Black Pine mine, Montana. Poster, 18th Annual V.M. Goldschmidt Conference, Vancouver, Canada, July 13–18, 2008; abstract in *Geochimica et Cosmochimica Acta*, 72, Special Supplement 12S, A632.
- Nakamura, Y. (1999) Precise analysis of a very small mineral by an X-ray diffraction method. *Journal of the Mineralogical Society of Japan*, 28, 117–121 (in Japanese with English abstract).
- Peacor, D.R., Dunn, P.J., Ramik, R.A., Sturman, B.D., and Zeihan, L.G. (1985) Philipsburgite, a new copper zinc arsenate hydrate related to kipushite, from Montana. *Canadian Mineralogist*, 23, 255–258.
- Pouchou, J.L. and Pichoir, F. (1984) A new model for quantitative X-ray microanalysis. 1. Application to the analysis of homogeneous samples. *Recherche Aéropatiale*, 3, 13–38.
- Schwendtner, K. and Kolitsch, U. (2007) Two new structure types: KFe₃(AsO₄)₂(HASO₄)₂ and K(H₂O)M²⁺(H_{1.5}AsO₄)(H₂AsO₄) (M²⁺ = Fe, Ga, In)—synthesis, crystal structure and spectroscopy. *European Journal of Mineralogy*, 19, 399–409.
- Sheldrick, G.M. (1997a) SHELXS-97, a program for crystal structure solution. University of Göttingen, Germany.
- (1997b) SHELXL-97, a program for crystal structure refinement. University of Göttingen, Germany.
- Turrillas, X., Delabouglise, G., Joubert, J.G., Fournier, T., and Muller, J. (1985) A new proton conductor HSbTeO₆·xH₂O: Conductivity dependence with temperature and water vapor partial pressure. *Solid State Ionics*, 17, 169–174.
- Untenecker, H. and Hoppe, R. (1987) Neue oxotellurate(VI): KNa₅[TeO₆]. *Journal of the Less-Common Metals*, 132, 93–105.
- Vanek, L., Němec, I., Cisařova, I., Mička, Z., and Fajnor, V. (2000) A new lithium hydrogen tellurate—LiH₂TeO₆. *Journal of Solid State Chemistry*, 150, 410–415.
- Waisman, D. (1992) Minerals of the Black Pine Mine, Granite County, Montana. *Mineralogical Record*, 23, 477–483.
- Wallace, C.A., Schmidt, R.G., Lidke, D.J., Waters, M.R., Elliott, J.E., French, A.B., Whipple, J.W., Zarske, S.E., Blaskowski, M.J., Heise, B.A., Yeoman, R.A., O’Neill, J.M., Lopez, D.A., Robinson, G.D., and Klepper, M.R. (1986) Preliminary geologic map of the Butte 1 × 2° quadrangle, Montana. U.S. Geological Survey Open File Report, 86-292, scale 1:250 000.
- Williams, S.A. (1978) Khinite, parakhinite, and dugganite, three new tellurates from Tombstone, Arizona. *American Mineralogist*, 63, 1016–1019.
- Yager, T.R. (2007) The Mineral Industry of South Africa. *USGS Minerals Yearbook 2005—South Africa*, 23 p.

MANUSCRIPT RECEIVED NOVEMBER 5, 2008

MANUSCRIPT ACCEPTED FEBRUARY 19, 2009

MANUSCRIPT HANDLED BY EDWARD GREW