Cannonite, Bi₂O(OH)₂SO₄, a new mineral from Marysvale, Utah, USA*

C. J. Stanley¹, A. C. Roberts², D. C. Harris², A. J. Criddle¹ and J. T. Szymański³

¹Department of Mineralogy, Natural History Museum, Cromwell Road, London SW7 5BD, UK

²Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, K1A 0E8, Canada

³CANMET, 555 Booth Street, Ottawa, Ontario, K1A 0G1, Canada

Abstract

Cannonite, ideally $Bi_2O(OH)_2SO_4$, is a new mineral from the Tunnel Extension mine, Ohio Mining District, Marysvale, Utah, USA. It occurs mostly as intergrown crystalline aggregates (<1 mm) of subhedral to euhedral equant to prismatic crystals (<200 µm) in cavities in quartz gangue. Other associated minerals are cuprobismutite, bismuthinite, and covelline. Cannonite is colourless and transparent with an adamantine lustre and white streak. It is brittle with an uneven to conchoidal fracture. In reflected light it is low reflecting, weakly to moderately bireflectant and weakly anisotropic. Internal reflections (colourless to white) are abundant. Measured reflectance values in air and oil are tabulated. Colour values relative to the CIE illuminant C for R_1 and R_2 in air respectively are: Y% 10.4, 11.7; Lambda_d 475, 475; $P_e\%$ 2.6, 3.0. Calculated refractive indices at 589 nm: R_1 1.91 and R_2 1.99. VHN₁₀₀ 229 (range 183–280); calculated Mohs hardness is 4.

X-ray studies show that cannonite is monoclinic with space group $P2_1/c$ and a 7.700(3), b 13.839(6), c 5.686(2) Å, $\beta 109.11(3)^{\circ}$. It has a cell volume of 572.5(4) Å³ with Z = 4. $D_{\text{calc.}}$ is 6.515 g/cm³. The strongest six lines of the X-ray powder pattern are $[d \text{ in Å (I) (hkl)}] 3.206 (100) (\overline{221})$; 1.984 (90) (340, $\overline{152}$); 2.924 (70) (131); 3.644 (60) (111); 3.466 (60) (040); 2.782 (50) ($\overline{112}$). Averaged probe analyses gave the empirical formula $Bi_{1.99}O(OH_{1.04})_2S_{0.99}O_4$ on the basis of 7 oxygen atoms. The name is for Benjamin Bartlett Cannon of Seattle, Washington, United States of America.

KEYWORDS: cannonite, new mineral, bismuth, Marysvale, Utah.

Introduction and general geology

CANNONITE, ideally Bi₂O(OH)₂SO₄, is a new mineral species found in a specimen collected from the Tunnel Extension mine of the Ohio Mining District, Marysvale, Utah, USA [latitude 38°28′N, longitude 112°14′W]. A description of the deposit is given in Radtke et al., (1967); in short, the mineralisation occurs as steeply dipping fissure infillings, along faults or shear zones, which cut the Bullion Canyon volcanics of middle Tertiary age. Radtke et al. also give an account of the mineralogy: 'Primary ore minerals include cuprobismutite, bismuthinite, tetrahedrite, emplectite, chalcopyrite, native gold and tetradymite. Secondary or alteration minerals include covellite, chalcocite, and a new hydrated bismuth

sulfate. Most of the gangue is composed of quartz'. Cassiterite also occurs in the quartz gangue. Their 'hydrated bismuth sulfate' is the mineral which we characterise and describe as cannonite. It appears to have formed as an alteration product of the primary Cu-Bi-S mineral assemblage. Cannonite is named after Benjamin Bartlett Cannon (the fifth) (1950-) who donated specimens from the mine and who first brought this hitherto uncharacterised mineral to our attention. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type specimens are preserved at the Natural History Museum, Great Britain, as specimen BM 1992, 240, and polished section E.1456, and in the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, under the catalogue number NMC 67428.

^{*} Geological Survey of Canada Contribution Number 16192.

Physical properties

Cannonite is colourless and transparent, with a white streak and adamantine lustre. It is brittle with an uneven to conchoidal fracture and shows no evidence of either a cleavage or a parting, nor is the mineral fluorescent. Crystal forms are only well developed where cannonite has formed in cavities in the quartz gangue. Mostly it occurs as intergrown crystalline aggregates (<1 mm) of subhedral to euhedral equant to prismatic crystals (<200 µm) or as irregular intergrown aggregates (Fig. 1) which have altered cuprobismutite and bismuthinite at grain boundaries and along cleavages.

Polished sections of the ore-bearing material were prepared using the techniques described in Stanley *et al.* (1991) with polishing finished by 0.25 µm diamond. Together with the associated minerals, cannonite takes a good polish. It has a VHN₁₀₀ of 229 with a range of 183–280 from 10

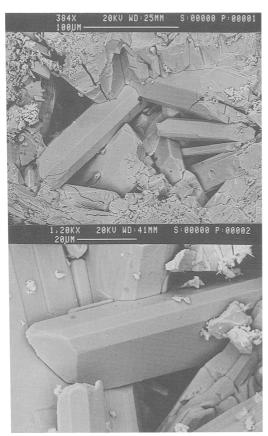


Fig. 1. Scanning electron photomicrographs of intergrown prismatic cannonite crystals (Scale bar: top 100 μm; bottom 20 μm).

indentations, the shapes of which were perfect with slight fracturing at the corners. The equivalent Moh's hardness is 4. The specific gravity could not be determined due to a lack of pure material and because of the size of the individual crystals.

In reflected light, cannonite is weakly to moderately bireflectant from grey to darker grey and is weakly anisotropic. Internal reflections, colourless to white, are abundant and the usual precautions were taken to ensure accurate reflectance measurements, which were obtained in air and in oil using the procedures summarised in Criddle *et al.*, (1983), with a SiC standard (Zeiss no 472). Pleochroism is absent. The data are given in Table 1 and Fig. 2. Calculated refractive indices at 589 nm are (for R_1 and R_2 respectively) 1.91 and 1.99 (using Koenigsberger equations).

Chemical composition

Electron probe microanalysis was used to determine the chemistry of cannonite, with H_2O being determined both by difference and by analogy to the synthetic compound. Initial micro-

TABLE 1. Reflectance data and colour values for cannonite

λnm	R_{I}	R_{Z}	$\mathit{im}_{R_{_{\widetilde{I}}}}$	$im_{R_{\underline{2}}}$
400 420 440 460 470	11.2 11.1 11.0 10.9 10.8	12.9 12.8 12.5 12.3 12.2	2.04 1.98 1.93 1.87 1.86	3.01 2.85 2.73 2.64 2.59
480 500 520 540 546	10.8 10.7 10.5 10.4 10.4	12.1 12.0 11.9 11.7 11.7	1.83 1.78 1.75 1.72 1.71	2.55 2.48 2.42 2.37 2.35
560 580 589 600 620	$ \begin{array}{c} 10.3 \\ 10.3 \\ \hline 10.3 \\ \hline 10.3 \\ \hline 10.2 \end{array} $	11.6 11.6 11.6 11.5 11.5	1.70 1.68 <u>1.68</u> 1.68	2.33 2.30 2.29 2.29 2.28
640 650 660 680 700	$ \begin{array}{c} 10.2 \\ 10.2 \\ \hline 10.2 \\ 10.2 \\ 10.1 \end{array} $	$ \begin{array}{r} 11.5 \\ 11.5 \\ \hline 11.4 \\ 11.4 \\ 11.4 \end{array} $	1.67 1.67 1.66 1.65 1.64	$\begin{array}{r} 2.27 \\ \underline{2.26} \\ 2.26 \\ 2.23 \\ 2.23 \end{array}$

COLOUR VALUES RELATIVE TO CIE ILLUMINANT C

	R_{1}	R_2	$im_{R}^{}$ 1	$im_{R_{\hat{Z}}}$
x	.305	.304	.300	.298
У	.310	.309	. 304	.301
Y%	10.4	11.7	1.72	2.36
λ.,	475	475	473	473
${\stackrel{\scriptscriptstyle{\wedge}}{P}}{}^{\mathbf{d}}_{\mathbf{e}}$	2.6	3.0	5.1	6.5

probe analyses at the Natural History Museum, Great Britain, were undertaken at 20 kV, with a beam current of 2.50×10^{-8} amps on the Faraday cage. There was some evidence of beam damage, even when a moving or rastered beam was used, and the results (using pure Bi and FeS standards) suggested an ideal formula of Bi₈O₉(SO₄)₃, a common decomposition product of hydrated bismuth oxide sulphates (Margulis *et al.*, 1967).

Analyses performed on a Cameca SX-50 electron microprobe at the Geological Survey of Canada with a moving and slightly defocused beam (~10 µm diameter) at 15 kV and 20 nA

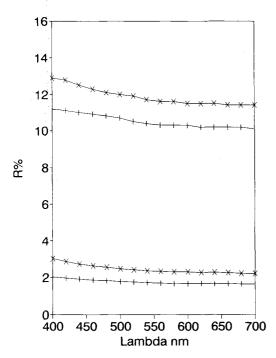


Fig. 2. Reflectance spectra in air and in oil for cannonite.

(with synthetic bismuthinite, natural baryte standards and the PAP correction program of Pouchou and Pichoir, 1984) gave an empirical formula based on 7 oxygen atoms of Bi_{1.99}O(OH_{1.04})₂S_{0.99}O₄. This is identical to synthetic [Bi₂O(OH)₂]SO₄, the structure of which has been described by Aurivillius (1964) and by Golič *et al.* (1982).

Although there was no direct evidence to suggest OH rather than H₂O, there being insufficient pure material for water analysis, structural considerations (Aurivillius, 1964; Golič *et al.*, 1982) suggest infinite double chains of formula Bi₂O(OH)₂²⁺ and thus the preferred ideal formula is Bi₂O(OH)₂SO₄ rather than Bi₂O₂SO₄.H₂O. The electron microprobe analyses are given in Table 2.

X-ray powder and single-crystal study

Two crystals, elongate $[\overline{1}02]$, were mounted and studied by precession single-crystal methods employing Zr-filtered Mo radiation. One crystal was mounted approximately parallel, and the other approximately normal to the precession camera dial axis. The reciprocal lattice levels collected were: $hk0 \rightarrow hk2$, $h0l \rightarrow h3l$, $0kl \rightarrow 2kl$, $\overline{1}02* \wedge b*$ and $\overline{1}01* \wedge b*$.

Cannonite is monoclinic with space group $P2_1/c$ (14). The refined unti-cell parameters: a7.700(3), b13.839(6), c5.686(2)Å, $\beta109.11(3)$ °, V572.5(4)Å³ and a:b:c=0.5564:1:0.4109, are based on 32 reflections, between 4.162 and 1.489 Å, in the X-ray powder pattern for which unambiguous indexing was possible. All possible reflections down to 1.45 Å were visually examined on single-crystal precession films. These unit-cell parameters are in their reduced form as indicated by a cell reduction computer program, and are virtually identical to those reported by Golič *et al.* (1982) for synthetic $[Bi_2O(OH)_2]SO_4$. The crystallography, combined with the formula

	Bí	S	0	н ₂ 0	Total (wt%)
1 range	74.03 72.87-75.01	5.68 5.55-5.81	16.97	[3.32]	[100.00]
2	74.10	5.69	17.02	3.19	100.00

^{1 -} Average of 10 analyses with 0 calculated by stoichiometry and ${\rm H}_2{\rm O}$ calculated by difference.

^{2 -} Ideal formula Bi₂O(OH)₂SO₄.

C. J. STANLEY ET AL.

TABLE 3. X-ray powder data for cannonite

<u>Iest.</u>	dAmeas.	dAcalc.	h <u>k</u> 1	Iest.	dÅmeas.	dAcalc.	hkl
30	7.30	7.28	100	10	2.080	2.082	24 2
30	6.94	6.92	020	3	2.049	2.050	341
30	6.45	6.44	110			1.986	340
50	0.10	5.01	120	90	1.984	1.982	Ī52
35	5.02	5.01	011	25	1.945	1.944	2 61
5	4.87	4.88	111			1.909	142
3	4.24	4.24	021	30	1.907	1.904	321
20	4.162	4.164	121	3	1.884	1.886	202
10	3.896	3.896	130	15	1.868	1.869	212
60	3.644	3.639	111			1.855	071
-		3.518	210	15	1.851	1.855	421
40	3.513	3.500	031			1.852	342
		3.494	211			1.824	350
60	3.466	3.460	040	30	1.822	1.822	123
25	3.314	3.312	121	20	1.791	1.790	412
100	3.206	3.201	221			1.776	431
70	2.924	2.920	131	3	1.773	1.776	013
20	2.840	2.843	231	25	1.750	1.751	171
50	2.782	2.782	112	35	1.733	1.734	023
3	2.690	2.686	002			1.686	323
5	2.609	2.607	202	10	1.684	1.682	441
5	2.558	2.562	212			1.681	432
10	2.500	2.498	241	5	1.671	1.671	360
		2.465	221	5	1.656	1.656	242
5	2.460	2.445	151	3	1.639	1.642	Ī81
25	2.423	2.425	300	20	1.626	1.626	333
10	2.389	2.389	310			1.592	072
10	2.308	2.307	060	10	1.589	1.590	043
20	2.290	2.288	102			1.589	362
10	2.225	2.228	331	_		1.575	272
		2.203	250	3	1.575	1.572	181
30	2.200	2.192	302			1.560	281
3	2.146	2.147	330	40	1.561	1.559	252
15	2.116	2.119	061			1.518	423
				10	1.514	1.512	4 52
				20	1.501	1.501	521
				10	1.489	1.489	431

^{114.6} mm Debye-Scherrer powder camera; Cu radiation, Ni filter (λ Cu $K\alpha$ = 1.54178 A)

intensities visually estimated

derived from the electron microprobe analyes, confirm that cannonite is the naturally occurring analogue of this synthetic compound.

Fully indexed 114.6 mm Debye-Scherrer camera X-ray powder data are presented in Table

3. The data are unique and do not bear resemblance to any inorganic compound listed in the PDF file up to and including Set 41. With Z=4 and using the empirical formula of $Bi_{1.99}O(OH_{1.04})_2S_{0.99}O_4$, the calculated density is

not corrected for shrinkage and no internal standard indexed with a 7.700, b 13.839, c 5.686 Å, β 109.11°

6.515 g/cm³, in excellent agreement with the measured density of 6.5(1) g/cm³ given by Golič *et al.* (1982) for the synthetic analogue.

Acknowledgements

We thank David Walker and Laura Radburn (GSC) for the scanning electron photomicrographs reproduced in Fig. 1, and Bob Symes and Richard Herrington (tNHM) for their comments on the manuscript.

References

- Aurivillius, B. (1964) The crystal structures of Bi₂O₂. SO₄.H₂O and BiOHSeO₄.H₂O. *Acta Chem. Scand.*, **18**, 2375–8.
- Criddle, A. J., Stanley, C. J., Chisholm, J. E., and Fejer, E. E. (1983) Henryite, a new copper-silver telluride from Bisbee, Arizona., *Bull. Mineral.*, **106**, 511–7.

- Golič, L., Graunar, M., and Lazarni, F. (1982) *Catena*-Di-μ-hydroxo-μ₃-oxo-dibismuth(III) sulphate. *Acta Cryst.*, **B38**, 2881–3.
- Margulis, E. V., Grishankina, N. S., Novoselova, V. N., and Maletina, E. D. (1967) Hydrolysis of bismuth sulphates. Russ. J. Inorg. Chem., 12, 1072-5.
- Pouchou, J. L. and Pichoir, F. (1984) A new model for quantitative X-ray microanalysis. *La Recherche Aerospatial*, 3, 167–92.
- Radtke, A. S., Taylor, C. M., and Frost, J. E. (1967) Bismuth and tin minerals in gold- and silver-bearing sulphide ores, Ohio Mining District, Marysvale, Utah. U.S. Geol. Survey Prof. Paper, 575-D, D127-30.
- Stanley, C. J., Jones, G. C., Hart, A. D., Keller, P., and Lloyd, D. (1991) Barstowite, 3PbCl₂.PbCO₃.H₂O, a new mineral from Bounds Cliff, St Endellion, Cornwall., *Mineral. Mag.*, 55, 121-5.

[Manuscript received 30 April 1992]