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Author(s)	Yosimura, Toyohumi
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CALEDONITE AND LEADHILLITE FROM THE TOROKU MINE, MIYAZAKI PREF., JAPAN

By

Toyohumi YOSIMURA

Contribution from the Department of Geology and Mineralogy, Faculty of Science, Hokkaidō Imperial University, No. 213.

I. INTRODUCTION

The Toroku mine in Miyazaki Prefecture, Kyūsyū, Japan, consists of workings on pneumatolytic-pegmatitic tin-ore veins which are noted for their boron minerals such as axinite, datolite, danburite(1) and tourmaline. These deposits were probably formed by emanations from the quartz porphyry, which is now seen as dikes exposed in the vicinity of the mine, or from related masses at greater depth. The country rocks are quartzite, slate and limestone of the Palaeozoic formation.(2) The later hydrothermal solution has replaced the limestone and deposited silver-lead ores. The Hukidani(3) adit of the Toroku mine has been developed in such a deposit for nearly a century.

A few years ago a beautiful drusy cavity was found in the ore body and a piece of the wall of the druse, thickly mounted with crystals of caledonite, leadhillite, cerussite and mimetite, was sent to the author by Mr. K. SINODA, the superintendent of that mine. The author, afterwards, had the opportunity of visiting this mine, and engaging in some mineralogical studies of these druse minerals at the Mineralogical Institute of Tōkyō Imperial University. In this paper the results of these examinations are presented with some new data recently obtained.

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(1) Z. HARADA: Jour. Fac. Sci. Hokkaidō Imp. Univ., Ser. IV, Vol. IV, 153–164, (1938).

(2) The age of the formation was suggested by Mr. G. IIZAKA on the basis of the determination of *Fusulina* collected from the limestone near the mine. G. IIZAKA: Jour. Geol. Soc. Tōkyō, Vol. **40**, p. 229 (1933).

(3) 吹谷坑.

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II. CALEDONITE

1. Crystal forms.

Caledonite occurs as beautiful blue crystals as long as 3 mm, usually elongated to the direction of the crystallographic a-axis. The dominant forms are: (001) (010) (011) (110); smaller and infrequent forms are: (111) (201) (012) (225) (223) (221). (225) is a new form. Reflections on the faces of form (201) were extraordinarily fine. Fig. 1 shows the stereographic projection of the forms of the idealized crystal of the caledonite, and Fig. 2 the clinographic drawing thereof.

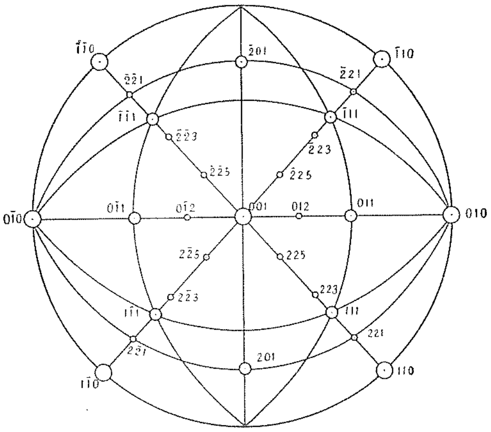

Fig. 1. Stereographic projection of the forms of caledonite.

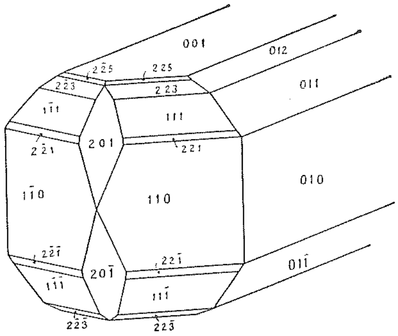

Fig. 2. Clinographic drawing of a crystal of caledonite.

Interfacial angles measured and calculated are contained in Table 1. According to the system of Miller-Dana, caledonite is rhombic with the axial ratios:—

$$a : b : c = 0.9163 : 1 : 1.4032$$

TABLE 1. Interfacial angles of caledonite.

	Measured	Calculated(1)
$100\wedge110$	42° 26′	42° 30′
$001\wedge101$	56 52	56 51.5
$001\wedge011$	54 30.5	54 31.5
$201\wedge20\bar{1}$	36 9.5	36 10
$111\wedge011$	41 43	41 47.5
$111\wedge225$	24 41	24 24.5

(225); new form.

SCHRAUF(2) and EREMEYEV(3) reported it to be monoclinic and measured the angle β as follows:

$\beta = 89°\ 18'$.......... Schrauf.
$\beta = 88°\ 22'$.......... Eremeyev.

As the present crystals gave fine reflections on the faces of (110) and (201) the readings on these faces were employed in calculating the following four interfacial angles.

$$110\wedge20\bar{1} = 45°\ 24'$$
$$1\bar{1}0\wedge20\bar{1} = 45°\ 25'$$

$$110\wedge201 = 45°\ 12'$$
$$1\bar{1}0\wedge201 = 45°\ \ 6'$$

The four angles must be equal to each other if caledonite is rhombic, while the actually measured differences between them are a little greater than those expected from the limit of error of goniometry as shown above. The author, therefore, tentatively calculated on the basis of these angles the following crystallographic elements;

$$\beta = 89°\ 28'$$
$$a : b : c = 0.9028 : 1 : 1.4033$$

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(1) Calculated from the constants given in "Dana: System of Mineralogy (1920) p. 924."

(2), (3) Literatures cited from "Dana: System of Mineralogy":
SCHRAUF: Ber. Ak. Wien, **64** (1871).
EREMEYEV: Mem. Acad. St. Pet., **31** (1883).

Although the Toroku caledonite is rhombic in its crystal-habit (Fig. 3)(1) and the optical orientations are also in accordance with the rhombic symmetry, the possibility of its belonging to the monoclinic system may not be denied without further detailed examinations.

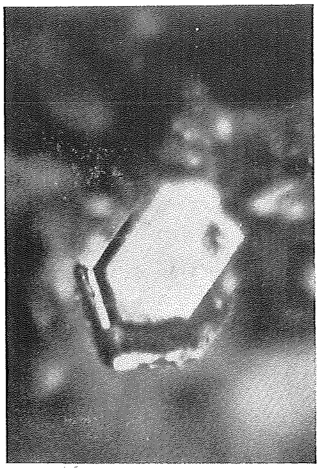

Fig. 3. A crystal of caledonite. ×40.

2. Physical properties.

Cleavage; (001) good, (010) (100) distinct. Specific gravity; $d_4^{23} = 6.13$. Hardness; $H = 3\frac{1}{2}$. Colour deep blue to cobalt-blue, sometimes with a greenish tinge.

Transparent. Lustre subadamantine. Pleochroism weak.

$$X \geq Y \geq Z$$

The optical orientations are;

$$X = a, \quad Y = b, \quad Z = c.$$

The optic axial plane parallel to (010), 2V very large. $\alpha_D = 1.820.$(2) Birefringence strong.

3. Chemical properties.

Easily soluble in acid with effervescence. Leaves a white residue consisting of leadsulphate. The results of chemical analysis are given in Table 2. About 5% of leadsulphate was lost on burning with a filter paper.

The following atomic ratios and the chemical formulas are obtained from the results of the analysis:—

$$(Pb+Cu) : (SO_3, CO_2, O_2H_2) = 1 : 1$$

Atomic ratio... $Pb : Cu = 8 : 3$

$$SO_4 : CO_3 : O_2H_2 = 4 : 2 : 5$$

Formula....... $(Pb, Cu)(SO_4, CO_2, O_2H_2)$,

or more empirically;

$$(Pb_8 Cu_3)\ \{(SO_4)_4 (CO_3)_2 (O_2H_2)_5\}$$

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(1) Compare this figure with the leadhillite crystal shown in Fig. 5.

(2) The indices of refraction of caledonite from Inyo Co. Calif. were measured by E. S. LARSEN: Bull. U. S. G. S. No. 679, p. 52 (1916).

$\alpha = 1.818$

$\beta = 1.866$ (−) $2V = 85° \pm 5°$.

$\gamma = 1.909$

TABLE 2. Chemical analysis of caledonite.

	wt. % 1.	wt. % 2.	wt. % 3.	Mol. ratio.	
PbO	66.58	66.80	66.69	298	412
CuO	9.39	8.75	9.07	114	
SO_3	12.48	12.38	12.43	155	415
CO_2	2.55	4.03	3.29	75	
H_2O	3.49	3.19	3.34	185	
As_2O_5	—	tr	tr		
FeO	—	—	—		
Insoluble	0.40	—	0.20		
	94.89	95.15	95.02		

1) Analysed by the writer in 1932 at the Mineralogical Institute, Tōkyō Imp. Univ.
2) Analysed by the writer in 1936 at the Min. Inst., Hokkaidō Imp. Univ.
3) Average of 1) and 2).

In Table 3 is given the comparison of the composition of the Toroku caledonite with three earlier analyses, and in Table 4 is compared the chemical formula with those previously reported.

TABLE 3. Comparison of chemical compositions of caledonite.

	1.	2.	3.	4.
PbO	66.69	69.71	67.7	66.93
CuO	9.07	9.24	10.7	9.26
SO_3	12.43	15.81	15.6	13.89
CO_2	3.29	1.43	1.9	3.06
H_2O	3.34	3.70	3.5	3.66
Insoluble	0.20	—	—	2.39
	95.02	99.94	99.4	99.11

Locality	Analyst	Literature
1) Toroku Mine:	Yosimura:	(1938)
2) Leadhills Mine:	Flight:	ST. MASKELYNE & FLIGHT; J. Chem. Soc., **27** 101 (1874).
3) Leadhills Mine:	N. Collie:	N. COLLIE; J. Chem. Soc, **55** 91 (1889).
4) Challacollo, Chile:	Liebert:	G. BERG; T. M. P. Mitt., **20** 390 (1901).

TABLE 4. Chemical formulas of caledonite.

Chemical formula	Literature
$6PbSO_4 . 4PbCO_3 . 3CuCO_3$	Brooke (1820).
$5PbSO_4 . 2Pb(OH)_2 . 3Cu(OH)_2$	Flight (1874).
$4(Pb, Cu)(SO_4 . CO_3) . 3(Pb, Cu)(OH)_2$	Collie (1889).
$2PbSO_4 . 2Pb(OH)_2 . CuSO_4 . Cu(OH)_2$	Rammelsberg (1895).
$5(SO_4)_4 . Pb(PbOH)_6 . 2(CO_3)_4 . Cu(CuOH)_6$	Groth. (1905).
$(Pb_8 Cu_3) \{(SO_4)_4 (CO_3)_2 (O_2H_2)_5\}$	Yosimura (1938).

III. LEADHILLITE

1. Crystal forms.

Leadhillite occurs as coarse-grained masses constituting the main portion of the druse. Isolated crystals are rarely seen. The forms noted are as follows:—

The dominant forms; (001) (110) (011) (437) $(\bar{4}34)$ $(\bar{4}18)$.

Small and impersistent forms; (101) (410) (012) (111) $(\bar{3}38)$.

The following angles measured on the two-circle goniometer are sufficiently close to those calculated(1) (Table 5).

TABLE 5. Leadhillite. Measured and calculated angles.

	Measured	Calculated
$001\wedge012$	46° 47′	47° 56′
$001\wedge\bar{4}34$	65 57	66 4
$00\bar{1}\wedge01\bar{1}$	65 29	65 42
$110\wedge\bar{4}3\bar{7}$	71 53	71 50
$110\wedge01\bar{1}$	35 50	37 43
$\bar{4}34\wedge01\bar{1}$	62 46	61 21
$41\bar{8}\wedge01\bar{1}$	54 40	57 13
$\bar{4}34\wedge012$	35 38	36 7
$\bar{4}10\wedge012$	72 36	72 43
$110\wedge012$	49 30	49 53

Four and multiples of four are seen frequently among the indices of the observed crystal forms of the Toroku leadhillite. In Fig. 4 is shown the stereographic projection of the idealized crystal form of this mineral and in Fig. 5 the clinographic drawing thereof. Development of the crystal forms of the leadhillite shown in Fig. 5 is clearly illustrative of the monoclinic symmetry of this mineral.

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(1) After Dana: System of Min., p. 929 (1920).

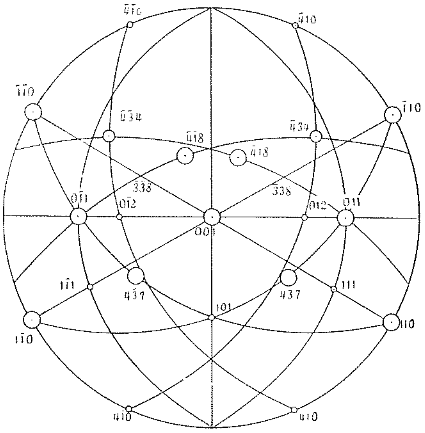

Fig. 4. Stereographic projection of the forms of leadhillite.

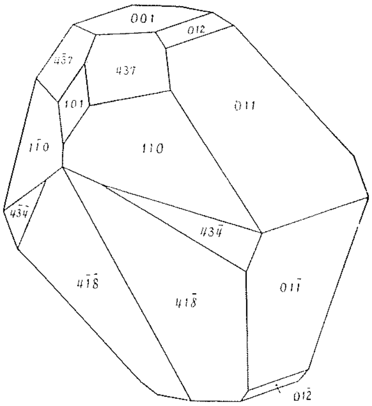

Fig. 5. Clinographic drawing of a crystal of leadhillite.

2. Physical properties.

Twinnings are seen frequently (Fig. 6), but it was difficult to determine their law. The cleavage is basal (001), perfect and easy. Adamantine lustre on the perfect cleavage is characteristic of this mineral, being reliable for distinction of leadhillite from cerussite which has no good cleavage. Colourless or white when pure, but usually stained brown, yellow or green owing to the contamination of limonite, mimetite or caledonite respectively.

Fig. 6. Twinned crystals of leadhillite. ×8.

Specific gravity; $d_4^{20} = 6.62$. Hardness; $H = 3$.

Optically negative, $(-)2V \doteqdot 10°$.

The acute bisectrix X is perpendicular to the perfect cleavage.

Indices of refraction are remarkably high and the birefringence is very strong. $\alpha \geqq 1.85$.

No impressions were left on a photographic plate on which it had been left for a week.

3. Chemical properties.

Easily soluble in acids with effervescence and leaves for a time a white residue. A brown impure specimen was subjected to the chemical analysis which yielded the results given in Table 6.

The insoluble matter which was separated by treating with hot nitric acid consisted chiefly of limonite contaminated with some oxide of arsenic.

TABLE 6. Chemical analysis of leadhillite.

		wt. % 1.	wt. % 2.	Mol. ratio.	
	PbO	66.42	76.62	296	19
	CuO	2.55	2.94	32	2
	SO_3	6.03	6.95	75	5
	CO_2	9.81	11.30	223	14
	H_2O^+	1.90	2.19	106	6
	As_2O_5	0.40	—		
	H_2O^-	0.28	—		
Insoluble	Fe_2O_3	9.04	—		
	As_2O_5 P_2O_5	1.85	—		
	Others	0.88	—		
		99.16	(100.00)		

(1) Leadhillite from the Toroku Mine; Analysis by the present author in 1936.
(2) Essential components of (1) corrected to 100%.

The formula was calculated as follows:

$$(Pb_{17}Cu_2)\ \{(SO_4)_5\ (CO_3)_{14}\}\ .\ 2Pb(OH)_2\ .\ 4H_2O$$

The chemical composition and the formula of the Toroku leadhillite are compared with other known examples in the following Tables 7 and 8. The mineral from the Toroku mine would better be termed "cupriferous leadhillite."

TABLE 7. Chemical compositions of leadhillite.

	1.	2.	3.	4.
PbO	76.62	81.3	80.80	82.44
CuO	2.94	—	—	—
SO_3	6.95	7.3	8.17	7.33
CO_2	11.30	11.5	9.18	8.14
H_2O	2.19	1.8	2.00	1.68
	(100.00)	101.9	100.15	99.59

1) Toroku Mine; YOSIMURA (1938).
2) Leadhills Mine; N. COLLIE (1889).
3) Sardinia; C. HINTZE (1875).
4) Granby, Montana; PIRSON and WELLS (1894).

TABLE 8. Chemical formulas of leadhillite

Formula	Author
$Pb_6\{(SO_4)_2(CO_3)_4\} . Pb(OH)_2 . H_2O$	HINTZE (1874).
$Pb_{14}\{(SO_4)_5(CO_3)_9\} . 4Pb(OH)_2 . H_2O$	LASPEYRES (1877).
$(Pb_{17}Cu_2)\{(SO_4)_5(CO_3)_{14}\} . 2Pb(OH)_2 . 4H_2O$	YOSIMURA (1938).

IV. OCCURRENCE AND GENESIS

1. Occurrence and genesis.

The silver-ore deposit of the Hukidani adit of the Toroku mine are pneumatolytic-metasomatic veins developed in a Palaeozoic limestone. The dominant constituent minerals are arsenopyrite, galena and zincblende; a small quantity of cassiterite is found with other pneumatolytic minerals such as fluorite, axinite, tourmaline, quartz, garnet and vesuvianite. Sometimes the cassiterite is worked as a tin-ore. Secondary oxidations are seen in a wide range along fissures near the surface resulting in numerous druses full of limonite and other oxidation products. A few of them are filled with plumbiferous minerals, the most important of which is leadhillite. In a drusy cavity with a wall thickly lined with leadhillite crystals, were found beautiful clusters of caledonite crystals (blue) and cerussite crystals (white).

Some tiny crystals of leadhillite (white) and mimetite (yellow) were also observed among them. All of them are the products of the secondary oxidation and have mutually intimate genetical relationships. Azurite, malachite, linarite and nontronite were also found as oxidation products in this mine, but were not seen in the druse mentioned here.

2. Cerussite.

Cerussite occurs in the druse as large crystals sometimes 2 cm. long. These crystals are elongated parallel to the crystallographic a-axis, with the following crystal faces;

Well-developed forms; (001) (021) (010) (110) (112) (121) (102).

Small and impersistent forms; (111) (211) (130) (120).

In Figs. 7 and 8 are presented the stereographic projection of the idealized crystal form of the Toroku cerussite and its clinographic drawing respectively.

Pseudohexagonal cyclic twinnings are frequently seen, terminated by a plane in which the faces (001) of the twinned individuals are

TABLE 9. Cerussite; measured and calculated angles.

	Measured	Calculated
$110\wedge1\bar{1}0$	62° 52′	62° 45′
$011\wedge0\bar{1}1$	71 49	71 44
$021\wedge0\bar{2}1$	110 30	110 40
$130\wedge1\bar{3}0$	57 20	57 19
$012\wedge0\bar{1}2$	39 22	39 45
$112\wedge1\bar{1}2$	58 16	58 16
$111\wedge\bar{1}11$	87 37	87 42
$121\wedge\bar{1}21$	68 0	67 59
$211\wedge100$	27 32	27 30

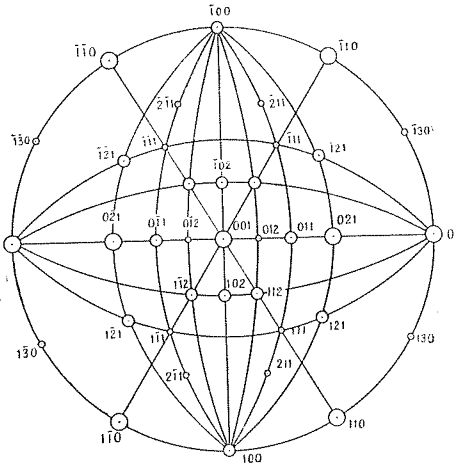

Fig. 7. Stereographic projection of the forms of cerussite.

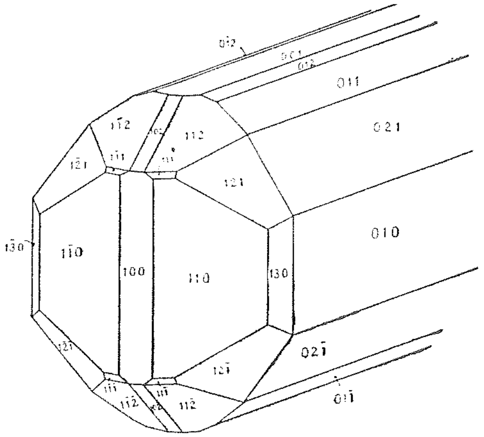

Fig. 8. Clinographic drawing of a crystal of cerussite.

orientated in common (Fig. 9). A clear colourless single crystal was subjected to the determination of the specific gravity which was found as:

$$d_4^{21} = 6.78$$

This value is a little higher than those described in ordinary textbooks of mineralogy.

Usually colourless, often somewhat tinged blue, green or yellow. Optically negative, 2V nearly zero.

Refringence examined was as follows:

$$\alpha = 1.807. \text{ Birefringence very strong.}$$

A pure specimen consisting of colourless crystals was analysed by the author with the following results (Table 10).

TABLE 10. Analysis of cerussite.

	1.	2.
PbO	82.5	83.5
CO_2	16.2	16.5
H_2O	0.0	—
Insoluble	0.0	—
	98.7	100.0

1) Toroku Mine ; YOSIMURA, (1938).
2) Theoretical value for $PbCO_3$.

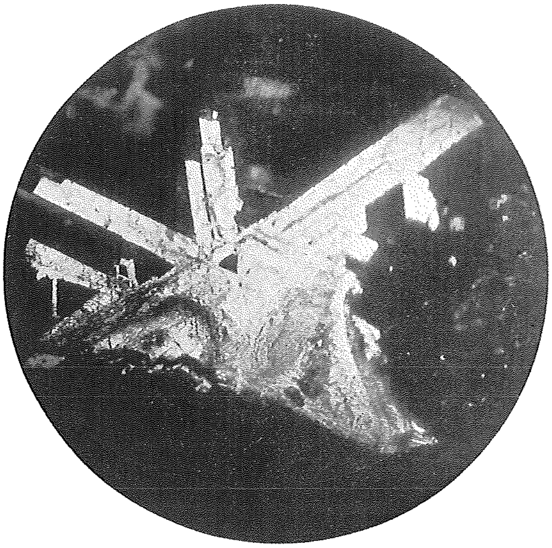

Fig. 9. The terminal plane of a pseudohexagonal cyclic twinning of cerussite. ×10.

Fig. 10. A crystal of mimetite showing hexagonal pyramidal face. ×50.

3. Mimetite.

Sulphur-yellow crystals of mimetite were found sporadically distributed on the leadhillite mass, often showing hexagonal-pyramidal crystal faces, as shown in Fig. 10. The abundance of arsenic oxide in this mineral was detected by the qualitative analysis. Optically uniaxial negative, and shows very weak birefringence under the microscope, while the indices of refraction are markedly higher than 1.85.