

Dukeite from the Kinkei mine, Chino City, Nagano Prefecture, Japan

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Abstract Dukeite is found in small cavities of quartz–chromian muscovite vein from the Kinkei mine, Chino City, Nagano Prefecture, Japan. It occurs as bright yellow hemispherical aggregates up to 2 mm in diameter composed of minute lath-like crystals in association with very minute rhombic crystals of waylandite. The specimens were collected from an outcrop of gold ore deposit. An electron microprobe analysis for the most Te-rich dukeite gave Bi₂O₃ 85.77, CrO₃ 11.83, TeO₃ 0.81, H₂O (calc.) 1.66, total 100.07 wt.%. The empirical formula is: Bi_{23.98}(Cr_{7.71}⁶⁺Te_{0.30}⁶⁺)_{Σ8.01}O₅₇(OH)₆·3H₂O on the basis of O = 66 excluding H₂O. The strongest eight lines of the X-ray powder diffraction pattern obtained by using a Gandolfi camera [*d* in Å (*I*) (*hkl*)] are: 7.67 (10) (002), 3.84 (12) (004), 3.77 (14) (220), 3.38 (100) (222), 2.69 (31) (224), 2.56 (8) (006), 2.18 (16) (600), 2.12 (9) (226). An electron microprobe analysis for the associated waylandite gave Bi₂O₃ 38.81, CaO 0.43, Al₂O₃ 22.11, Fe₂O₃ 5.54, P₂O₅ 23.19, As₂O₅ 1.18, H₂O (calc.) 9.11, total 100.37 wt.%. The empirical formula is: (Bi_{0.99}Ca_{0.05})_{Σ1.04}(Al_{2.57}Fe_{0.41})_{Σ2.98}(P_{1.94}As_{0.06})_{Σ2.00}O₈(OH)₆ on the basis of O = 11 excluding H₂O. Dukeite and waylandite were formed by the decomposition of chromite, phosphates such as monazite-(Ce), xenotime and apatite, and Bi-minerals such as native bismuth and tellurobismuthite.

Key words: dukeite, waylandite, Kinkei mine

Introduction

Dukeite, Bi₂₄Cr₈⁶⁺O₅₇(OH)₆·3H₂O, is an extremely rare mineral described by Burns *et al.* (2000). It was recognized as a museum specimen from the mineral collection deposited at Duke University, North Carolina, USA. The specimen was labelled as pucherite and collected from the Posse mine, São José de Brejaúba, Minas Gerais, Brazil. Dukeite is late-stage products in association with pucherite, schumacherite, hechtsbergite and bismutite (Burns *et al.*, 2000).

During the study on minerals from the Kinkei mine, Chino City, Nagano Prefecture, Japan, we have found dukeite and waylandite in quartz–chromian muscovite rock.

The present paper deals with the second occurrence of dukeite in the world and the associated waylandite.

Occurrence

We collected the studied specimen from an outcrop of the gold deposits of the Kinkei mine, Chino City, Nagano Prefecture, Japan (35°56'16"N, 138°9'36"E). Gomi (1998) introduced the history and mining geology of the Kinkei mine. According to his description, the gold ore deposits were developed from the 1500s and were mined intermittently to 1950. The ore bodies are located in mainly talc-muscovite-chlorite quartz schist belonging to Sanbagawa metamorphic terrain. At the time, we can recognize such ore minerals as gold, bismuth, tellurobismuthite, tetradymite, tsumoite, and gersdorffite in quartz veins and abandoned ore at the dump.

Dukeite occurs as bright yellow hemispherical aggregates up to 2 mm in diameter composed of minute lath-like crystals around 5 μm in length

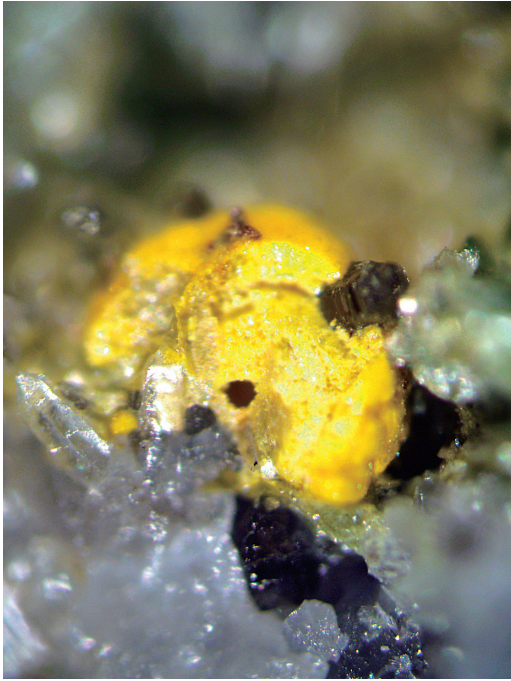


Fig. 1. Hemispherical aggregate of dukeite in cavity of quartz vein. Field view: approximately 3×4 mm.

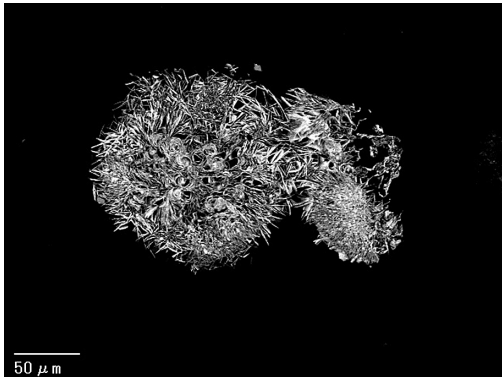


Fig. 2. Back-scattered electron image of dukeite aggregate composed of minute lath-like crystals.

on small rock crystals in cavities of quartz vein (Figs. 1 and 2). The quartz vein is characterized by the association with abundant greenish chromian muscovite (fuchsite) (Fig. 3) and also minor of chromian dravite, chromian andalusite, chromite, florencite-(Ce) (Nakamura *et al.*, 2009), monazite-(Ce), xenotime, apatite, and

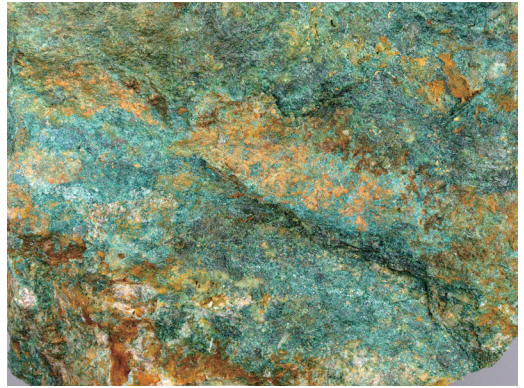


Fig. 3. Quartz-chromian muscovite rock including dukeite-bearing quartz veins. Field view: approximately 6×4.7 cm.

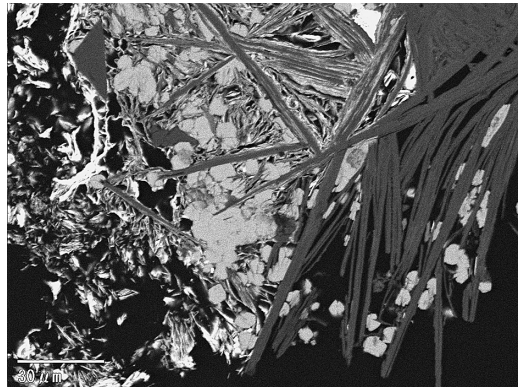


Fig. 4. Back-scattered electron image of minute rhombic waylandite (light), fibrous or lath-like dukeite (bright), and lamellar chromian muscovite (dark).

rutile. Under the electron microscope, very minute rhombic crystals of waylandite are observed in association with dukeite and chromian muscovite (Fig. 4).

X-ray Crystallography

The powder X-ray diffraction patterns of dukeite were obtained by using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered $\text{CuK}\alpha$ radiation. The calculated unit cell parameters were $a = 15.070(3)$ and $c = 15.366(4)$ Å. The powder X-ray diffraction data are given in Table 1

Table 1. Powder X-ray diffraction data for dukeite from the Kinkei mine, and the Posse mine (Burns *et al.*, 2000).

<i>h</i>	<i>k</i>	<i>l</i>	1			2		3	
			d obs.	d calc.	<i>I</i> / <i>I</i> ₀	d obs.	<i>I</i>	d	<i>I</i>
1	0	1				9.915	5	9.926	2
0	0	2	7.67	7.68	10	7.650	50	7.647	12
1	1	0						7.534	2
2	0	0	6.45	6.53	3	6.492	5	6.524	2
2	0	1				6.010	10	6.001	3
1	1	2				5.392	3		
2	0	2				4.966	10	4.963	4
2	1	1				4.699	3		
2	1	2				4.131	3		
2	0	3				4.012	30	4.017	16
0	0	4	3.84	3.84	12	3.812	40	3.823	22
2	2	0	3.77	3.77	14	3.745	20	3.767	13
3	1	1				3.519	1		
2	2	2	3.38	3.38	100	3.382	100	3.379	100
2	0	4				3.299	2	3.299	2
4	0	0	3.25	3.26	5	3.272	10	3.262	3
4	0	1				3.189	10	3.190	3
4	0	2				2.998	10	3.001	3
3	2	1				2.938	5	2.938	2
4	1	0				2.840	1		
4	0	3				2.747	3	2.748	1
2	2	4	2.69	2.69	31	2.681	70	2.683	34
4	1	2						2.668	1
3	2	3						2.581	1
0	0	6	2.56	2.56	8	2.541	30	2.549	12
3	3	0						2.511	1
4	0	4						2.482	1
4	2	0		2.47		2.467	3	2.466	1
4	2	1	2.45	2.44	4	2.431	30	2.435	11
3	3	2	2.41	2.39	3	2.382	3		
4	2	2				2.340	20	2.347	7
4	1	4	2.28	2.29	1	2.277	1		
4	2	3				2.216	25	2.220	6
6	0	0	2.18	2.18	16	2.175	40	2.175	16
2	2	6	2.12	2.12	9	2.106	40	2.111	15
4	2	4						2.072	3
4	3	2				2.064	10		
4	0	6				1.999	3	2.008	1
6	1	1				1.968	1		
4	2	5				1.916	20	1.920	8
6	0	4	1.892	1.893	6	1.888	20	1.890	7
7	0	1				1.848	1	1.850	1
4	4	2	1.829	1.830	6	1.826	20	1.829	6
6	2	0	1.808	1.810	2	1.807	3		
6	2	1				1.789	1		
3	3	6							
4	2	6				1.766	10	1.772	1
6	2	2				1.754	10	1.761	1
7	1	0				1.724	1		
5	2	5							
2	2	8	1.711	1.711	7	1.701	50	1.705	13
6	2	3						1.705	4
4	4	4	1.691	1.691	4	1.685	10	1.690	3
6	0	6	1.657	1.658	5	1.651	20	1.654	7
6	2	4						1.636	1
4	2	7				1.633	15	1.635	2
8	0	1				1.618	5	1.622	3
5	3	5				1.590	5		
7	1	4				1.570	1		
8	0	3				1.550	30	1.554	7
0	0	10	1.534	1.537	2	1.526	5	1.529	2
4	4	6				1.509	5	1.515	1
8	0	4						1.500	1
6	4	0						1.497	1
6	4	1	1.490	1.490	3	1.487	15	1.490	4
7	2	4				1.468	3		
6	4	3				1.434	5	1.436	2
2	2	10	1.422	1.423	2	1.414	10	1.417	2
4	2	9				1.396	10	1.399	1
8	2	2	1.398	1.400	1			1.400	1
8	2	3				1.371	1		
6	4	5	1.344	1.346	1	1.342	20	1.344	5
8	0	7						1.307	2
6	0	10						1.251	2
6	4	7	1.236	1.237	1			1.235	1
2	2	12	1.211	1.212	1			1.207	3

1: Dukeite from the Kinkei mine, $a = 15.070(3)$, $c = 15.366(4)$ Å.

2: Dukeite from the Posse mine, Brazil, $a = 15.039(5)$, $c = 15.259(5)$ Å. (Burns *et al.*, 2000)

3: Calculated powder X-ray pattern from the crystal structure of dukeite from the Posse mine, Brazil. $a = 15.067$, $c = 15.293$ Å.

with those of dukeite from the Posse mine (Burns *et al.*, 2000). The present unit cell parameters are slightly larger than those of the original one. It is considered that the TeO_4 tetrahedra larger than the CrO_4 enlarge the unit cell, because the present dukeite includes small amounts of Te.

Chemical Composition

The chemical analyses of the present dukeite and the associated waylandite were carried out using a WDS (JXA 8900L) (20kV, 20nA, 2 μ m beam diameter). Table 2 shows the chemical composition of most Te-rich and Te-poor dukeite from the Kinkei and the Posse mines (Burns *et al.*, 2000). Also the chemical composition of

Table 2. Chemical composition of dukeite from the Kinkei mine and the Posse mine (Burns *et al.*, 2000).

Wt.%	1	2	3	4
Bi_2O_3	85.77	85.60	85.06	86.03
CrO_3	11.83	11.98	11.65	12.31
TeO_3	0.81	0.43	—	—
V_2O_5	—	—	0.59	—
$\text{H}_2\text{O}^{\text{calc}}$	1.66	1.65	1.67	1.66
Total	100.07	99.66	98.97	100.00
O = 66				
Bi	23.98	24.02	23.95	24.00
Cr	7.71	7.83	7.64	8.00
Te	0.30	0.16	—	—
V	—	—	0.43	—
Σ	8.01	7.99	8.07	8.00
H	12.00	12.00	12.18	12.00

1, 2: Kinkei mine (This study)

3: Posse mine (Burns *et al.*, 2000)

4: $\text{Bi}_{24}\text{Cr}_8\text{O}_{57}(\text{OH})_6 \cdot 3\text{H}_2\text{O}$

Table 3. Chemical composition of waylandite from the Kinkei mine, the Kawazu mine (Yamada *et al.*, 1999), Wampewo pegmatite (Von Knorring and Mrose, 1963) and the Pestormel mine (Clark *et al.*, 1986).

Wt.%	1	2	3	4	5
Bi_2O_3	38.81	34.85	28.28	34.84	40.04
BaO	—	—	—	1.01	—
SrO	—	2.87	—	—	—
CaO	0.43	0.72	2.93	0.75	—
Al_2O_3	22.11	23.52	29.27	26.52	26.28
Fe_2O_3	5.54	4.18	—	***0.81	—
CuO	—	—	—	0.81	—
P_2O_5	23.19	20.71	22.15	23.96	24.39
As_2O_5	1.18	—	—	—	—
SiO_2	—	—	4.68	0.15	—
SO_3	—	3.08	—	—	—
H_2O	*9.11	**10.07	***12.89	**11.15	9.29
Total	100.37	100.00	100.20	100.00	100.00

*, calculation, **, difference, ***, H_2O^+ 12.34 + H_2O^- 0.55, ****: as FeO

O = 14

Bi	0.99	0.88	0.63	0.83	1
Ba	—	—	—	0.04	—
Sr	—	0.16	—	—	—
Ca	0.05	0.08	0.27	0.07	—
Σ	1.04	1.12	0.90	0.94	—
Al	2.57	2.70	2.96	2.90	3
Fe	0.41	0.31	—	0.06	—
Cu	—	—	—	0.06	—
Σ	2.98	3.01	2.96	3.02	—
P	1.94	1.71	1.61	1.88	2
As	0.06	—	—	—	—
Si	—	—	0.40	0.01	—
S	—	0.22	—	—	—
Σ	2.00	1.93	2.01	1.89	—
H	6.00	6.55	7.06	6.89	6

1: Kinkei mine (This study)

2: Kawazu mine (Yamada *et al.*, 1999)

3: Wampewo pegmatite (Von Knorring & Mrose, 1963)

4: Restormel mine (Clark *et al.*, 1986)

5: $\text{BiAl}_3(\text{PO}_4)_2(\text{OH})_6$

waylandite from the Kinkei mine, the Kawazu mine (Yamada *et al.*, 1999), Wampewo pegmatite (Von Knorring and Mrose, 1963) and the Restormel mine (Clark *et al.*, 1986) are demonstrated in Table 3. The present materials are characterized by including small amounts of Te in dukeite, and As and Fe in waylandite. Two empirical formulae of dukeite are: $\text{Bi}_{23.98}(\text{Cr}_{7.71}^{6+}\text{Te}_{0.30}^{6+})_{\Sigma 8.01}\text{O}_{57}(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ and $\text{Bi}_{24.02}(\text{Cr}_{7.83}^{6+}\text{Te}_{0.16}^{6+})_{\Sigma 7.99}\text{O}_{57}(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ on the basis of O = 66 assuming with 6H₂O by calculation. The empirical formula of waylandite is: $(\text{Bi}_{0.99}\text{Ca}_{0.05})_{\Sigma 1.04}(\text{Al}_{2.57}\text{Fe}_{0.41}^{3+})_{\Sigma 2.98}(\text{P}_{1.94}\text{As}_{0.06})_{\Sigma 2.00}\text{O}_8(\text{OH})_6$ on the basis of O = 14 assuming with 3H₂O by calculation.

Discussion

Why is extremely rare dukeite? The one of most reason is that the combination with Bi and Cr is not easily expected in ordinary geological environment because Bi is a chalcophile element but Cr is a lithophile element. The gold ore bodies of the Kinkei mine probably were formed when chromite-bearing ultramafic rock was metasomatized by later intrusion of high temperature Si, Al, and K-rich hydrothermal solution including such heavy metal component as Au, Bi, Te, Ni, Co etc. As a result of such geological event the rare assemblage of Cr and Bi may be realized at the Kinkei mine. Under a microscope chromite is enclosed by quartz and shows distinctly relict texture. Released Cr from decomposed chromite was firstly fixed into such silicates as muscovite, dravite, and andalusite. At the latest stage dukeite was produced by decomposition of tellurobismuthite, tetradymite or tsumoite as source of Bi and Te, and relict chromite as source of Cr. Then also waylandite formed by decomposition of probably muscovite as source

of Al and apatite except the above Bi-bearing minerals.

Incidentally the only locality name of the second dukeite, Val-d'Ajol, Lorraine, France, is reported (Web site of Mineral Data), but the occurrence is uncertain because of no references. This is the substantial second occurrence in the world.

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