Andyrobertsite and Calcioandyrobertsite: Two New Minerals from the Tsumeb Mine, Tsumeb, Namibia

Mark A. Cooper and **Frank C. Hawthorne**
Department of Geological Sciences
University of Manitoba
Winnipeg, Manitoba, Canada R3T 2N2

William W. Pinch
Department of Earth Sciences
Royal Ontario Museum
100 Queen's Park
Toronto, Ontario, Canada M5S 2C6

Joel D. Grice
Research Division, Canadian Museum of Nature
PO Box 3443, Station D
Ottawa, Ontario, Canada K1P 6P4

ABSTRACT

Andyrobertsite, ideally $KCdCu_5(AsO_4)_4[As(OH)_2O_2](H_2O)_2$, and **calcioandyrobertsite**, ideally $KCaCu_5(AsO_4)_4[As(OH)_2O_2](H_2O)_2$, are two new minerals from the Tsumeb mine, Namibia. Both minerals form a lamellar intergrowth that is crystallographically continuous, and hence only average physical properties can be measured. There is only one specimen known, an aggregate of overlapping plates that radiate outward from a common center; the individual plates are up to 0.1 x 5 x 10 mm and the aggregate is pyramidal, approximately 1.4 cm long and 1 cm across the base. The aggregate is perched on cuprian adamite and zincian olivenite with minor tennantite. Andyrobertsite and calcioandyrobertsite have a platy habit with forms {100} (dominant), {210}, {001}, {10$\bar{2}$} and {011}; no twinning was observed. They are electric blue with a pale-blue streak, a vitreous luster, and they do not fluoresce under longwave or shortwave ultraviolet light. The aggregate has a Mohs hardness of 3, is brittle with a conchoidal fracture, and has good cleavage parallel to (100). The strongest five reflections in the X-ray powder diffraction pattern of a bulk sample are [d(Å), I, hkl]: 9.64(100)(100); 3.145(50)(130,122); 4.46(40)(120); 3.048(40)($\bar{2}$22); 2.698(40)(320). The refined cell dimensions for a monoclinic cell with $P2_1/m$ space-group symmetry are a = 9.810(4), b = 10.034(6), c = 9.975(4) Å, β = 101.84(4)°, V= 961.0(6) Å^3, a:b:c = 0.9777:1:0.9941, Z = 2. The calculated density for an aggregate crystal of andyrobertsite and calcioandyrobertsite in a 50:50 proportion of the end-members is 4.011 g/cm^3. In transmitted light, andyrobertsite [calcioandyrobertsite] is biaxial negative with α = 1.720(3) [1.713(3)], β = 1.749(1) [1.743(1)], γ = 1.757(1) [1.749(1)], 2V(meas.) = 50(5) [50(5)]°, 2V(calc.) = 55 [48]°, with X ^ a = 12° (in β obtuse), Y = b, Z = c; it is non-pleochroic. Electron-microprobe data for andyrobertsite (calcioandyrobertsite) are As_2O_5 = 47.58(49.56), CuO = 31.72(32.86), ZnO = 0.19(0.04), CdO = 6.48(1.26), MnO = 0.64(0.86), CaO = 1.36(3.52), K_2O = 4.00(4.05), H_2O(calc.) = 4.44(4.61), sum = 96.41(96.75) weight %; the corresponding unit formulae (based on 22 anions) are $K_{1.03}(Cd_{0.61},Ca_{0.30}Mn_{0.11})(Cu_{4.85}Zn_{0.03})(AsO_4)_{4.04}[As(OH)_2O_2](H_2O)_2$ and $K_{1.01}(Cd_{0.12}Ca_{0.74}Mn_{0.14})(Cu_{4.85}Zn_{0.01})(AsO_4)_{4.06}[As(OH)_2O_2](H_2O)_2$, where the OH and H_2O groups were assigned from knowledge of the crystal structure; the infrared spectrum indicates the presence of OH and H_2O in the structure. The minerals are named for Andrew C. Roberts (born 1950), mineralogist with the Geological Survey of Canada; he has contributed significantly to the science of mineralogy and has had extensive interactions with the collecting community, providing expertise and scientific support to many collectors around the world.

INTRODUCTION

It was a warm, sunny afternoon in mid-September, 1996. One of us (WWP) stopped to chat with Carol Smith in the parking lot of the Holiday Inn in Denver during the annual Denver Gem and Mineral Show. In the course of the conversation, Carol mentioned a large and spectacular crystal of "keyite" that she had seen for sale in the room of mineral dealer Carter Rich. Immediate investigation

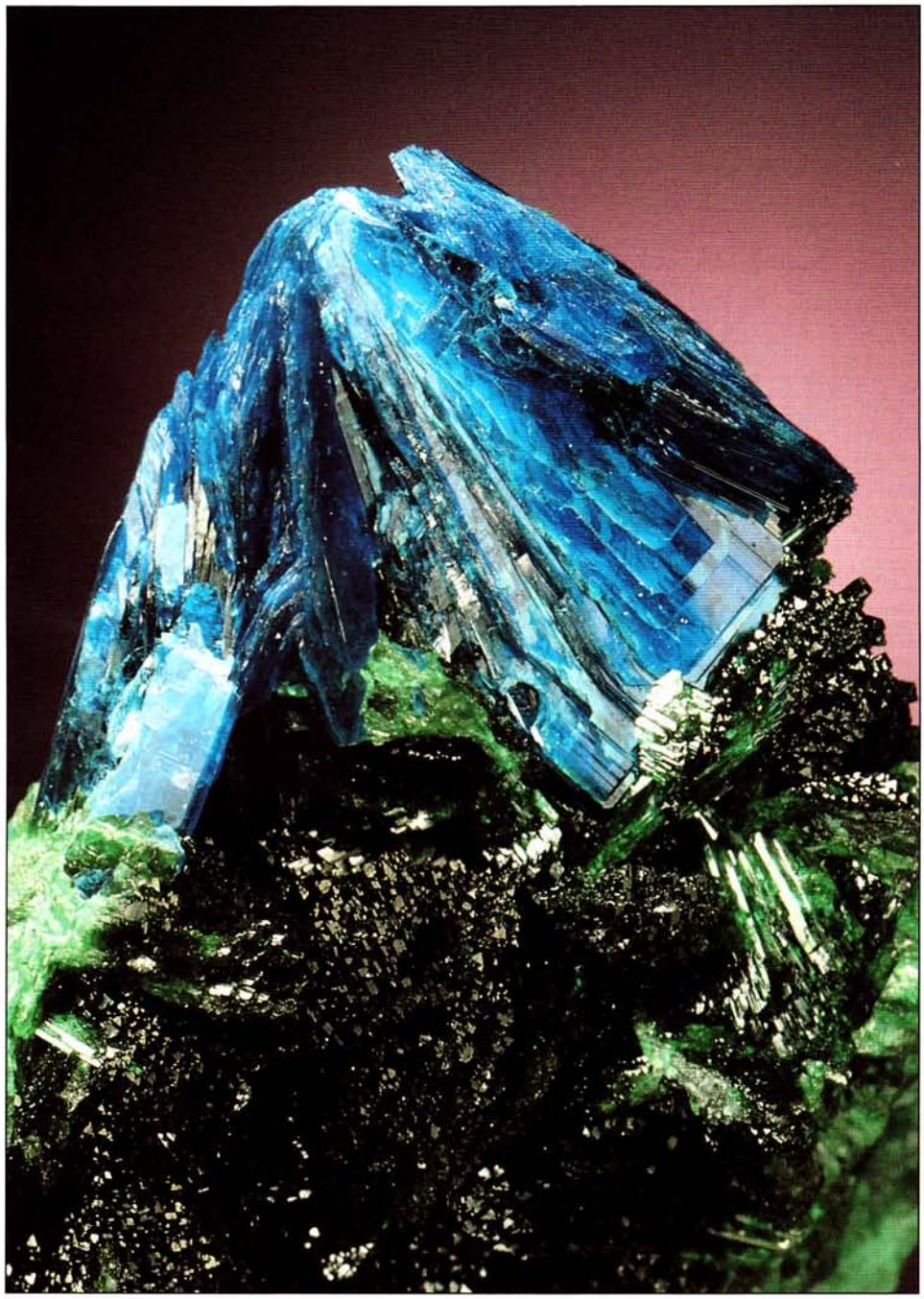

Figure 1. **Andyrobertsite-calcioandyrobertsite (electric blue), 1.5 cm high and 1.8 cm across the base. William Pinch specimen, Jeff Scovil photo.**

revealed a beautiful electric-blue crystal cluster, perhaps the most spectacular rare-mineral specimen any of us had ever seen. The label stated "Keyite crystals, with Zn-deficient analysis provided, from Tsumeb, S.W.A."; but the mineral clearly did not resemble keyite, even though the microprobe analysis contained Cd, Cu and As. The absence of Zn and the presence of K indicated that this must be a new mineral.

HISTORY OF THE SPECIMEN

The specimen first belonged to Richard Baughart, a mining engineer working at Tsumeb; it was reported to have been found in the early 1950's. At a later date, it was acquired by Ben Staskun, a close friend of Baughart. Staskun donated it to a well-known U.S. university. In the early 1990's, the university sold the mineral for a few dollars in a dispersal sale. It was purchased by Steve Kudums who sent a piece of it to Tony Nikisher of *Excalibur Minerals* for analysis by SEM-EDS. Dr. Kudums then exchanged the specimen with Carter Rich for a zincite crystal from Franklin, New Jersey. Carter Rich put the piece up for sale, and it was purchased by one of the authors (WWP) in Denver on September 15, 1996.

The new mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type material has been deposited with the Royal Ontario Museum (specimen numbers M47022 and M47110) and the Smithsonian Institution (specimen number NMNH 171487).

PHYSICAL PROPERTIES

The single specimen consists of an aggregate of overlapping plates which radiate outward from a common center; individual plates are up to 0.1 x 5 x 10 mm. The aggregate is pyramidal in shape, approximately 1.4 cm long and 1 cm across the base, and is perched on cuprian adamite and zincian olivenite (see cover photo). The minerals have a platy habit with forms {100} (dominant), {210}, {001}, {10$\bar{2}$} and {011}; no twinning was observed.

Andyrobertsite and calcioandyrobertsite are electric blue (Fig. 1) with a pale-blue streak and a vitreous luster; crystals do not fluoresce under longwave or shortwave ultraviolet light. The minerals are brittle with a conchoidal fracture and a good cleavage parallel to (100); Mohs hardness is 3 and the calculated density is 4.011 g/cm^3 for a 50:50 mixture of the end members.

OPTICAL PROPERTIES

In transmitted light, andyrobertsite and calcioandyrobertsite are greenish blue and non-pleochroic; dispersion is moderate, asymmetric with r < v. The optical orientation is X ^ *a* = 12° (in β obtuse), Y = *b*, Z = *c*; 2V, measured by the Tobi method, is 50(5)°. The refractive indices (Table 1) were measured in monochromatic light (λ = 590 nm); α was measured on a spindle stage, β and γ were measured on a grain mount. Although crystals have pervasive fine-scale chemical zoning and measured optical properties are necessarily an aggregate of different chemical compositions, we could measure optical properties on parts of crystals that are predominantly Cd-rich (andyrobertsite) and Cd-poor (calcioandyrobertsite); the measured optical properties and corresponding chemical compositions are listed in Table 1.

Table 1. **Optical properties, average chemical compositions and unit formulae for andyrobertsite and calcioandyrobertsite.**

	Andyrobertsite	*Calcioandyrobertsite*
α	1.720(3)	1.713(3)
β	1.749(1)	1.743(1)
γ	1.757(1)	1.749(1)
2*V* (obs)°	50(5)	50(5)
2*V* (calc)°	55	48
As_2O_5	47.58	49.56
CuO	31.72	32.86
ZnO	0.19	0.04
CdO	6.48	1.26
MnO	0.64	0.86
CaO	1.36	3.52
K_2O	4.00	4.05
(H_2O)	4.44	4.61
Sum	96.41	96.75
Unit formulae		
As	5.04	5.06
Cu	4.85	4.85
Zn	0.03	0.01
Σ	4.88	4.86
Cd	0.61	0.12
Mn	0.11	0.14
Ca	0.30	0.74
Σ	1.02	1.00
K	1.03	1.01
OH	2	2
H_2O	2	2

CHEMICAL COMPOSITION

Crystals were analyzed chemically with a Cameca SX-50 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, a beam size of 20 μm and counting times on peak and background of 30 and 15 seconds, respectively. The following standards were used: Cd: Cd metal; Cu: olivenite; As: cobaltite; K: orthoclase; Ca: diopside; Mn: spessartine; Zn: gahnite. Data were reduced using the φρZ method of Pouchou and Pichoir (1985).

Back-scattered-electron (BSE) imaging shows fine lamellar zoning on a scale of microns (Fig. 2). Detailed electron-microprobe analysis shows the zoning to involve variable Cd, Ca and Mn

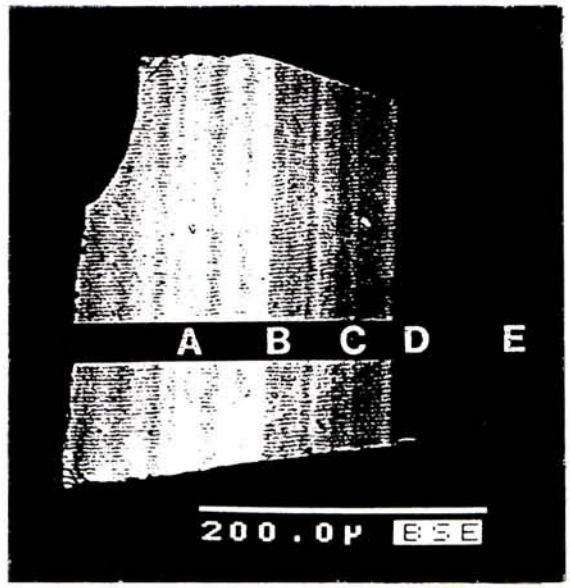

Figure 2. **Back-scattered-electron image of a crystal of andyrobertsite-calcioandyrobertsite showing lamellar alternation of the two minerals. The edge of the crystal closest to E is the outer growth margin.**

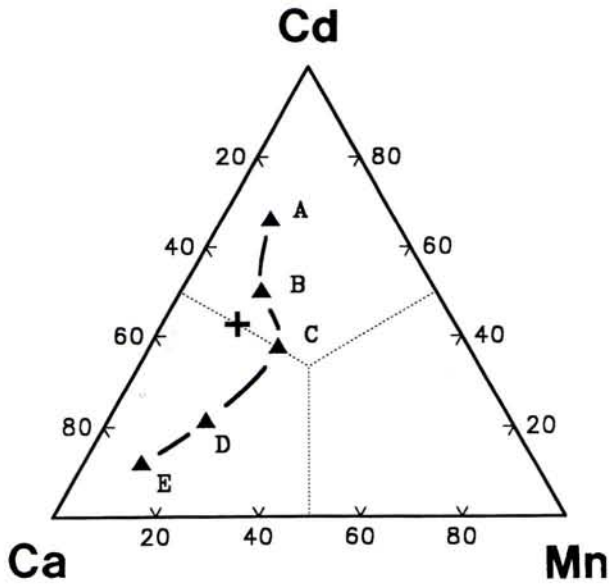

Figure 3. **The variation in chemical composition of the crystal of andyrobertsite-calcioandyrobertsite shown in Figure 2. The cross marks the bulk composition of the crystal.**

Table 2. **Chemical compositions of andyrobertsite and calcioandyrobertsite from Figure 2.**

	A	*B*	*C*	*D*	*E*	+
As_2O_5	47.19	47.87	48.75	48.97	49.6	48.35
CuO	31.38	32.07	32.39	32.87	32.75	32.17
ZnO	0.08	0.06	0.21	0.10	0.00	0.13
CdO	7.12	5.29	4.09	2.33	1.30	4.60
MnO	0.57	0.92	1.52	1.17	0.69	0.87
CaO	1.15	1.58	1.78	2.86	3.71	2.01
K_2O	4.09	4.03	4.01	4.04	4.07	4.01
(H_2O)	4.41	4.47	4.55	4.57	4.61	4.51
Sum	95.99	96.29	97.30	96.91	96.27	96.63
As	5.04	5.04	5.04	5.03	5.06	5.05
Cu	4.84	4.88	4.84	4.88	4.83	4.85
Zn	0.01	0.01	0.03	0.02	0.00	0.02
Cd	0.68	0.50	0.38	0.21	0.12	0.43
Mn	0.10	0.16	0.26	0.20	0.11	0.15
Ca	0.25	0.34	0.38	0.60	0.78	0.43
K	1.07	1.04	1.01	1.01	1.01	1.02
(H)	6	6	6	6	6	6

+ average composition along the continuous line-traverse A → E.

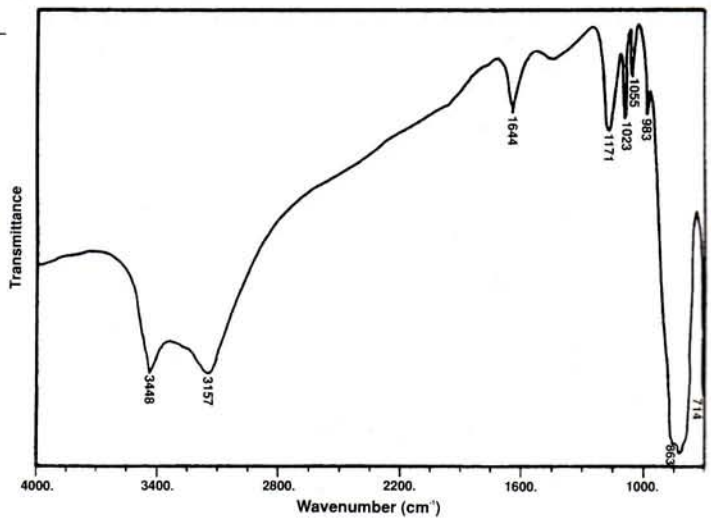

***Figure* 4. The infrared spectrum of andyrobertsite-calcioandyrobertsite.**

with (approximately) constant K, Cu and As. K_2O values were corrected for overlap of the K$K\alpha$ peak and the Cd *L* peak. Selected analyses from the crystal shown in Figure 2 are listed in Tables 1 and 2. The chemical formulae were calculated on the basis of 22 anions including two OH groups and two H_2O groups, as derived from solution and refinement of the crystal structure (Cooper and Hawthorne, 1999) and are given in Table 1. The crystal in Figure 2 involves a ternary solid-solution of Cd, Ca and Mn, all of which occur at the same site in the structure (Cooper and Hawthorne, 1999); the composition varies from A (andyrobertsite) to E (calcioandyrobertsite), and also shows significant variation in the Mn content (Fig. 3). It is apparent from Figure 3 that there are two distinct mineral species present in the crystal of Figure 2, the Cd-dominant species and the Ca-dominant species. Analysis of several grains showed that the Cd species is more abundant, and hence this was assigned the root name; the Ca-rich species was assigned a name by prefixing the root name with "calcio."

Andyrobertsite is the eleventh mineral containing essential Cd, and is also the first doubly acid arsenate mineral (i.e., contains an $[As(OH)_2O_2]$ group).

X-RAY DIFFRACTION

A single-crystal fragment was mounted on a Siemens P4 four-circle X-ray diffractometer and the unit cell (Table 5) was determined by indexing of 48 automatically aligned reflections in the range $40 < 2\theta < 60°$. The crystal structure was determined in the space group $P2_1/m$ (structural details will be reported elsewhere). The X-ray powder-diffraction pattern is reported in Table 5, together with the experimental conditions and the refined cell dimensions.

INFRARED SPECTROSCOPY

Experimental methods are identical to those reported by Roberts *et al.* (1994). The spectrum (Fig. 4) shows a broad absorption at ~3300 cm^{-1} and a sharp weaker absorption at 1644 cm^{-1}, indicating the presence of H_2O in the structure; the sharp absorption at 3448 cm^{-1} is compatible with the presence of OH in the structure.

Table 3. **Chemical compositions of zincian olivenite and cuprian adamite.**

	Zincian Olivenite	*Cuprian Adamite*
As_2O_5	41.41	41.27
ZnO	4.41	26.43
CuO	51.76	31.63
TOTAL	97.58	99.33
As	1.01	1.00
Zn	0.15	0.90
Cu	1.82	1.10
TOTAL	1.97	2.00

Table 4. **Minerals containing essential cadmium.**

Name	*Formula*	*Reference*
Andyrobertsite*	$KCdCu_5^{2+}(AsO_4)_4[As(OH)_2O_2](H_2O)_2$	(1)
Cadmium	Cd	(2)
Cadmoselite	CdSe	(3)
Černýite	Cu_2CdSnS_4	(4)
Greenockite	CdS	(5),(6)
Hawleyite	CdS	(7)
Keyite	$Cu_3^{2+}(Zn,Cu^{2+})_4Cd_2(AsO_4)_6(H_2O)_2$	(5),(8)
Monteponite	CdO	(9)
Niedermayrite	$Cu_4Cd(SO_4)_2(OH)_6(H_2O)_4$	(10)
Otavite	$CdCO_3$	(5)
Quadratite	$Ag(Cd,Pb)AsS_3$	(11)

References: (1) this study; (2) Oleinikov *et al.* (1979); (3) Bur'yanova *et al.* (1957); (4) Kissin *et al.* (1978); (5) Pinch and Wilson (1977); (6) Hurlburt (1957); (7) Traill and Boyle (1955); (8) Cooper and Hawthorne (1996); (9) Anthony *et al.* (1990); (10) Giester *et al.* (1998); (11) Graeser *et al.* (1998).
* Minerals found at Tsumeb are shown in bold type.

Table 5. **X-ray powder-diffraction data for andyrobertsite.**

$I_{est.}$	$I_{calc.}$	dÅ$_{meas.}$	dÅ$_{calc.}$	hkl	$I_{est.}$	$I_{calc.}$	dÅ$_{meas.}$	dÅ$_{calc.}$	hkl
100	100	9.64	9.601	100		3		1.966	051
5	4	7.61	7.678	10$\bar{1}$		2		1.964	150
30	23	7.00	6.997	011	10b	2	1.953	1.962	$\bar{5}$01
3	1	5.00	5.017	020		2		1.954	$\bar{2}$05
30	12	4.81	4.801	$\bar{2}$00		3		1.953	005
	10		4.764	$\bar{1}$02		3		1.927	$\bar{5}$02
40	38	4.46	4.447	120	5	1	1.921	1.917	015
5	5	4.31	4.304	$\bar{1}$12		2		1.917	$\bar{3}$42
*25	20	4.027	4.030	$\bar{1}$02		5		1.889	341
*5	6	3.842	3.839	$\bar{2}$02	10	3	1.885	1.886	510
5	4	3.723	3.712	211		4		1.870	$\bar{2}$24
*15	11	3.493	3.499	022	3	2	1.849	1.849	$\bar{1}$52
*10	10	3.243	3.245	$\bar{3}$01		3		1.827	$\bar{5}$21
50	33	3.145	3.158	130	5	3	1.82$\bar{1}$	1.826	$\bar{5}$03
	49		3.142	122		2		1.821	$\bar{2}$25
*40	49	3.048	3.049	$\bar{2}$22		2		1.820	025
30	12	2.979	2.994	$\bar{2}$03		6		1.796	152
	21		2.971	$\bar{3}$02	10	4	1.793	1.793	$\bar{5}$20
*5	11	2.908	2.906	103		3		1.793	$\bar{4}$24
3	7	2.878	2.872	301		2		1.792	$\bar{3}$43
	4		2.759	032	*15	18	1.766	1.767	$\bar{1}$44
	4		2.754	23$\bar{1}$	3	7	1.746	1.749	044
30	9	2.747	2.744	230		2		1.734	$\bar{4}$40
	7		2.737	32$\bar{1}$	3	1	1.728	1.730	$\bar{3}$25
	5		2.730	023		2		1.728	$\bar{1}$25
*40	40	2.698	2.698	320	3		1.716	1.716	$\bar{5}$23
*15	15	2.648	2.648	$\bar{2}$22		1		1.714	$\bar{1}$53
*30	19	2.565	2.571	$\bar{2}$23		4		1.700	$\bar{3}$50
		8	2.522	$\bar{2}$32	5	5	1.692	1.694	$\bar{4}$05
30	13	2.515	2.515	123		2		1.692	205
	12		2.509	040	*5	4	1.672	1.672	060
*5	12	2.491	2.491	$\bar{1}$04	3	4	1.656	1.661	$\bar{1}$06
3	5	2.452	2.455	302	3	3	1.611	1.614	$\bar{3}$35
	2		2.441	004	*5	8	1.588	1.588	$\bar{5}$22
5	2	2.398	2.400	400		3		1.565	$\bar{2}$62
5	4	2.381	2.385	$\bar{3}$12	3	2	1.561	1.563	442
	2		2.380	$\bar{4}$11		3		1.557	253
3	2	2.322	2.318	$\bar{2}$14		2		1.554	$\bar{3}$52
*15	11	2.283	2.281	$\bar{2}$32		9		1.544	$\bar{6}$22
10	2	2.227	2.231	$\bar{1}$24		10		1.540	$\bar{4}$50
	5		2.221	$\bar{3}$32	25b	3	1.540	1.536	$\bar{5}$05
*5	4	2.203	2.202	$\bar{4}$21		3		1.533	$\bar{2}$62
3	4	2.152	2.152	$\bar{2}$24		4		1.533	$\bar{3}$05
3	5	2.125	2.130	$\bar{1}$42	3	3	1.526	1.527	$\bar{4}$52
*5	3	2.102	2.100	$\bar{2}$42	*5	3	1.509	1.509	235
3	3	2.061	2.059	124	3b	1	1.485	1.483	126
*10	5	2.036	2.036	$\bar{4}$21		1		1.482	$\bar{3}$60
3	3	1.989	1.985	$\bar{3}$41	15	5	1.466	1.468	$\bar{5}$25
						4		1.466	325
					3	1	1.442	1.444	443
						1		1.444	630
					*10	6	1.415	1.415	$\bar{5}$5$\bar{1}$

114.6 mm Debye-Scherrer powder camera; Cu radiation, Ni-filter (λCu$K\alpha$ = 1.54178Å)
Intensities estimated visually; b = broad line
* = lines used for unit-cell refinement
Calculated intensities derived from crystal structure
Not corrected for shrinkage and no internal standard
Indexed on a = 9.810(4), b = 10.034(3), c = 9.975(4) Å, β = 101.84(4)°, V = 961.0(6) Å^3

ASSOCIATED MINERALS

The andyrobertsite-calcioandyrobertsite crystal cluster is perched on dark olive-green zincian olivenite and grass-green cuprian adamite with minor tennantite. The olivenite and adamite were analyzed by electron microprobe; the results are given in Table 3.

Early crystals of cuprian adamite at the base of the sample are overgrown by later zincian olivenite, forming the matrix on which andyrobertsite-calcioandyrobertsite crystallized. The andyrobertsite-calcioandyrobertsite crystals show complex oscillatory zoning (Cd, Ca, Mn) on a scale of a few microns; however, there is a broader zonation over several tens of microns, corresponding mainly to Ca → Cd substitution (A → E, Figs. 2, 3). These compositional variations in all four minerals suggest a fluid becoming relatively depleted in Zn, relative to Cu, prior to the crystallization of andyrobertsite-calcioandyrobertsite, followed by an evolving reversal in the relative activities in solution of Cd and Ca, from Cd > Ca to Ca > Cd during crystallization of andyrobertsite-calcioandyrobertsite.

The discovery of andyrobertsite and calcioandyrobertsite brings the number of minerals with essential Cd to eleven; these are listed in Table 4. Greenockite and hawleyite are reported to occur together by Anthony *et al.* (1990), but no locality is given. With the exception of this possible association and Tsumeb, the other minerals in Table 4 are each the only mineral containing essential Cd at the localities in which they occur. Except for the recently discovered niedermayrite, all known oxide and oxysalt minerals containing essential Cd occur at Tsumeb (Pinch and Wilson, 1977), another unique feature of this amazing mineral deposit.

ACKNOWLEDGMENTS

We thank Andy Roberts for measuring the X-ray powder-diffraction pattern of these minerals and refining the cell dimensions, and J. A. Mandarino and A. Rosenzweig for their comments on this paper. This work was supported by the Natural Sciences and Engineering Research Council of Canada (grants to FCH).

REFERENCES

ANTHONY, J. W., BIDEAUX, R. A., BLADH, K. W., and NICHOLS, M. C. (1990) *Handbook of Mineralogy*. Volume III: *Halides, Hydroxides, Oxides*. Mineral Data Publishing, Tucson.

BUR'YANOVA, E. Z., KOVALEV, G. A., and KOMKOV, A. I. (1957) The new mineral cadmoselite. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, **86**, 626–628 (in Russian).

COOPER, M. A., and HAWTHORNE, F. C. (1996) The crystal structure of keyite, $Cu_3^{2+}(Zn,Cu^{2+})_4Cd_2(AsO_4)_6(H_2O)_2$, an oxysalt mineral with essential cadmium. *Canadian Mineralogist*, **34**, 623–630.

COOPER, M. A., and HAWTHORNE, F. C. (1999) The crystal structure of andyrobertsite, a novel arsenate mineral from Tsumeb, Namibia. *Canadian Mineralogist* (submitted).

GIESTER, G., RIECK, B., and BRANDSTÄTTER, F. (1998) Niedermayrite, $Cu_4Cd(SO_4)_2(OH)_6 \cdot 4H_2O$,a new mineral from the Lavrion Mining District, Greece. *Mineralogy and Petrology*, **63**, 19–34.

GRAESER, S., LUSTENHOUVER, W., and BERLEPSCH, P. (1998) Quadratite Ag(Cd,Pb)(As,Sb)S_3—a new sulfide mineral from Lengenbach, Binntal (Switzerland). *Schweizerische Mineralogische und Petrographische Mitteilungen*, **78**, 489–494.

HURLBURT, C. S., Jr. (1957) The wurtzite-greenockite series. *American Mineralogist*, **42**, 184–190.

KISSIN, S. A., OWENS, D. R., and ROBERTS, W. L. (1978) Cernyite, a copper-cadmium-tin sulfide with the stannite structure. *Canadian Mineralogist*, **16**, 139–146.

OLEINIKOV, B. V., OKRUGIN, A. V. and LESKOVA, N. V. (1979) Native cadmium in traps of the Siberian Platform. *Doklady Akademiia Nauk, SSSR*, **248**, 1426–1428 (in Russian).

PINCH, W. W., and WILSON, W. E. (1977) Tsumeb Minerals; A descriptive list. *Mineralogical Record*, **8**, 5–110.

POUCHOU, J. L., and PICHOIR, F. (1985) "PAP" $\phi(\rho Z)$ procedure for improved quantitative microanalysis. *Microbeam Analysis*, 104–106.

ROBERTS, A. C., ERCIT, T. S., CRIDDLE, A. J., JONES, G. C., WILLIAMS, R. S., CURETON, F. F., and JENSEN, M. C. (1994) Mcalpineite, $Cu_3TeO_6 \cdot H_2O$, a new mineral from the McAlpine mine, Tuolumne County, California, and from the Centennial Eureka mine, Juab County, Utah. *Mineralogical Magazine*, **58**, 417–424.

TRAILL, R. J., and BOYLE, R. W. (1955) Hawleyite, isometric cadmium sulphide, a new mineral. *American Mineralogist*, **40**, 555–559.