

SENGIERITE: A PRELIMINARY DESCRIPTION

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ABSTRACT

A hydrous copper, uranium, vanadium mineral from Katanga, Belgian Congo, with the formula $2\text{CuO} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$, is believed to be a new mineral and is called sengierite in honor of Mr. Edgard Sengier. X-ray diffraction, chemical analysis, spectrographic study, crystallographic measurement, and optical study combine to suggest that the material described is related to carnotite and tyuyamunite, but differs chemically in that it is a definite copper-bearing species. In crystallization it may be quite similar to the other two minerals.

INTRODUCTION

An unusual radioactive mineral has been found in fissures cutting an argillaceous phase of the Mines Series, in the Elizabethville-Jadotville area of Katanga in the Belgian Congo. Chemical, x-ray and crystallographic data indicate that the mineral differs from species previously described. This particular portion of the Mines Series (pre-Cambrian) is described by geologists of the Union Minière as R.A.T. (Roche Argilo-Talqueuse) and consists essentially of chlorite and talc. The mineral occurs in the form of small, green, platy crystals which correspond approximately to the empire green of Ridgway (1912), have a vitreous luster and coat fracture surfaces in a flake-like fashion as shown in Fig. 1.

The fissures containing the crystals occur along a fault which brings the R.A.T. into contact with a dolomite containing minor sulfide mineralization in the form of siegenite. The mineral is accompanied by black oxides containing iron, copper, cobalt, and nickel and also some lustrous yellow volborthite. Less frequently it is found associated with vandenbrandeite, fibrous malachite, garnierite, and chrysocolla. Pitchblende is also found in small pockets along the fault where it has been partly altered to vandebrandeite and kasolite. The mineral is believed to be of supergene origin produced by deposition from solutions containing uranium, vanadium, and copper derived from earlier minerals.

The name *sengierite* is proposed for the new mineral in honor of Mr. Edgard Sengier, Executive Director of the Société Générale de Belgique and Managing Director of the Union Minière du Haut Katanga, in recognition of his efforts in directing war-time mineral production from the Belgian Congo. The Congo production of copper, tin, cobalt, industrial diamonds, and various minerals was much more of a material factor in Allied success than has been generally realized.

The locality which yields the mineral was first recognized by Dr. H. G.

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FIG. 1. Crystals of sengierite distributed on a surface of fractured rock (about one and one half times natural size).

Schuling, Chief Geologist of the Union Minière and Dr. Anton Gray, Chief Geologist of the Kennecott Copper Corporation. The mineral itself was first identified by Mr. Vaes. Confirming studies have since been made at Columbia University on the basis of data and techniques not available at Jadotville. The laboratory work at the University has been carried on with the assistance of Mr. H. D. Holland. We are also indebted to Professor T. I. Taylor of the Department of Chemistry for cooperation in spectrographic studies. We likewise appreciate the courtesy of Dr. Michael Fleischer of the U. S. Geological Survey who read the manuscript on behalf of the Society and offered a number of constructive suggestions.

CRYSTALLIZATION

Sengierite is orthorhombic in crystallization and apparently belongs to the bipyramidal class. The crystals rarely measure as much as two

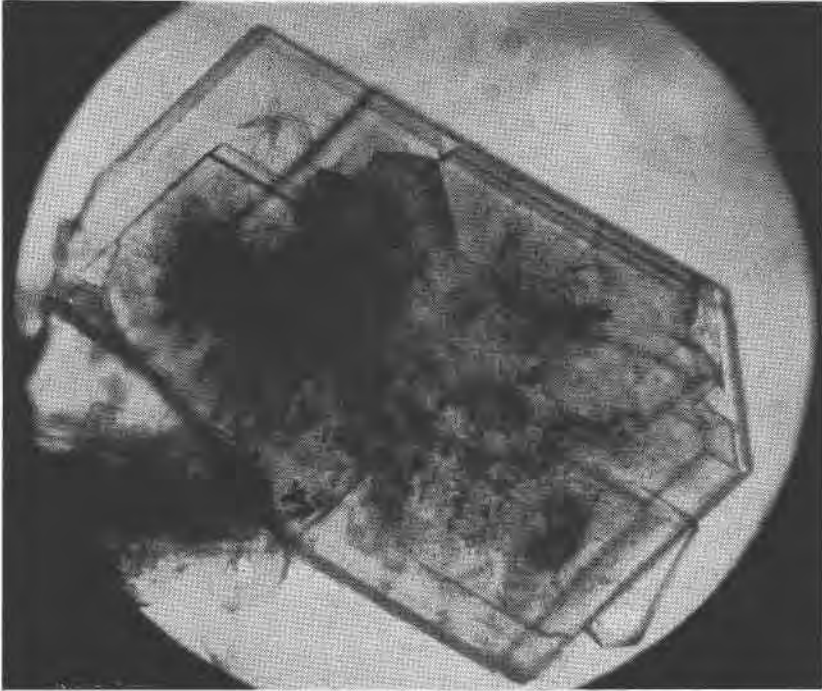


FIG. 2. Photomicrograph of a crystal of sengierite. Magnification about 50.

millimeters across and are ordinarily not more than a fraction of a millimeter in width. The habit is tabular with the thickness usually one-fifth to one-tenth the width. The outline is rhombic, the two opposite acute corners of the section often being truncated by a pinacoid. Crystals show excellent cleavage parallel to (001) and are frequently only singly terminated. The occasional occurrence of doubly terminated bipyramidal crystals leads to the conclusion that the mineral belongs to the bipyramidal class. Figure 2 shows such a doubly terminated crystal. Angles were measured with a two circle goniometer although imperfections in crystal development interfered with the attainment of as much precision as should be possible with such an instrument. Oscillatory development parallel to the basal plane introduces ray-like reflections with the goniometer for certain faces. On the basis of the unit face assumed, the axial ratio is $a:b:c=0.762:1:0.739$.

The forms most frequently observed are (001), (111) and (010). The rhombic prism (110) and dome (011) and the rhombic bipyramids (331) or (441) are often present.

In measuring the interfacial angles six different crystals were selected

with a binocular microscope. Measurements of the rhombic prism (110) were repeated three times for each individual face, the average being recorded. Among the interfacial angles measured $(110) \wedge (\bar{1}\bar{1}0)$ were repeated on 5 crystals; the angles $(\bar{1}\bar{1}0) \wedge (\bar{1}\bar{1}0)$ on three crystals; the angles $(\bar{1}\bar{1}0) \wedge (\bar{1}\bar{1}0)$ on 5 crystals, all giving either good or fair measurements. The weighted average of all measurements yields the angle $(110) \wedge (\bar{1}\bar{1}0)$ of $74^\circ 37'$ used to compute the $a:b$ ratio of $0.762 \pm .001$.

The $b:c$ ratio has been determined on the basis of measurements between the pinacoid (001) and the rhombic bipyramid faces. The bipyramid faces tend to develop multiple reflections along the vertical circles, hence the measurements are less accurate than those of the rhombic section. The weighted average of measurements on six crystals is $(001) \wedge (111) = 50^\circ 40'$ which yields a $b:c$ ratio of $1:0.739 \pm 0.073$.

Although observed angles were not sufficiently well developed on the crystals available for measurement, it seems likely that the forms (331) and (441) are present. Although other bipyramidal forms may be observed, the angles were not considered sufficiently significant for purposes of record.

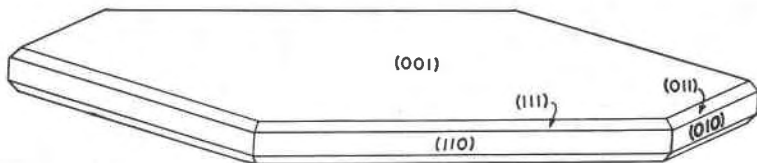


FIG. 3. Sengierite, showing the pinacoids (001) and (010), with the rhombic prism (110), dome (011) and the rhombic bipyramid (111).

OPTICAL PROPERTIES

The dispersion is $v < r$ and the pattern is symmetrical. The angle $2V$ on the basis of micrometer ocular readings is $37^\circ-39^\circ$: Sengierite is biaxial, negative, and yields a good interference figure with strong dispersion. The acute bisectrix is perpendicular to (001) and the plane of the optic axes is parallel to (010). The indices of refraction were determined by the immersion method using melts as follows:

$$\alpha = 1.77; \quad \beta = 1.94; \quad \gamma = 1.97.$$

Interference colors are somewhat obscured by the natural color of the mineral. The pleochroism is distinct with $X=c$ =bluish green; $Y=b$ =olive green; $Z=a$ =yellowish green to colorless. A view of the crystals as observed with the microscope appears in Fig. 3.

CHEMICAL PROPERTIES

An approximate chemical analysis of sengierite on 0.1460 grams of material was made by Mr. Bracq of the Jadotville-Panda Laboratory of the Union Minière as follows:

	Analysis	Recast	Theoretical Composition
CuO	14.82	15.77	14.55
V ₂ O ₅	15.96	16.98	16.65
UO ₃	47.45	50.47	52.34
(Fe, Al) ₂ O ₃	1.43		
H ₂ O	15.77	16.78	16.46
	95.43	99.70	100.00

The above yields the formula $2\text{CuO} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$. Unfortunately, samples with sufficient quantities of separable material to make possible the analytical precision desired do not appear to be available.

In order to obtain confirmation of the chemical nature of the mineral a spectrographic plate was secured showing the lines for sengierite in comparison with the lines of copper, vanadium, and uranium and referred to iron. A portion of this plate enlarged is shown in Fig. 4. It may be observed that each of the lines of sengierite may be matched by a corresponding line for either Cu, V, or U in the portion of the spectrographic plate reproduced. This same comparison would apply throughout the range from 3020 to 4400 Angstroms. In view of this comparison, the spectrographic data would indicate that the essential metallic elements of the sengierite are Cu, V, and U, in confirmation of the chemical determinations.

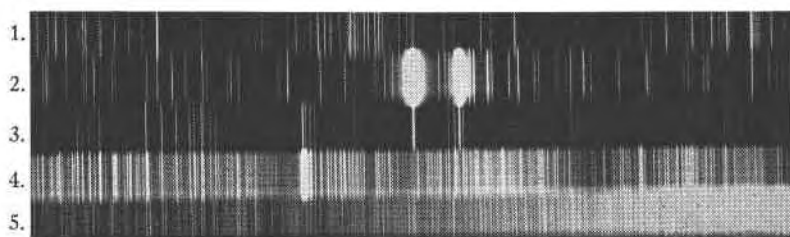


FIG. 4. Comparison of a spectrogram of sengierite with spectrograms of iron, copper, vanadium, and uranium between 3020 Å and 3475 Å.

1. Iron
2. Copper
3. Sengierite
4. Vanadium
5. Uranium

The water content of sengierite was determined on a sample weighing 0.080 gr. and containing 0.0090 gr. of gangue. The loss during heating was found to be as follows:

Temperature	Per cent Loss	Mol. H ₂ O
100° C.	3.94	2.5
300° C.	10.56	6.5
Calcination	15.77	10.

When heated at 300° C. and re-exposed to air for two days the mineral regained water, the loss being 6.48 per cent or 4 molecules H₂O. Thus, it seems likely that the mineral contains 10 molecules of H₂O, six of which are quite stable.

When heated in a closed tube, sengierite loses water, assumes a bronze shade with a metallic luster and becomes opaque. The mineral dissolves readily even in dilute hydrochloric acid. In concentrated acid a brown ring is formed around the grains of the mineral, indicative of the presence of vanadium. The solution gives a test for copper, and after repeated precipitations with ammonia, accompanied by dissolving the precipitate formed in hydrochloric acid, the solution yields enough uranium soluble in acetic acid to yield the microchemical reaction with sodium acetate. Tests for calcium, potassium, magnesium, and phosphate applied to solutions of sengierite have all been negative.

X-RAY DATA

The *x*-ray diffraction pattern obtained for sengierite by radiation from copper through a nickel filter was compared with patterns obtained under similar conditions from samples of carnotite and tyuyamunite from the Egleston Collection of Columbia University. It was found that the patterns obtained from specimens of carnotite, Florence Mining Claim, Camp Marvel, Naturita, Colorado; of "carnotite" from the Copper Prince Mine, Rock Creek, Colorado; "tyuyamunite and carnotite" from Paradox Valley, Colorado; and tyuyamunite, Hudspeth County, Texas, could be arranged on the basis of line spacings to form a series in which carnotite and tyuyamunite are end members, and in which the other two specimens occupy intermediate positions. The pattern obtained from sengierite was similar to the patterns obtained from members of this carnotite-tyuyamunite series, but differed sufficiently from each of the four patterns to suggest its identity outside the series. Sengierite, with 2CuO in the position occupied by K₂O in the carnotite formula and structurally similar, is perhaps not a direct end-member of a carnotite-sengierite series but is presumably a cuprian mineral closely related to carnotite.

TABLE 1. COMPARISON OF INTERPLANAR SPACINGS OF SENGERITE, TYUYAMUNITE, AND CARNOTITE

Sengierite, Katanga		Tyuyamunite, Hudspeth Co., Tex.		Carnotite, Naturita, Colo.		
<i>d</i> in Å	Est. Int.	<i>d</i> in Å	Est. Int.	<i>d</i> in Å	Est. Int.	
9.883	10	10.180	10	11.142	3	
6.566	1	6.620	3	6.425	10	
5.736	1	—	—	—	—	
4.915	10	5.019	9	5.063	3	
4.160	2	—	—	—	—	
4.020	3	4.021	2	—	—	
3.710	3	—	—	—	—	
—	—	3.366	3	3.493	6	
3.153	10	3.202	5	3.208	3	
—	—	3.123	3	3.092	8	
2.951	2	—	—	2.998	3	
2.836	2	—	—	2.822	1	
2.721	1	2.693	1	2.742	2	
2.549	3	—	—	2.552	3	
2.433	3	2.484	1	2.452	2	
—	—	—	—	2.356	$\frac{1}{2}$	Average error = ± 0.005 Å
2.252	1	2.275	1	2.267	1	Max. error = ± 0.015 Å
2.128	3	2.159	1	2.146	3	
2.086	3	2.096	1	2.081	2	
2.052	1	2.039	4	—	—	
2.001	4	—	—	2.016	2	
—	—	1.964	1	1.934	3	
—	—	1.911	2	1.901	2	
1.857	3	1.870	1	1.864	1	
1.802	1	—	—	1.816	1	
1.760	3	—	—	1.756	1	
1.715	2	—	—	—	—	
1.667	1	—	—	1.670	2	
1.632	1	—	—	—	—	
1.588	1	—	—	1.599	2	
1.508	1	—	—	1.500	2	

Table 1 contains data on interplanar spacings for sengierite, carnotite, and tyuyamunite, calculated from the x -ray patterns.

IDENTITY OF SENGERITE

In view of the large number of hydrous uranium minerals the review of the literature in connection with establishing the unique character of a new species is not as simple a procedure as might be desired. However, search of the ordinary journals and the various mineral listings fails to

TABLE 2. SUMMARY OF THE PROPERTIES OF THE HYDROUS URANIUM VANADIUM MINERALS

Properties	Sengterite	Carnotite	Tuyyamunite	Rauvite	Uvanite
Chemical formula	$2\text{CaO} \cdot 2\text{UO}_2 \cdot \text{V}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$	$\text{K}_2\text{O} \cdot 2\text{UO}_2 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$	$\text{CaO} \cdot 2\text{UO}_2 \cdot \text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	$\text{CaO} \cdot 2\text{UO}_2 \cdot 6\text{V}_2\text{O}_5 \cdot 20\text{H}_2\text{O}$	$2\text{UO}_2 \cdot 3\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$
Calculated analyses	$\text{CaO} = 14.6$ $\text{UO}_2 = 52.3$ $\text{V}_2\text{O}_5 = 16.6$ $\text{H}_2\text{O} = 16.5$	$\text{K}_2\text{O} = 10.4$ $\text{UO}_2 = 63.5$ $\text{V}_2\text{O}_5 = 20.1$ $\text{H}_2\text{O} = 6.0$	$\text{CaO} = 6.4$ $\text{UO}_2 = 65.2$ $\text{V}_2\text{O}_5 = 20.7$ $\text{H}_2\text{O} = 7.7$	$\text{CaO} = 2.7$ $\text{UO}_2 = 27.5$ $\text{V}_2\text{O}_5 = 52.5$ $\text{H}_2\text{O} = 17.3$	$\text{UO}_2 = 41.2$ $\text{V}_2\text{O}_5 = 39.3$ $\text{H}_2\text{O} = 19.5$
Crystal system	Orthorhombic $a:b:c$	Orthorhombic $0.81:1:-$	Orthorhombic $1.303:1:2.337$	—	Orthorhombic? —
Habit	Rhombic plates acute $< 74^\circ 37'$	Rhombic plates acute $< 78^\circ$	Elongated plates $(110) \wedge (110) = 75^\circ$	Fine aggregates	Fine aggregates
Cleavage	(001) perfect	(001) perfect	(001) perfect (010) and (100) dist.	—	(two) pinacoids
Hardness, tenacity Sp. Gr.	$2\frac{1}{2}$ —brittle ± 4	4—very brittle 4.46	brittle 3.31—4.35	very brittle —	— —
Luster color streak	Vitreous to adamantine emerald green light green	— yellow to greenish yellow.	Pearly (001); adamantine canary yellow light yellow	— Purple red light brown to yellow.	— brownish yellow —
Indices α β γ	1.76 to 1.77 1.92 to 1.94 1.94 to 1.97 (Vaes) (Kerr)	1.75 to 2.06 1.925 1.895 1.95 1.92 2.08 (Larsen and Berman)	1.670 to 1.77 1.870 to 1.93 1.895 to 1.97 (Larsen and Berman)	1.87 to 1.90	1.817 1.879 2.057
Orientation	$X=c$; bluish green to colorless $Y=b$; olive green $Z=a$; yellowish green	$X=c$; grayish yellow $Y=b$; lemon yellow $Z=a$; lemon yellow	$X=c$; almost colorless $Y=b$; canary yellow $Z=a$; darker yellow	—	X —light brown Y —dark brown Z —greenish yellow
Optic Angle $2V$	37° — 39°	39° — 44° small	36° 40°— 55°	—	52°
Sign	—	—	—	—	+
Plane	\parallel (010)	\parallel (010)	\parallel (010)	—	—
Bxa	\perp (001)	\perp (001)	\perp (001)	—	—
Dispersion	$r < s$ strong	$r < s$ strong	$r < s$ rather strong	—	—

reveal the description of a mineral corresponding exactly to sengierite.

The hydrous copper-uranium minerals are zeunerite, uranospathite, slightly-copper-bearing tyuyamunite, torbernite and metatorbernite, cuprosklodowskite, vandenbrandeite, and uranochalcite. Of these, only the cuprian tyuyamunite also contains vanadium. The hydrous vanadium-uranium minerals uvanite, carnotite, rauvite, and "ferganite"* contain vanadium but not copper. The compositions of the other hydrous uranium minerals have only UO_3 and H_2O in common with that of sengierite.

Of the copper-uranium and vanadium-uranium minerals mentioned above, all except vandenbrandeite, uvanite, rauvite, carnotite, and tyuyamunite contain either arsenic, phosphorus, or sulfur, all of which have been shown to be essentially absent from sengierite. The chemical, optical, and crystallographical properties of the above-mentioned copper-uranium and vanadium-uranium minerals most closely approximating the properties of sengierite are listed in Table 2. It would appear as shown by the chart that carnotite and tyuyamunite are the minerals in this group which are most closely related to sengierite. This has been confirmed by the x -ray diffraction data mentioned above.

Carnotite was first described by Friedel and Cumenge in 1899 from a locality at Montrose, Colorado, as a distinct hydrous uranium vanadate, and reported to have the composition cited below. Shortly thereafter Hillebrand and Ransome (1900) analyzed material from the same locality but obtained a somewhat different composition. In 1910 Crook and Blake described carnotite from Olary, South Australia. The composition cited by these authors was quite similar to that of Hillebrand and Ransome, and is given below. Crook and Blake measured the angles of small rhombic crystals of carnotite and found that the acute angle of the rhombic section was 78° .

Hillebrand again published descriptions of carnotite in 1924. He had found that the water content of carnotite varies strongly with atmospheric conditions and adopted a standard drying procedure for all samples prior to analysis. His bulk analysis for selected carnotite from Temple Mountain, Utah, dried at 20° over sulfuric acid of specific gravity 1.05 is cited below. Hess and Foshag (1926) examined carnotite from Colorado. Their analyses agreed with the hypothetical formula $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 2/3\text{H}_2\text{O}$. Optical measurements gave the value $\alpha = 2.06$ $\gamma = 2.08$, $2V = 50^\circ$. In a later description by the same authors (1927), these results were supplemented by further optical data and an analysis of air-dried material reproduced in Table 3.

* Shown by Nenadkevitch (1912) to correspond to tyuyamunite as pointed out by Dr. Fleischer.

TABLE 3. ANALYSES OF CARNOTITE MENTIONED IN THE TEXT

	Friedel and Cumenge (1899)	Hillebrand and Ransome (1900)	Crook and Blake (1910)	Hillebrand, Hess and Foshag	
				(1924)	(1927)
UO ₃	63.54	61.53	60.8	62.26	65.62
V ₂ O ₅	20.12	20.72	21.4	20.57	21.12
K ₂ O	10.37	7.31	6.6	10.00	9.58
CaO		3.03	1.3	0.66	0.64
H ₂ O	5.95	(-105°) 2.72 (+105°) 2.36	5.0	4.90	1.35
P ₂ O ₅		0.90	trace		trace
BaO(SrO)		1.03			
MgO		0.25	trace	0.30	0.22
Na ₂ O		0.15	2.3	0.16	0.35
PbO			1.7		
CuO				0.07	
SO ₃				0.26	
Fe ₂ O ₃				0.55	0.04
Al ₂ O ₃					0.10
Insol.				0.04	0.32
	99.98	100.00	99.1	99.77	99.40

TABLE 4. ANALYSES OF TYUYAMUNITE

	Nenadkevitch (1912)	Hillebrand (1924) (Fergana)	Hess (1924)	Rode (1925)
UO ₃	63.09	55.85	55.22	56.07
V ₂ O ₅	21.	17.92	17.62	18.92
K ₂ O		0.17	0.47	
CaO	5.99	4.80	5.36	5.08
H ₂ O	7.04	16.61	14.79	17.53
BaO			0.26	0.32
MgO		0.09		0.12
Na ₂ O		0.20		
CuO		0.10		
Fe ₂ O ₃		0.13	1.10	0.86
Tl	trace	trace		
Insol.		3.26	8.51	0.31
	97.12	99.13	100.33	98.71

From these analyses it appears that the formula $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$ where n is a function of the relative humidity and temperature of the surroundings, adequately describes the composition of carnotite. Copper is present only in small amounts. Confusion with sengierite is therefore hardly possible. This is supported further by the meager crystallographic evidence on carnotite which is available.

Tyuyamunite, first described in 1912 by Nenadkevitch, is a hydrous calcium-vanadium-uranium mineral. Some analyses of this mineral are given in Table 4. From these and other analyses the formula was deduced to be $CaO \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$, where n , as in the case of carnotite, depends somewhat on the humidity and temperature of the surroundings. Tyuyamunite has been considered a calcium analogue of carnotite. However, since n is usually much larger than in carnotite, some doubt has been expressed as to the isomorphism of these two minerals.

Crystallographic descriptions of tyuyamunite are to be found, among others, in articles by Hillebrand (1924), Hess (1924), and Dolivo-Dobrovosky (1925). The first of these authors cites Dr. H. E. Merwin who examined scales of tyuyamunite on two specimens supposedly from Paradox Valley, Colorado. He found that the scales were probably orthorhombic and tabular parallel to $c(001)$. The forms present at the boundaries were $a(100)$, $b(010)$, $m(110)$, and $l(120)$. The prism angles mm were 75° and $105^\circ \pm 1^\circ$, and the prism (ll) 67° and $113^\circ \pm 1^\circ$. The crystals were found to be biaxial and negative; the acute bisectrix emerges normal to the plates, and the plane of the optic axes is parallel to $b(010)$. It was found that $2E = 100^\circ - 115^\circ$ and $2V = 45^\circ - 51^\circ$. The refractive indices measured by immersion under the microscope, are $\gamma = 1.965 - 1.968$; $\beta = 1.927 - 1.932$, and $\alpha =$ (calculated) $1.75 - 1.80$. On another specimen it was found that $\gamma = 1.92$, $\beta = 1.895$, α (calculated) $= 1.78$.

Hess (1924) confirms this data. His measurement of $2V = 48^\circ$, $\alpha = 1.72$, $\beta = 1.868(?)$ and $\gamma = 1.953$ agree only approximately with Dolivo-Dobrovosky's values of $2V = 48^\circ$, $\gamma - \beta = 0.028$, $\gamma - \alpha = 0.154$. The latter author gives the axial ratio as $1.303:1:2.337$ on the basis of goniometer measurements of minute platy crystals from Tyuya Muyun. The angles measured were $(001):(110) = 52\frac{1}{2}^\circ$, $(001):(111) = 70\frac{3}{4}^\circ$.

As in the case of carnotite, it is probable that tyuyamunite is related to, but perhaps not identical in crystallization, with sengierite. The grouping of the three minerals together, however, seems justifiable with the potassium, calcium, and copper-bearing members being represented respectively by carnotite, tyuyamunite, and sengierite. While the crystallographic similarity is perhaps not as close as between the long-familiar

autunite and torbernite in the uranite group, the justification for distinctive nomenclature is comparable.

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