THE OCCURRENCE AND PROPERTIES OF METATYUYAMUNITE, $Ca(UO_2)_2(VO_4)_2 \cdot 3\text{–}5H_2O$*

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Abstract

Metatyuyamunite [$Ca(UO_2)_2(VO_4)_2 \cdot 3\text{–}5\ H_2O$], a new mineral, is a dehydration product of tyuyamunite [$Ca(UO_2)_2(VO_4)_2 \cdot 5\text{–}8.5\ H_2O$]. This lower hydrate of tyuyamunite has been collected from more than 35 localities on the Colorado Plateau and from several localities in Fall River County, S. Dak., and Campbell and Johnson counties, Wyo. The optical properties and specific gravity of metatyuyamunite and tyuyamunite are significantly different. Metatyuyamunite samples from two localities in Mesa County, Colo., have been chemically analyzed. The hydration of metatyuyamunite has been examined as a function of water vapor pressure. Plateaus on the dehydration curve are at values of 5 and 8.5 moles of water per mole of $Ca(UO_2)_2(VO_4)_2$. Metatyuyamunite was rehydrated to tyuyamunite by placing it in a moist atmosphere. The *x*-ray diffraction powder patterns of metatyuyamunite and tyuyamunite are distinctly different, indicating a change in phase. Base-exchange studies show that the metatyuyamunite structure may contain several per cent potassium. *X*-ray diffraction powder patterns of this base-exchanged product do not reveal the presence of carnotite [$K_2(UO_2)_2(VO_4)_2 \cdot 1\text{–}3\ H_2O$]. Two samples of metatyuyamunite from Mesa County, Colo., are not in radium-uranium equilibrium, and their Ra/U ages are 25,000 and 150,000 years.

Introduction

Variations in the water content of tyuyamunite have been studied by Hillebrand (1924, p. 202), Rohde (1925, p. 377), and Murata, Cisney, Stieff, and Zworykin (1951, p. 323). Merwin (1924, p. 210) found that the density of the mineral increases as it is dehydrated. An analogous variation in the water content of minerals of the torbernite and meta-torbernite groups has been discussed in papers by Beintema (1938, p. 155), J. W. Frondel (1951, p. 249), C. Frondel (1951*a*, p. 678; 1951*b*, p. 681), Mrose (1950, p. 529), and Nuffield and Milne (1953, p. 476). The water content of sengierite (Vaes and Kerr, 1949, p. 109) should be studied when and if sufficient amounts of the mineral can be made available.

Both the torbernite group and synthetic KUO_2VO_4 have a layer type structure (Beintema, 1938, p. 155; Sundberg and Sillen, 1950, p. 377). In KUO_2VO_4, sheets of $(UO_2VO_4)^-$ are separated by K^+ layers. Tyuyamunite $Ca(UO_2)_2(VO_4)_2 \cdot 5\text{–}8.5H_2O$ has a layer structure with the metal-oxygen sheets bonded together by Ca^{++} ions. This layer structure is stable for values of nH_2O up to 8.5, and the water content ranges down to 3. The hydration-dehydration effect is reversible in the range $3\text{–}8.5H_2O$.

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Metatyuyamunite, a new mineral, contains 3–5 moles of water per mole of $Ca(UO_2)_2(VO_4)_2$ and has distinct *x*-ray powder diffraction pattern and optical properties. Various hydrates within the range of stability have been found in nature, and unless specimens are collected in moisture-proof containers, they may dehydrate before they are examined in the laboratory. Crystal lattice studies of tyuyamunite, carnotite, and sengierite have been made by Donnay and Donnay (1954, p. 323).

OCCURRENCE OF METATYUYAMUNITE

The first specimen of metatyuyamunite examined in the present study was collected by L. R. Stieff in 1948, from an outcrop at the lower portal of the Jo Dandy mine, Montrose County, Colo. Purification of this sample for detailed mineralogic study was not possible because of the fine-grained nature of the metatyuyamunite and the presence of clay. Since 1948, metatyuyamunite has been collected from more than 35 localities on the Colorado Plateau and also from several localities in Fall River County, S. Dak., and in Campbell and Johnson counties, Wyo. The specimens from the Colorado Plateau occur in the Shinarump conglomerate (Triassic), Chinle formation (Triassic), Todilto limestone (Jurassic), and Salt Wash sandstone member of the Morrison formation (Jurassic). In most localities tyuyamunite and metatyuyamunite form pulverulent masses or are disseminated in sandstone or limestone. Tyuyamunite and metatyuyamunite are difficult to purify as they are commonly mixed with carnotite—the potassium uranyl vanadate—and other impurities.

Yellow crystals forming radial aggregates of metatyuyamunite from the Small Spot (pl. 1) and May Day mines, Calamity Mesa, Mesa County, Colo., have been studied in detail. The crystals, which are as long as 3 mm., filled fractures in the Salt Wash sandstone member of the Morrison formation (Jurassic). The metatyuyamunite formed on gypsum, which coated the fracture walls. In these samples the metatyuyamunite and tyuyamunite occurred in such a manner that by very careful work they could be hand-separated and purified.

PHYSICAL PROPERTIES

Metatyuyamunite is canary yellow to greenish yellow. It has perfect micaceous (001) cleavage. Cleavage on (010) and (100) is distinct. The crystals have an adamantine luster and massive material is distinctly waxy. Hardness is about 2 and the material is not brittle. The specific gravity of metatyuyamunite ranges from 3.8 to 3.9. On the hydration of metatyuyamunite to tyuyamunite the specific gravity drops to 3.6. Both tyuyamunite and metatyuyamunite fuse relatively easily, and this property can be used to distinguish these minerals from carnotite when the samples contain only tyuyamunite or metatyuyamunite and carnotite. Both tyuyamunite and metatyuyamunite may turn yellow green on exposure to sunlight (Chirvinsky, 1924, p. 291).

Optical Properties

Both tyuyamunite and metatyuyamunite are orthorhombic, biaxial negative, and occur as basal plates. These minerals are colorless to pale yellow in transmitted light and faintly pleochroic with X nearly colorless, Y very pale canary yellow, and Z pale canary yellow. X is perpendicular to the plate, and the plate is elongated in the Z direction (pl. 1). The optical orientation is the same as that given by Merwin (1924, p. 208) and Dolivo-Dobrovolskiy (1925, p. 367). The dispersion is $r<v$ weak. The interference figure does not show strong enough dispersion to prove orthorhombic symmetry. The indices of refraction given in Table 1 were determined using arsenic tribromide, precipitated sulfur, and arsenic disulfide immersion liquids (Meyrowitz and Larsen, 1951, p. 746). The indices of refraction change significantly in air (Table 1) owing to the rapid hydration or dehydration of the material. Therefore, index of refraction determinations must be made immediately after making the slide.

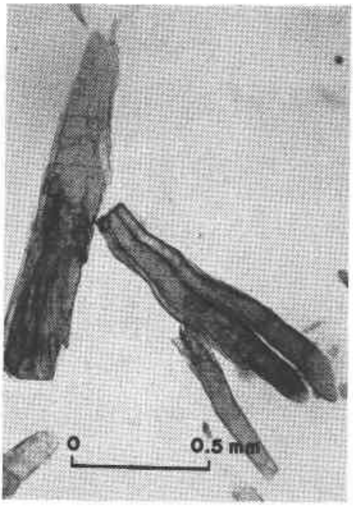

Plate 1. Photomicrograph of bladed crystalline metatyuyamunite, Small Spot mine, Calamity Mesa, Mesa County, Colo.

Norman Herz, of the U. S. Geological Survey, determined the axial

TABLE 1. OPTICAL PROPERTIES OF TYUYAMUNITE AND METATYUYAMUNITE

Orientation		"Tyuyamunite" (1)	"Tyuyamunite" (2)	Metatyuyamunite (3)	Metatyuyamunite (4)
c	α	1.72 ±0.01	1.75 to 1.80 (calculated)	1.68 (calc.)	1.62 (calc.)
a	β	1.868±0.005	1.927 to 1.932	1.835±0.002	1.842±0.002
b	γ	1.953±0.005	1.965 to 1.968	1.865±0.002	1.899±0.002
2V		48°	45° to 51°	45°	48°

(1) Sample from Henry Mountains, Utah (Ross, 1924). $Y=b$ only optical orientation given.
(2) Sample from Paradox Valley, Colo. (Merwin, 1924).
(3) Sample from Small Spot mine, Mesa County, Colo. Measurements at conditions prevailing in Washington, D. C.
(4) Sample from May Day mine, Mesa County, Colo. Measurements at conditions prevailing in Washington, D. C.

angle, 2V, with a universal stage. α was calculated. The changes in the indices of refraction caused by the variation of water content are shown in Table 2. The indices of refraction for specimens from the Small Spot mine are given for material that was kept over water in a closed container for 16 days, with a water vapor pressure of about 16 mm. Hg (col. 1); for material that was stored for 16 days in a desiccator over concentrated H_2SO_4, which has a water vapor pressure of 0.6 mm. Hg (col. 2); and for material that was heated to 100° C. (col. 3). On dehydration the indices of refraction and 2V increase, but the optical orientation, dispersion, and pleochroism remain essentially the same.

TABLE 2. VARIATION IN OPTICAL PROPERTIES OF TYUYAMUNITE AND METATYUYAMUNITE FROM SMALL SPOT MINE CAUSED BY HYDRATION AND DEHYDRATION

Orientation		Hydrated sample (1)	Desiccated sample (2)	Sample heated to 100° C. (3)
c	α	1.57 (calculated)	1.88 (calculated)	1.73 (calculated)
a	β	1.805±0.002	1.959±0.002	1.960±0.002
b	γ	1.851±0.002	1.976±0.002	2.02 ±0.01
2V		42°	47°	49°

CHEMICAL COMPOSITION

C. S. Annell of the Geological Survey made semiquantitative spectrographic analyses (Table 3) to guide the quantitative chemical analyses of the Small Spot and May Day materials (Table 4).

TABLE 3. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF METATYUYAMUNITE IN PER CENT

Analyst: C. S. Annell, U. S. Geological Survey

Locality	More than 10	1–10	0.1–1.0	0.01–0.1
Small Spot mine	U	V Ca	Al	Si Co K Ba
May Day mine[1]	U	V Ca	Sr Al Ba	Si Fe

[1] This spectrogram was made in a region in which potassium could not be detected. A flame photometer analysis by C. A. Kinser, U. S. Geological Survey, indicated that potassium was present in the 1–10 per cent range.

TABLE 4. CHEMICAL ANALYSES OF TYUYAMUNITE AND METATYUYAMUNITE

	Tyuyamunite				Metatyuyamunite		Theoretical composition	
	(1)	(2)	(3)	(4)	(5)	(6)	Metatyuyamunite 3 H_2O (7)	Tyuyamunite 8 H_2O (8)
Na_2O	0.02							
K_2O	.18	0.5		2.89		3.10		
CaO	5.63	5.9	5.56	5.42	6.22	5.83	6.49	5.88
BaO	.54			.28		.30		
SrO				.08		.09		
MgO	.09							
CuO	.04							
UO_3	55.91	57.7	60.00	57.68	66.80	62.12	66.21	59.95
V_2O_4			2.01	1.27	2.25	1.33		
V_2O_5	18.76	19.5	16.40	18.39	18.27	19.79	21.05	19.06
H_2O	18.83	16.3	16.03	13.53	6.57	7.33	6.25	15.11
Rem.				0.10		.11		
Total	100.00	99.9	100.00	99.64	100.11	100.00	100.00	100.00
Sp. gr.			3.6		3.8	3.9		

(1) Calamity Creek, Mesa County, Colo. (Hillebrand, 1924, p. 213).
(2) Henry Mountains, Utah (Schaller, 1924).
(3) Small Spot mine, Mesa County, Colo. Recalculation of sample 5 based on change in water content following hydration to tyuyamunite. Analysts: A. M. Sherwood and R. G. Milkey.
(4) May Day mine, Mesa County, Colo. Analyst: A. M. Sherwood.
(5) Small Spot mine, Mesa County, Colo. Analyst: A. M. Sherwood.
(6) May Day mine, Mesa County, Colo. Recalculation of sample 4 based on change in water content following dehydration to metatyuyamunite. Analyst: A. M. Sherwood.
(7) Theoretical composition of metatyuyamunite with 3 moles of water [$Ca(UO_2)_2(VO_4)_2 \cdot 3H_2O$].
(8) Theoretical composition of tyuyamunite with 8 moles of water [$Ca(UO_2)_2(VO_4)_2 \cdot 8H_2O$].

Hydration of the Small Spot material increased its water content from 6.57 to 16.03 per cent and its *x*-ray diffraction powder pattern showed larger interplanar spacings. The 2.89 per cent potassium content in the May Day specimen does not seem to be due to admixed carnotite. This sample is discussed further in the section on base exchange.

WATER CONTENT

The number of moles of water as a function of the partial pressure of the water has been determined for the Small Spot material (Fig. 1).

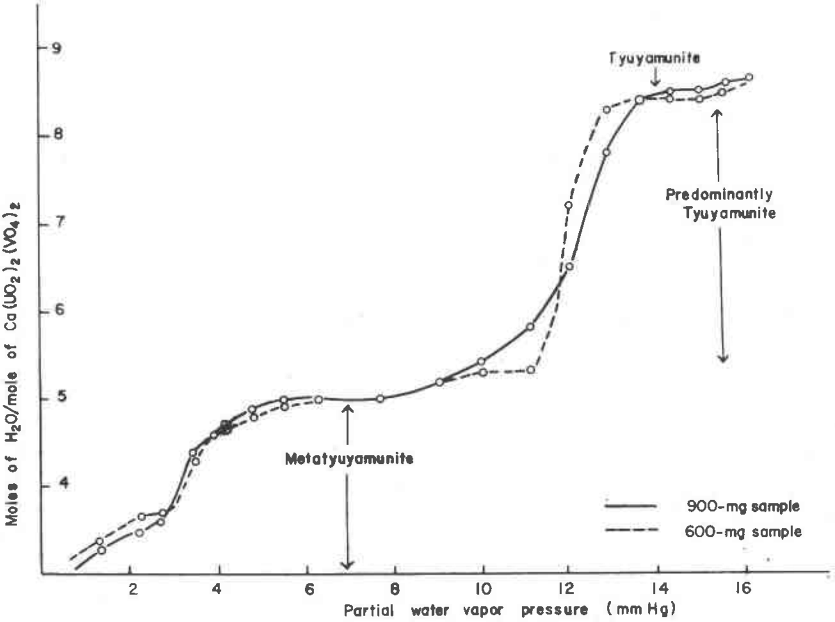

FIG. 1. Hydration of metatyuyamunite and tyuyamunite as a function of the partial pressure of water.

Two samples of the mineral weighing 600 and 900 mg. respectively were dehydrated in a desiccator containing concentrated sulfuric acid. The desiccator was kept in a constant temperature room (24° C.). All weighings were made in this room using a semimicrobalance. Equilibrium was assumed to have been reached when constant weight (within 0.2 to 0.3 mg.) was reached. The minimum interval between weighings was one day, and the sample was mixed thoroughly between weighings.

The partial pressure was varied by changing the concentration of aqueous sulfuric acid over which the sample was stored. The time required for equilibrium to be established at a new partial pressure varied from 3 to 19 days. The partial pressure of the water vapor at each dilution was calculated from the approximate relative humidity of the sulfuric acid solutions using the table of Stevens (1916, p. 430), which shows the approximate relative humidity of dilute sulfuric acid solutions of various percentage compositions.

The water content of the dehydrated material was determined in the following manner. After the samples had come to equilibrium over concentrated sulfuric acid, a small portion of each sample was transferred to weighed porcelain microcrucibles. The crucible and contents were placed in the desiccator and weighed each day until the weight was constant. The weight of the crucible and contents was determined within 1 to 2 minutes after it was removed from the desiccator. The percentage of water was calculated from the loss on ignition. Several attempts were made to determine the water content by the Penfield method. These were not successful because the samples picked up water before the determination could be made.

X-RAY DIFFRACTION DATA

The plateaus in the dehydration curve at values of 5 and 8.5 moles of water per mole of $Ca(UO_2)_2(VO_4)_2$ indicate that the structures of metatyuyamunite and tyuyamunite are complete. *X*-ray diffraction powder patterns for the two minerals are distinctly different (pl. 2 and Tables 5 and 6). Samples containing 3 to 5 moles of water per mole of $Ca(UO_2)_2(VO_4)_2$ show slight differences among themselves in spacings due to changes in water content, but the spacings correspond essentially to those given for metatyuyamunite. Analogous differences exist in the tyuyamunite powder patterns in the range of 5 to 8.5 moles of water.

The differences in the *x*-ray diffraction powder patterns of tyuyamunite and metatyuyamunite are due to changes in the interlayer spacings between the $(UO_2VO_4)^-$ sheets as the water content is changed either by hydration or by dehydration. Dehydrated specimens have smaller $\{001\}$ interplanar spacings than do the more hydrated specimens. Murata, Cisney, Stieff, and Zworykin (1951) have already noted the correlation between water content and interlayer spacings.

George Ashby, of the Geological Survey, found that the space occupied by interlayer water in tyuyamunite is nearly the same as that occupied by interlayer water in montmorillonite. Tyuyamunite heated at 500° C. for 72 hours gives a single *x*-ray powder line in the low-angle region with an interplanar spacing about 5.8 Å. Assuming that 5.8 Å is the basal spacing of anhydrous tyuyamunite, the interlayer water space can be calculated as 2.7 Å for metatyuyamunite and 4.4 Å for tyuyamunite. The analogous water spaces for montmorillonite are 2.76 Å and 4.54 Å

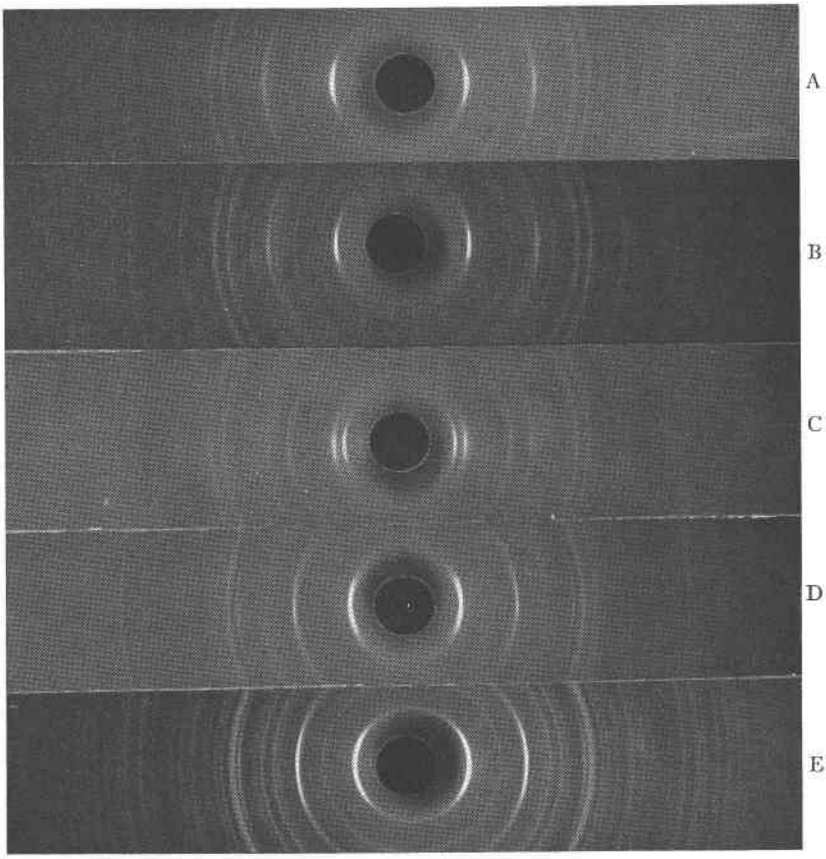

PLATE 2. *X*-ray diffraction powder patterns of metatyuyamunite and tyuyamunite.

A. Metatyuyamunite from Small Spot mine, Mesa County, Colo. Sample in equilibrium with water vapor pressure of 0.6 mm. Hg. Film 5117.

B. Metatyuyamunite from Small Spot mine, Mesa County, Colo. Sample in equilibrium with water vapor pressure of 4.8 mm. Hg. Film 5170.

C. Metatyuyamunite and tyuyamunite from Small Spot mine, Mesa County, Colo. Note the two closely spaced lines at low angles of 2θ. Film 3342.

D. Tyuyamunite from Small Spot mine, Mesa County, Colo. Sample in equilibrium with water vapor pressure of 15.1 mm. Hg. Film 3343.

E. Tyuyamunite synthesized by K. J. Murata. Film 3336.

(Barshad, 1949, p. 675). These spacings suggest that metatyuyamunite has a single water layer and tyuyamunite has a double water layer.

In Table 5 the interplanar spacings are given for synthetic metatyuyamunite and metatyuyamunite from the Small Spot mine in equilibrium with a partial water vapor pressure of 0.6 mm. of Hg. Table 6 gives the

Table 5. X-Ray Diffraction Powder Data for Metatyuyamunite
(Cu/Ni Radiation = 1.5418 Å; *d* in Å)
Data from D. D. Riska, U. S. Geological Survey

Synthetic metatyuyamunite (Film 109)		Metatyuyamunite $Ca(UO_2)_2(VO_4)_2 \cdot 3H_2O$ Small Spot mine, Mesa County, Colo. In equilibrium with water vapor pressure of 0.6 mm. Hg (Film 5117)	
$d_{obs.}$	I^*	$d_{obs.}$	I^*
9.94	vf		
8.51	vs	8.51	vs
6.51	w	6.66	f
5.19	w	5.22	w
4.48	f	4.48	f
4.22	s	4.22	s
3.77	w	3.77	w
3.55	f	3.55	f
3.24	mb	3.26	mb
3.04	mb	3.05	mb
2.85	vfb	2.81	f
2.72	f		
2.59	w	2.58	w
2.48	vfb		
2.19	fb		
2.13	wb	2.12	wb
2.05	f	2.05	f
2.01	f	1.99	f
1.96	f	1.95	f
		1.91	vfb
		1.88	vfb
		1.85	vfb
1.77	fb	1.77	fb
		1.73	vfb
1.69	vfb	1.69	vf
1.66	vfb	1.66	vf
		1.61	vfb
		1.57	vf
1.53	vf	1.53	vf
1.49	vf	1.50	vf

* vs = very strong, s = strong, m = medium, w = weak, f = faint, vf = very faint, b = broad.

interplanar spacings of metatyuyamunite from the Small Spot mine in equilibrium with a partial water vapor pressure of 4.8 mm. of Hg and of tyuyamunite from the same mine with a partial water vapor pressure of 16.1 mm. of Hg. The patterns of metatyuyamunite ($\sim$4.5 H_2O) and

TABLE 6. X-RAY DIFFRACTION POWER DATA FOR METATYUYAMUNITE AND TYUYAMUNITE (Cu/Ni RADIATION=1.5418; *d* IN Å)
Data from D. D. Riska, U. S. Geological Survey

Metatyuyamunite $Ca(UO_2)_2(VO_4)_2 \cdot \sim 4.5\ H_2O$. Small Spot mine, Mesa County, Colo. In Equilibrium with water vapor pressure of 4.8 mm. Hg. $a_0 = 10.63$ Å, $b_0 = 8.36$ Å, $c_0 = 16.96$ Å. (Film 5170)

$d_{obs.}$	$d_{calc.}$	I*	hkl
8.55	8.48	vs	002
6.55	6.57	f	110
5.25	5.19 5.32	w	112 200
4.48	4.50	w	202
4.21	4.18 4.24	s	020 004
3.77	3.79 3.75	w	121 022
3.56	3.56 3.54	f	114 122
3.25	3.26 3.23	m	310 221
3.04	3.04 3.06	m	312 222
2.82	2.83 2.83 2.84 2.80	w	006 313 223 024
2.71	2.70 2.71	f	130 215
2.58	2.58 2.59 2.56 2.60 2.60 2.57	m	322 314 125 224 116 132

Tyuyamunite $Ca(UO_2)_2(VO_4)_2 \cdot \sim 8.5\ H_2O$. Small Spot mine, Mesa County, Colo. In equilibrium with water vapor pressure of 16.1 mm. Hg. $a_0 = 10.63$ Å, $b_0 = 8.36$ Å, $c_0 = 20.40$ Å. (Film 3343)

$d_{obs.}$	$d_{calc.}$	I*	hkl
10.16	10.20	vs	002
6.51	6.57	f	110
5.28	5.31	vf	200
5.10	5.10 5.14	m	004 201
4.10	4.10	fb	212
3.40	3.40	mw	006
3.24	3.24 3.24 3.23 3.26	mw	221 205 024 310
3.03	3.02 3.02	fb	215 116
2.88	2.86	fb	206
2.65	2.66 2.66 2.67 2.64 2.64	fb	400 117 131 401 026
2.55	2.55 2.55 2.55 2.56 2.56 2.57	fb	008 315 207 225 126 402
2.17		fb	
2.11		fb	

TABLE 6 (*continued*). X-RAY DIFFRACTION POWDER DATA FOR METATYUYAMUNITE AND TYUYAMUNITE (Cu/Ni RADIATION = 1.5418; *d* IN Å)
Data from D. D. Riska, U. S. Geological Survey

<table>
<tr><th colspan="4">Metatyuyamunite $Ca(UO_2)_2(VO_4)_2\cdot\sim 4.5\ H_2O$. Small Spot Mine, Mesa County, Colo. In equilibrium with water vapor pressure of 4.8 mm. Hg. $a_0=10.63$ Å, $b_0=8.36$ Å, $c_0=16.96$ Å. (Film 5170)</th><th colspan="4">Tyuyamunite $Ca(UO_2)_2(VO_4)_2\cdot\sim 8.5\ H_2O$. Small Spot mine, Mesa County, Colo. In equilibrium with water vapor pressure of 16.1 mm. Hg. $a_0=10.63$ Å, $b_0=8.36$ Å, $c_0=20.40$ Å. (Film 3343)</th></tr>
<tr><th>$d_{obs.}$</th><th>$d_{calc.}$</th><th>I*</th><th>hkl</th><th>$d_{obs.}$</th><th>$d_{calc.}$</th><th>I*</th><th>hkl</th></tr>
<tr><td>2.49</td><td>2.50
2.50</td><td>vf</td><td>411
206</td><td>2.04</td><td></td><td>mw</td><td></td></tr>
<tr><td>2.42</td><td></td><td>mb</td><td></td><td>1.98</td><td></td><td>vfb</td><td></td></tr>
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<tr><td>1.48</td><td></td><td>f</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

* vs = very strong, s = strong, m = medium, mw = medium weak, w = weak, f = faint, vf = very faint, b = broad.

tyuyamunite (~8.5 H_2O) have been indexed, and the powder patterns in Plate 2 show the change in the inner lines.

The single crystal data given by Donnay and Donnay (1954)—orthorhombic, $a = 10.63$ Å, $b = 8.36$, $c = 16.96$; pseudo *Pnan*—and referred to tyuyamunite are actually for the dehydrated form which all of us now call metatyuyamunite. We have used their data to index our pattern of metatyuyamunite. Our pattern of tyuyamunite has been indexed using the same a and b as above, but with $c = 20.40$ Å, assuming an expansion in that direction.

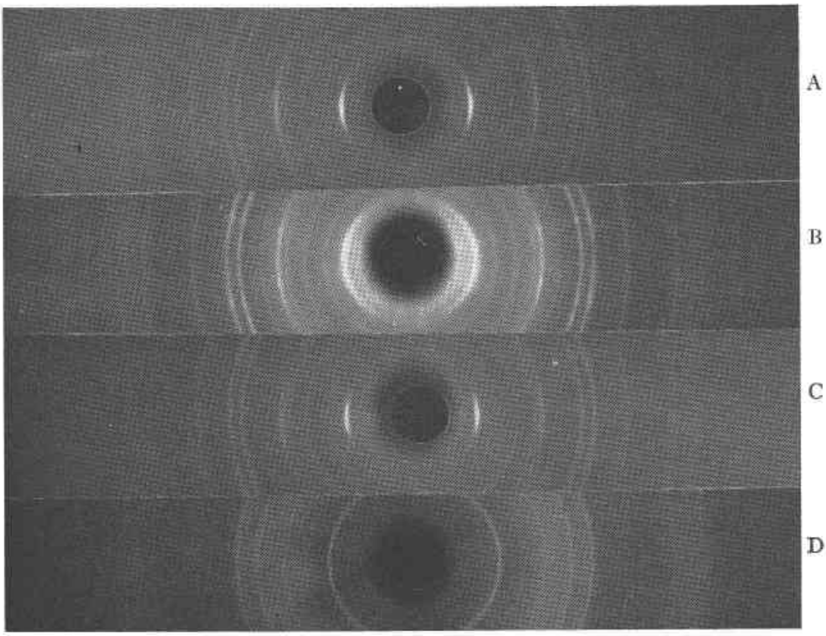

PLATE 3. *X*-ray diffraction powder patterns of metatyuyamunite, base-exchanged metatyuyamunite, and carnotite.

A. Metatyuyamunite, Small Spot mine, Mesa County, Colo. In equilibrium with water vapor pressure of 0.6 mm. of Hg.; this material does not contain potassium.
B. Metatyuyamunite, May Day mine, Mesa County, Colo. This material contains 2.89 per cent K_2O. Same hydration as *A*. Film 5219.
C. Base-exchanged metatyuyamunite from Small Spot mine, Mesa County, Colo. Same hydration as *A*. Film 5220.
D. Carnotite. Synthesized by K. J. Murata. Film 238.

BASE EXCHANGE

The metatyuyamunite from the May Day mine contains 2.89 per cent K_2O. These crystals are optically homogeneous, and no evidence of the presence of carnotite could be found from *x*-ray examination of the material. To study the effect of the presence of K_2O in the material from the May Day mine, C. A. Kinser, of the Geological Survey, base-exchanged some of the CaO in the Small Spot sample with K_2O. A 100-mg. sample of metatyuyamunite was treated with 25 ml. of solution containing 3.0 mg. of K_2O as KCl. After base-exchanged reaction had taken place, the solution contained 0.80 mg. K_2O and 1.22 mg. CaO. The 2.20 mg. of K_2O that was removed from the solution by the reaction should liberate 1.30 mg. of CaO. The base-exchanged sample from the Small Spot mine, an untreated sample from the Small Spot mine, and the base-exchanged potassium-containing May Day mine material were stored in an atmosphere with a partial pressure of water of 1.2 mm. of Hg at 24° C. *X*-ray diffraction powder patterns were made of the three samples. For comparative purposes *x*-ray diffraction powder patterns are shown for metatyuyamunite from the Small Spot mine, metatyuyamunite from the May Day mine, base-exchanged metatyuyamunite, and carnotite in Plate 3. These experiments show that samples of metatyuyamunite can contain significant amounts of potassium. The transition point from orthorhombic symmetry of tyuyamunite to monoclinic symmetry of carnotite has not been determined. The base-exchange reaction easily converts tyuyamunite to carnotite, but the reaction from carnotite to tyuyamunite proceeds very slowly (Murata, Cisney, Stieff, and Zyorykin, 1951).

RADIUM-URANIUM AGE

Radium-uranium equilibrium is established when the rates of radium formation and decay are equal. Ninety-nine per cent of radium-uranium equilibrium will be attained in approximately 500,000 years (Knopf, 1931, p. 110). If minerals do not contain radium in proportion to the equilibrium amount of 3.32×10^{-7} g. Ra/g. U, this condition may be attributed to either one or both of the following causes:

1. The mineral may be less than 500,000 years old if the radiogenic lead content is very low.
2. The material may have been influenced by very recent selective leaching of radium or enrichment of uranium.

The metatyuyamunite samples from both the Small Spot mine and the May Day mine contain less than 0.001 g. Pb/g. sample. These well-crystallized specimens seem to be fresh and unaltered; therefore, the loss of large amounts of radium by selective leaching does not seem probable. For these reasons it is assumed that these samples can be dated approximately by the radium-uranium-equilibrium method.

Nuclear-track studies of both metatyuyamunite and carnotite showed the absence of radiocolloids (local concentration of radium or other relatively short half-lived daughter products), which suggests that the minerals have not been recently leached of uranium with respect to radium. Furthermore, the number of alpha tracks associated with these minerals is small, relative to their uranium content, confirming a lack of radium-uranium equilibrium.

For the two metatyuyamunite specimens, Table 7 gives their uranium content, theoretical radium content assuming radioactive equilibrium, experimentally determined radium content, and age.

TABLE 7. RADIUM CONTENT, DEPARTURE FROM EQUILIBRIUM, AND RADIUM-URANIUM AGE OF METATYUYAMUNITE SPECIMENS FROM MESA COUNTY, COLO.

Location	Per cent U[1]	Theoretical g. Ra/g. sample[2]	Experimental g. Ra/g. sample[3]	Per cent equilibrium	Approximate age (years)
May Day mine, Mesa County, Colo.	52.00	1.73×10^{-7}	1.08×10^{-7}	62.4	150,000
Small Spot mine, Mesa County, Colo.	55.59	1.84×10^{-7}	0.333×10^{-7}	18.1	25,000

[1] Analyses by A. M. Sherwood and R. G. Milkey, U. S. Geological Survey.
[2] Computed from g. Ra/g. U in equilibrium $=3.32\times10^{-7}$ g. Ra/g. U.
[3] Analyses by John Rosholt, U. S. Geological Survey.

Crystalline carnotite from the Bridger Jack Flat, Cane Springs Pass, Utah, is also of very recent geologic age. Using the data given by Knopf (1931, p. 351) and modern decay constants, the age of the carnotite from Bridger Jack Flat is approximately 170,000 years. Additional samples of crystalline carnotite from the Parco Mine, Yellow Cat group, Grand County, Utah, and from the Jo Dandy mine, Montrose County, Colo., have ages of 40,000 and 15,000 years, respectively, as determined by us in 1950. Thus, the age of some crystalline metatyuyamunite and carnotite specimens from the Colorado Plateau is Quaternary. These minerals have been formed from the vanadium-uranium deposits of the Plateau whose age has been determined as not older than Late Cretaceous or early Tertiary (Stieff and Stern, 1953).

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