Tyuyamunite from the Tyuya-Muyun radium mine in Fergana.

By PETR N. CHIRVINSKY (П. Н. Чирвинскій),

Professor of Applied Geology and Mineralogy and Dean of the Mining Faculty in the Don Polytechnic Institute, Novocherkassk.

[Read January 20, 1925; communicated by the Editor.]

TYUYAMUNITE (тюямунит)[1] from Tyuya-Muyun (Тюя-Муюн) was established as a mineral species by K. A. Nenadkevich in 1912.[2] It is closely allied to carnotite, differing from this in containing calcium in place of potassium, and also, according to W. F. Hillebrand,[3] in the degree of hydration. On this account the mineral has been also known as calciocarnotite. The chemical composition is given by the formulae:

Tyuyamunite . . .	$CaO . 2UO_3 . V_2O_5 . mH_2O$.
Carnotite . . .	$K_2O . 2UO_3 . V_2O_5 . nH_2O$.

The ferganite of I. A. Antipov[4] from this same locality, is perhaps identical with tyuyamunite, and will be further mentioned below.

Carnotite has played an important part in the radium industry in the United States of America, and tyuyamunite takes a similar place in Russia.

Tyuya-Muyun is a prominent rounded hill traversed by the gorge of the Aravan river and is a northern spur of the Alai Mountains in

[1] In his German MS., from which the abridged translation here given was prepared, the author writes Tüjamunit.

[2] K. A. Nenadkevich, Le 'tiujamunite', une nouvelle espèce minérale. (Russ.) Bull. Acad. Sci. St.-Pétersbourg, 1912, ser. 6, vol. 6 (pt. 2), pp. 945-946. Title from the wrapper of the journal. In German abstracts (Chem. Zentr., 1913, vol. i, p. 326; Neues Jahrb. Min., 1914, vol. ii, p. 211; Zeits. Kryst. Min, 1915, vol. 55, p. 180) of this paper the name is spelt Tjujamunit and Tjuiamunit. The original Russian form was тюямунитъ. Still other forms of the name that have appeared in the literature are Tuyamunite, Tyuyamuyunite, and тюямуюнит.

[3] W. F. Hillebrand, Carnotite and tyuyamunite and their ores in Colorado and Utah. Amer. Journ. Sci., 1924, ser. 5, vol. 8, pp. 201-216. [Min. Abstr., vol. 2, p. 404.]

[4] I. A. Antipov, Gornyi Zhurnal, St. Petersburg, 1908, year 84, vol. iv, pp. 255-263; abstract in Neues Jahrb. Min., 1909, vol. ii, Ref. p. 38.

Russian Turkestan. In the aboriginal language the name means camel's hump. It is situated 62 kilometres south-east of the railway station Fedchenko and about the same distance south of the town of Andijan in Fergana. The mine and the surrounding district have been actively studied from a scientific point of view during recent years, and several papers and reports have been published. A complete account has been given by D. I. Shcherbakov,[1] and a large work by V. G. Khlopin (Radium and its winning from Russian ores) shortly to be issued by the Russian

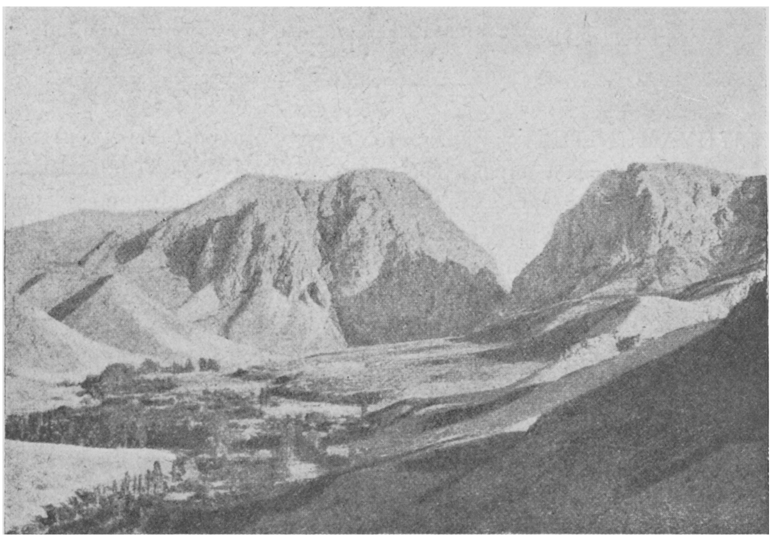

FIG. 1.—The limestone hill of Tyuya-Muyun in Russian Turkestan. The radium mine is shown on the low hill to the right.

Academy of Sciences will give further information together with new analyses of tyuyamunite.

The geological relations of the deposit may be summarized as follows. The ore forms metasomatic gash-veins and fills Karst caverns in limestone, which around the ore is dolomitized. The limestone beds, of Carboniferous age, are much dislocated and inverted. They are bordered by carbonaceous Silurian slates with a graptolitic fauna. To the north and to the south of the mine these pass into siliceous jasper-like slates with

[1] D. I. Shcherbakov (= Stzerbakoff, Щербаков), Deposits of radioactive ores and minerals of Fergana. (Russ.) 'K.E.P.S.' [Commission for the investigation of the natural productive forces of Russia], Leningrad, 1924, no. 47, 59 pp., 2 figs.

interbedded limestones. The whole series of sediments is penetrated by intrusive sills of diabase and dikes of keratophyre, together with volcanic tuffs and breccias.

The mine was probably worked in the bronze age, since a stone hammer (of diorite) has been found in the old workings; and more recently it was worked for copper by the Chinese. Only the upper oxidized portion ('iron hat') has been exposed, and the underground workings extend to a depth of only 75 metres. The ore has been taken mainly from two caverns ('bug holes'), of which the upper, measuring 16 × 8 × 8 metres, is known as the 'yellow cavern' and the lower as the 'green cavern'. Analyses of the ores made by different chemists between the years 1903 and 1923 are quoted below.

	I (1903).	II (1919).	III (1919).	IV (1921).	V (1923).	VI (1923).
CuO ...	10·88	3·10	3·10	3·55	3·90	5·12
U_3O_8 ...	4·61 (UO_3)	1·49	1·31	1·60	0·14	0·80
V_2O_5 ...	6·37	3·29	3·02	5·00	3·03	1·83
CaO ...	38·42	32·01	30·02	39·82	47·57	49·28
BaO ...	1·40	4·63	4·87	3·50	4·00	nil
Fe_2O_3 ...	1·52	7·06	6·45	5·40	0·51 (with Al_2O_3)	0·15 (with Al_2O_3)
Al_2O_3 ...	0·71	4·41	3·72	1·40		
SiO_2 ...	0·63	12·02	14·79	3·30	0·80	0·43
SO_3 ...	2·67	2·40	2·82	3·84	2·08	nil
CO_2 ...	30·02	25·49	28·12	30·26	35·60	39·72
H_2O ...	1·41	3·86	0·87	1·10	0·30	0·54
	98·88	100·19	99·09	98·77	97·93	97·87

In I also MgO 0·24. In II also PbO 0·08, alkalis 0·21, P_2O_5 0·12, As_2O_5 0·02, Bi_2O_3, ThO_2 traces.

According to these analyses the ore contains from 58 to 88 % $CaCO_3$ as calcite gangue. The barium is present as barytes, and the copper as malachite and turanite ($5CuO . V_2O_5 . 2H_2O$; K. A. Nenadkevich, 1909).

Between the years 1904 and 1914 the mine yielded 1,000 tons of ore, from 700 tons of which 2·3 grams of metallic radium was extracted. The remaining 300 tons and the residues have been taken over by the new State Radium Works on the Kama river. The State Expedition of 1922[1] estimated the quantity of ore in sight at 5,000 tons, an amount which would correspond to 60 tons of uranium and 15–20 grams of radium. This expedition discovered, close to the old mine,

[1] S. P. Aleksandrov, The Tyuya-Muyun radium expedition in 1922. (Russ.) Gornyi Zhurnal, Moscow, 1922, year 98, no. 10–12, pp. 415–416; and other notes in the same journal in 1923 and 1924.

another vein of the same character, which has been named the 'Academy vein'; and 30 tons of rich mineral specimens were brought back. Indications of other veins were discovered in 1923 and 1924,[1] and the whole district appears to be mineralized.

In this connexion mention may be made of a new mineral, named *kolovratite* by V. I. Vernadsky,[2] which has been found in the neighbourhood of the Tyuya-Muyun mine and appears to be widely distributed in Fergana. A zone of quartz-schists with kolovratite extends with a few breaks for 200 kilometres along the Alai and Turkestan ranges. Notable localities with workable quantities of ore are Kara-Chagyr and Uch-Kurgan. According to analyses by I. A. Preobrazhensky different ore samples containing this mineral have yielded:

NiO	6·50	8·38	12·22 %
V_2O_5	11·55	5·94	6·20

The mineral is a vanadate of nickel and is feebly radioactive. It is named after the late L. C. Kolovrat-Chervinsky, a Russian radiologist.

Material that I have had an opportunity of examining is a series of ore specimens that came to me in 1924 from two sources. One specimen was given by K. A. Nenadkevich and others were collected last summer at the mine by one of my students, A. Lavrov. The dark ore specimens show a banded and in part a brecciated structure. Cavities are lined with botryoidal, crystalline crusts of calcite, barytes, turanite, malachite, and other minerals. Masses of dark-brown, compact limestone are traversed by veins of coarsely crystalline calcite. These veins are more or less parallel to the bands (1–3 mm. thick) and lenses (up to 5 mm. thick) of tyuyamunite. This mineral is rendered conspicuous by its yellow colour, and it shows a fine scaly texture. The colour is only lemon-yellow on fresh surfaces, such as may be exposed by scraping with a knife. In daylight, and especially quickly (in a few minutes) in direct sunlight, the colour changes to dirty greenish-yellow, but this change takes place only on the

[1] A. E. Fersman and D. I. Shcherbakov (= Stzerbakoff), The deposits of the radium-ore in the Fergana district: the report of the scientific expedition of 1924. (Russ.) Scientific-technical Dept. of the Supreme Council of National Economy, Moscow, 1925, no. 74, 36 pp. 4 figs.

A. E. Fersman, The Tyuya-Muyun radium mine (expedition of 1924). (Russ.) 'Priroda' [Nature], Leningrad, 1924, col. 57–88, 8 figs.

[2] V. I. Vernadsky, A new nickel-bearing mineral, kolovratite. (Russ.) Compt. Rend. Acad. Sci. Russie, 1922, pp. 37–38.

D. I. Shcherbakov, 1924, loc. cit., pp. 46–52.

S. P. Aleksandrov, Radium industry in Russia. (Russ.) Gornyi Zhurnal, Moscow, 1924, year 100, no. 1, p. 17.

surface. On other specimens, showing tabular crystals of brown barytes up to 4 cm. long, the tyuyamunite is scattered as single scales and appears to belong to a later generation. Sometimes the mineral forms compact cryptocrystalline masses. It usually rests, not directly on the barytes, but on thin, greenish (copper-bearing) crusts and on clear crusts of calcite which here and there coat the barytes crystals. The specimen given by K. A. Nenadkevich has a more earthy appearance. It is grey in colour and shows many yellowish and greenish veins (to $\frac{1}{2}$ cm. across) and small cavities containing tyuyamunite and other minerals. The rare alaite ($V_2O_5 . H_2O$; K. A. Nenadkevich, 1909) was not detected on these specimens.

The streak of tyuyamunite is pale-yellow. The mineral is quite soft, the degree of hardness being about 2. G. P. Chernik's value of 'over 3' appears to be too high. The specific gravity has been given by G. P. Chernik as 3·41, whilst I. A. Antipov gave 3·31 for ferganite. For a sample of tyuyamunite from Paradox Valley, Colorado, H. E. Merwin (in Hillebrand, loc. cit.) found values ranging from 3·67 to 4·35, varying with the amount of water present in the mineral.

The largest, but poorly developed, crystals were taken from Nenadkevich's specimen. These are platy in form and measure 0·75 × 0·60 mm., 0·70 × 0·45 mm., &c. Their faces are not quite even, being corroded and dull, and sometimes curved. The large plane, which may be taken as (001), shows a greasy to pearly lustre, and parallel to it there is a perfect micaceous cleavage. Although the plates are thin, they are often only translucent, especially when corroded on the surface. But splinters and small crystals, especially from A. Lavrov's specimens, are quite transparent and more suitable for microscopical examination.

These show a vitreous lustre and were found to be orthorhombic. In addition to the perfect (001) cleavage, the plates show sharp cleavage cracks parallel to (010), which often extend continuously through the whole plate. A third rather less perfect cleavage is parallel to (100). Owing to these three cleavages, the plates readily break up into minute cuboidal fragments. As shown in fig. 2 (1–8) the crystals are often elongated in the direction of the brachy-axis, and they are sometimes striated in this direction. Less frequently, they are more or less equally developed in the three directions, and the material then presents a compact massive appearance. The tabular crystals are often terminated (fig. 2), but whether these terminations represent prism-faces or pyramid-faces is not certain. The plane angle on (001) between these edges has been measured under the microscope as 105°, the angle *CDE* in fig. 2 (1) and

(4). On one crystal an edge corresponding to (120) was observed. Comparing this angle with the values measured by other observers on allied minerals, we have :

	mm = (110):(1$\bar{1}$0).	a:b.
Tyuyamunite from Fergana (P. N. Chirvinsky, 1925) ...	75°	0·77:1
Tyuyamunite from Colorado (H. E. Merwin, 1924) [1] ...	75	0.77:1
Ferganite from Fergana (S. F. Glinka, 1908) [2]	74	0·75:1
Carnotite from South Australia (T. Crook, 1910) [3] ...	78	0.81:1
Carnotite from Colorado (E. S. Larsen, 1921) [4]	78	0.81:1

These values differ markedly from that of the corresponding angle for the minerals of the uranite group, although in chemical composition and

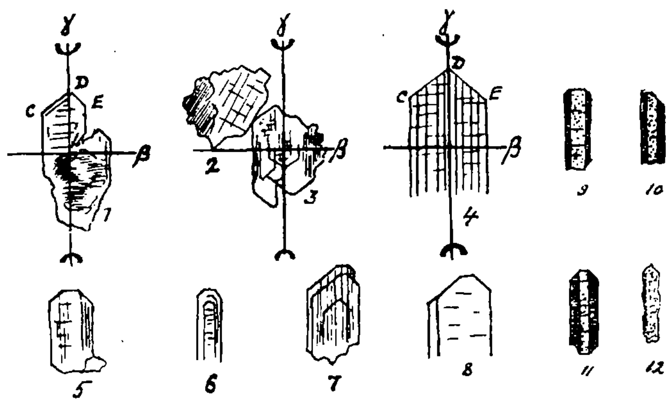

FIG. 2.—Tyuyamunite (1–8, ×50) and an undetermined mineral (9–12, × 100) from Tyuya-Muyun, Fergana. Cleavage cracks and the optical orientation are indicated.

general physical characters they show some analogies. For autunite the corresponding angle is 89° 17′ and $a:b = 0{\cdot}9876:1$.

Pleochroism is very weak, perhaps a tinge of greenish, or is quite absent. The mean refractive index is high [5]—higher than 1·73 (Thoulet's solution). The birefringence $\gamma-\beta$ on the basal plane is about 0·024. The extinction is symmetrical. In convergent light is seen a bisymmetric interference-figure of wide angle and very distinct dispersion $\rho<v$. In

[1] H. E. Merwin in W. F. Hillebrand, loc. cit. [Min. Abstr., vol. 2, p. 404.]
[2] S. F. Glinka in I. A. Antipov, loc. cit.
[3] T. Crook and G. S. Blake, Min. Mag., 1910, vol. 15, p. 174.
[4] E. S. Larsen, Bull. U.S. Geol. Survey, 1921, no. 679, p. 52.
[5] Values for the refractive indices are given by E. S. Larsen (loc. cit., p. 148) and H. E. Merwin (loc. cit.).

air the cusps of the hyberbolic brushes lie outside the field of view, but in cedar-oil ($n = 1{\cdot}516$) with the Seibert no. 5 ocular they come very near the edge of the field. The optical sign is negative. The sign of elongation of the longer plates is positive. In one crystal plate an optic axis was observed normal to the plate. The optic axial plane is (010), bisecting the angle of 105°, and the acute negative bisectrix is normal to (001). The optical orientation is thus $\alpha = c$, $\beta = b$, $\gamma = a$. This is in agreement with the observations of S. F. Glinka for ferganite, T. Crook for carnotite from South Australia, E. S. Larsen for tyuyamunite from Utah, and H. E. Merwin for tyuyamunite from Colorado.

In mineral acids (HCl, HNO_3, and H_2SO_4), even in the cold, tyuyamunite dissolves quietly and quickly. At the first instant of contact with the acid the powder acquires an orange or brownish-red colour, and is then quickly decolorized. Crystal flakes in acid develop fissures and a fibrous structure. Their birefringence rapidly diminishes, and there finally remains a colourless and transparent phantom (pseudomorph), not readily seen and without action on polarized light. This perhaps represents the small amount of silica and tungstic acid shown in G. P. Chernik's analysis. The solution in hydrochloric acid is first yellow, but after a few hours becomes bluish-green, probably due to the formation of UCl_4. A microchemical test with $PtCl_4$ proved the absence of potassium. Acetic acid, either cold or warm, has no appreciable action on the mineral.

The chemical composition of tyuyamunite is given by the analyses of K. A. Nenadkevich, 1912 (anal. I quoted below; CaO includes also SrO), and G. P. Chernik,[1] 1922 (anal. II, uranium oxide as U_3O_8; K_2O includes Li_2O; also PbO 0·07, Bi_2O_3 less than 0·01, Al_2O_3 0·32, SiO_2 0·26, WO_3 trace). W. F. Hillebrand's recent analyses (1924, loc. cit.) are also quoted for comparison: III of tyuyamunite from Calamity Creek, Mesa Co., Colorado (also MgO 0·09. Na_2O 0·02, Fe_2O_3 0·78); IV from Fergana (MgO 0·09, $Na_2O(+Li_2O)$ 0·20, Fe_2O_3 0·13).

	UO_3.	V_2O_5.	CaO.	BaO.	CuO.	Tl.	K_2O.	H_2O.	Insol.	Total.
I.	63·09	21·?	5·99	—	—	trace	—	7·04	—	97·12
II.	59·78	26·05	3·97	0·04	trace	—	0·09	10·12	—	100·71
III.	54·97	18·44	5·54	0·53	0·04	nil	0·18	18·52	1·00	100·11
IV.	55·85	17·92	4·80	—	0·10	trace	0·17	16·61	3·26	99·13

All authors agree in the formula $CaO.2UO_3.V_2O_5.mH_2O$, but

[1] G. P. Chernik, Analyses of the urano-vanadic ores from the Tyuya-Muyun deposit in Fergana. (Russ.) Bull Acad. Sci. Russie, 1922, ser. 6, vol. 16, pp. 505–514.

Nenadkevich gave $4H_2O$ and Chernik gave $8H_2O$. Hillebrand determined the content of water under controlled conditions, his material having been previously exposed over dilute sulphuric acid (of sp. gr. 1·05, vapour-pressure 16 mm.) at 20° C. The molecular ratios of water in his two analyses III and IV are 10·7 and 9·45 respectively (with $UO_3 = 2$). A similar variation in the water-content of minerals of the uranite group is well known [1]; and a further analogy is given by the water in zeolites.

The doubtful analysis by I. A. Antipov of ferganite from Tyuya-Muyun gave U_3O_8 77·00, V_2O_5 17·60, Li_2O 1·22 [in another place 3·49], H_2O 10·75, total 106·57 %. This is recalculated as UO 69·30 %, and the formula given as $3UO.V_2O_5.6H_2O$ or $U_3(VO_4)_2.6H_2O$. It has already been suggested by K. A. Nenadkevich that ferganite is identical with tyuyamunite; and it is shown above that the crystal figured by S. F. Glinka has the same form and optical orientation as the crystals now described. On the other hand, ferganite may represent a leached or weathered product of tyuyamunite. The progressive decrease in the strength of the birefringence observed when tyuyamunite is acted upon by acids is possibly due to an extraction of the bases. This would perhaps account for the low birefringence noted by S. F. Glinka in Antipov's material. The powdery coating on the larger corroded crystals of tyuyamunite noted above may perhaps also represent such an alteration product.

An undetermined mineral.—On some of the tyuyamunite specimens collected by A. Lavrov there were found in small amount some minute prismatic crystals (fig. 2, 9–12). These are collected mostly at the borders of the veinlets. They are sometimes well formed and show rectangular and six-sided cross-sections. Their length is usually 0·10–0·20 mm. Terminal faces are present and are sometimes rounded. The surface is somewhat corroded and is in part covered with a reddish-brown amorphous substance (iron hydroxide ?). In reflected light the crystals appear brown with adamantine lustre, but by transmitted light they are greenish-yellow with a darker colour than tyuyamunite. There are perfect cleavages parallel to the faces of the prism-zone and across the prism, though these are not very conspicuous. Optical extinction is straight, and the sign of elongation of the prism-zone is positive. Pleochroism is absent. The mean refractive index is very high, and the birefringence is not less than 0·020–0·025. Nothing definite could be made out in convergent light. In mineral acids the crystals dissolve

[1] See, for example, A. H. Church, Min. Mag., 1877, vol. 1, p. 234; A. F. Hallimond, Min. Mag., 1916, vol. 17, p. 326; 1920, vol. 19, p. 43.

readily without effervescence, and, like tyuyamunite, they are soon decolorized, finally leaving a gelatinous pseudomorph. These pseudomorphs are optically isotropic, and they retain the reddish-brown coating on their surface. It is not impossible that these crystals may represent tyuyamunite of another habit.

In this connexion mention may be made of an undetermined mineral associated with tyuyamunite recently analysed by G. P. Chernik (1922, loc. cit.). A thin, crystalline crust of dark-green colour, with fairly strong radioactivity, sp. gr. 4·46, and hardness 4, gave as the main constituents: U_3O_8 38·27, V_2O_5 38·28, CuO 7·23, BaO 0·84, K_2O 0·80, H_2O 7·80.

Genesis.—The ore-deposit was no doubt the product of post-volcanic hydrothermal action. Only secondary minerals in the upper oxidized zone have so far been found, and nothing is known of the primary ore-minerals from which these were derived. A case has been recorded of the presence of tyuyamunite on the bones of a human body that had remained in the mine for three years during the revolution. This has been taken to indicate that the mineral is still being formed. It was long ago shown experimentally by G. Werther (1848) and C. Winkler (1873) that minerals of the uranite group are readily formed even at ordinary temperatures. In the artificial preparation of zeunerite by the action of arsenic acid and uranyl nitrate on freshly precipitated copper carbonate, it was found that the green scales were larger from a cold than from a warm solution.