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TURANITE FROM TYUYA-MUIUN, KIRGIZIA: NEW DATA ON MINERAL

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The new data has been obtained for turanite described in the beginning of the last century at the Tyuya-Muyun deposit; there are the results of study of the holotype specimen from the Fersman Mineralogical Museum RAS (Moscow) and new field collections. Turanite forms spherulite aggregates in assemblage with tangeite, malachite, barite, quartz, calcite; also turanite forms the cavernous aggregations with tangeite. Turanite is olive-green, transparent, often it is represented by polysynthetic twins; the mineral is brittle. The Mohs hardness is 4.5-5, VHN = 436 (354-570 kg/mm^2). The cleavage is perfect on (011). Density (calc) = 4.452 g/cm^3. The unit cell parameters calculated by the X-ray powder pattern are as follows: a = 5.377(6) Å, b = 6.276(7) Å, c = 6.833(7) Å, α = 86.28(2), β = 91.71(3), γ = 92.35(2)°, V = 229.8(1) Å^3. Chemical composition is as follows (the holotype specimene/new collections; wt %): CuO 62.94/64.81, V_2O_5 28.90/29.86, H_2O 5.85 (calculation by the crystal structural data)/5.81 (calculation by the charge balance), total 97.69/100.52. The empirical formula is $Cu_{4.97}(VO_4)_{2.00}(OH)_{4.08}$.
The IR spectra of turanite and tangeite are given. The mineral genesis is hydrothermal. The turanite study results along with the earlier determined crystal structure confirm its status as the original mineral species. At the same time, a revision of information about findings of turanite in Nevada, USA, is necessary.
3 tables, 4 figures, and 12 references.

Studying minerals of vanadium from South Fergana, the authors have realised that the data on turanite, $Cu_5(VO_4)_2(OH)_4$, at present, is scanty and scarcely satisfactory. In the beginning of the last century, K.A. Nenadkevich described two new vanadium minerals from the radium deposit Tyuya-Muyun, alaite and turanite, named them by location of the Tyuya-Muyun pass, «...proper in the limits of north-eastern part of Alai foothills representing the south border of the Turan basin...» (Nenadkevich, 1909). The article probably had a preliminary character, since there were only a brief description of occurrences of two minerals and also their formulas without chemical analyses. In that article, basing on stoichiometry, the author concluded its closeness to mottramite. At the end K.A. Nenadkevich noted, «...analyses and more detailed description of chemical and physical properties of these minerals will be published in Proceedings of Geological Museum of Academy». But in «Proceedings...» this work was not published for any reasons. A.E. Fersman in his review on geochemistry and mineralogy of Tyuya-Muyun (Fersman, 1928) mentioned turanite together with other vanadates: tangeite, vanadinite, and Turkestanian volborthite*. He noted turanite as the most usual vanadate in the upper horizons, in particular, in the Yellow cave. Larsen and Berman (1937) gave optical properties of turanite, which they obtained on material from Tyuya-Muyun. The interplanar spaces (without the hkl indexes) were published for the first time by Guillemin (Guillemin, 1956).

In addition to Tyuya-Muyun, turanite was found in Nevada, USA: application Van-Nav-Sand, Fish Creek region, Eureka district (Pullman and Thomssen, 1999), the Gold Querry mine, Maggie Creek region (Castor and Ferdock, 2004). These works have a character of reports, and turanite is mentioned here only in reviews of occurrences of Nevada, without some analytical data or references on articles, instrumentally confirming the mineral diagnostic. We have examined by the X-ray method two specimens from the Fish Creek region, Eureka district but both are volborthite.

Absence of the reliable instrumental data on chemical composition and crystal structure of the mineral has resulted in that turanite has got the mark «?» in reference books. Therefore, our goal was to check turanite specimens of the Fersman Mineralogical Museum collections. Determination of the crystal structure of turanite (Sokolova et al., 2004) has clarified a question of its status. Our additional study of the turanite properties has finally confirmed the mineral individuality. In this work the data on chemical composition of turanite, more high-quality X-ray powder data, and the IR spectrum of turanite are published for the first time. More information on assemblage and morphology of mineral aggregations is given also.

*Turkestanian volborthite, $2V_2O_5{\cdot}2H_2O{\cdot}3CaO{\cdot}3CuO$ (Fersman, 1928), is tangeite.

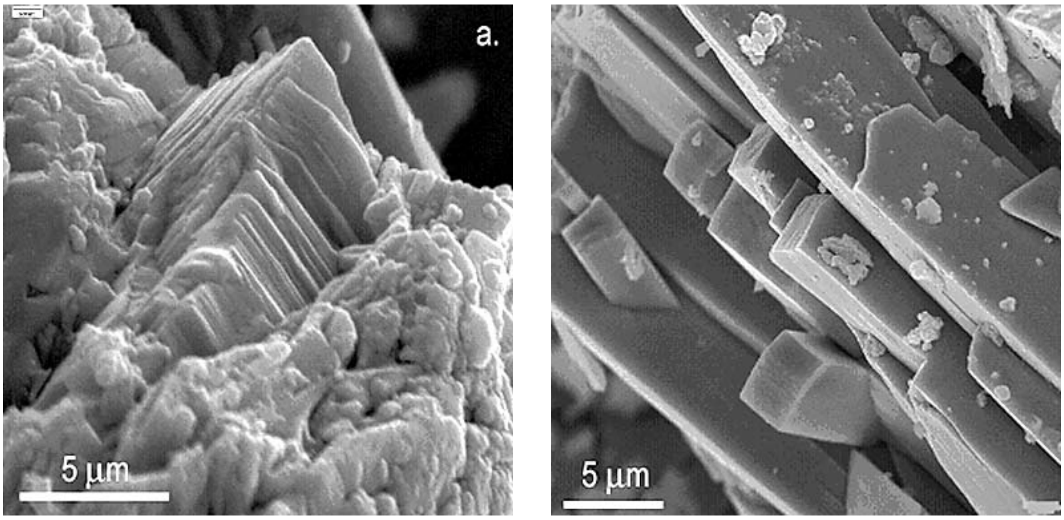


__Fig. 1__. Crystals of turanite and tangeite: a) crystals of turanite; b) aggregate of tangeite crystals from assemblage with turanite. REM-photo

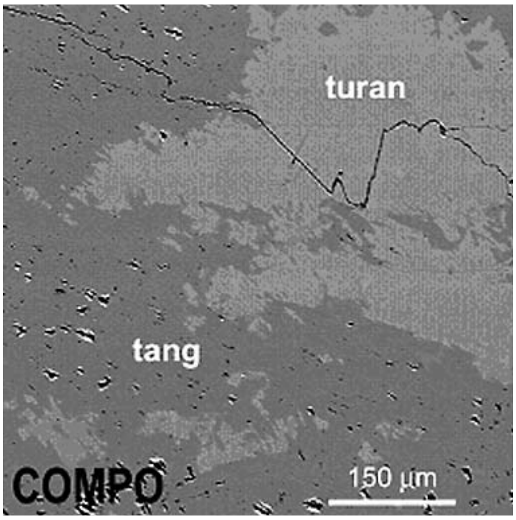
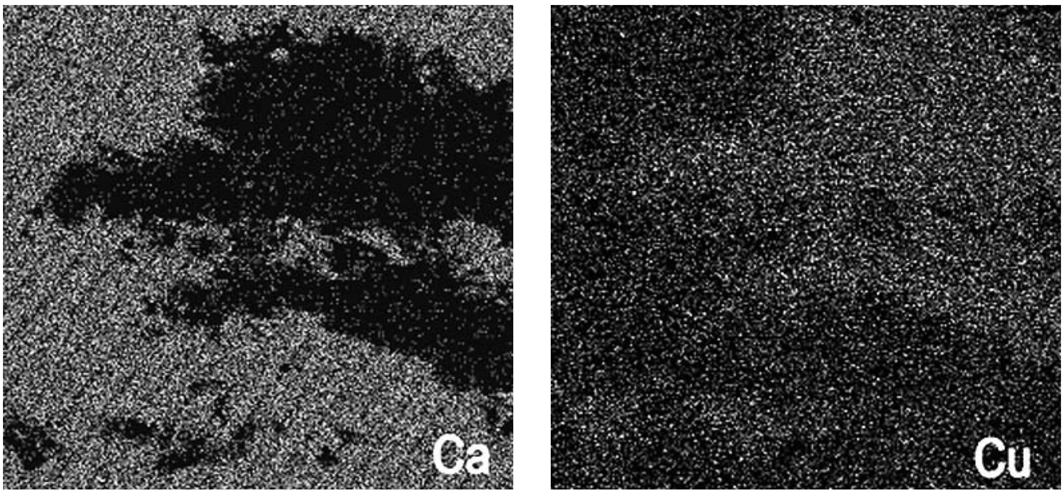


__Fig. 2__. Turanite (turan) – tangeite (tang) aggregate in composition of «olive-green ore». Image in the COMPO regime (a) and in characteristic X-ray radiation Ca (b) and Cu (c)



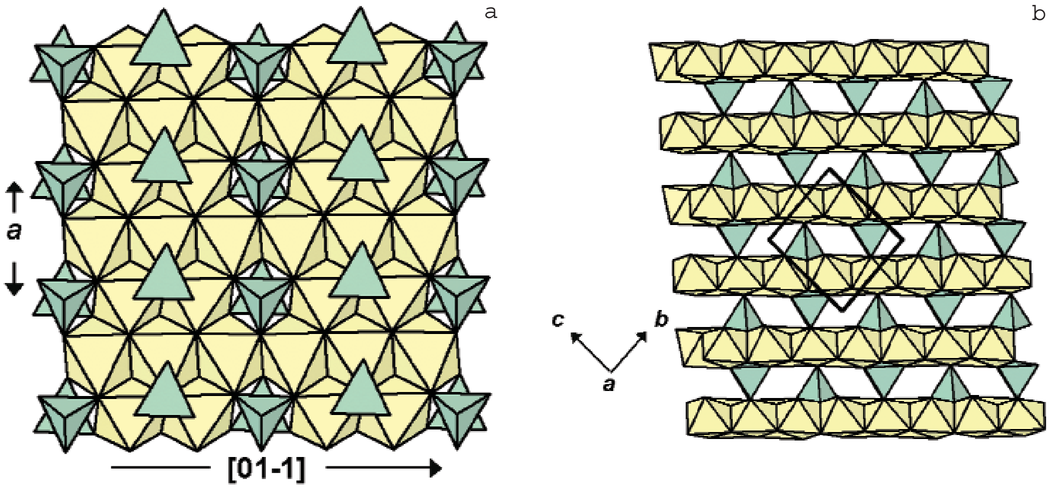


***Fig. 3**. Crystal structure of turanite (by Sokolova et. al., 2004): a) layers of the Cu octahedra and the V tetrahedra in a projection along {001]; b) mixed octahedral-tetrahedral interlayer, view along [100]. The Cu octahedra are yellow; the V tetrahedra are green*

Geology of the deposit

The radium-uranium Tyuya-Muyun deposit has been discovered in 1902; it is located in 30 km to the southeast from the city Osh (Kirgizia), at the left side of middle stream of the Aravan River. It is localized within the bounds of a small range, which was characterized very picturesquely and at the same time exactly by D.P. Mushketov, «...from a distance it appears in the form of sharply outlined, gloomy, long monolith dipped in some extraneous to it, surrounding shapeless mass» (Mushketov, 1926). In the beginning of the last century, the deposit has attracted attention of many researchers, fist of all V.I. Vernadsky, K.A. Nenadkevich, A.E. Fersman, D.I. Shcherbakov. That was connected not only with increased interest to radium at that time, but also unique morphology and genesis of pipe-like ore bodies of the deposit. V.I. Kazanskii (1970) has summarized a history of study of Tyuya-Muyun and also its geological structure. The ore bodies confined to old karst cavities are located in Lower-Carboniferous steeply dipping limestones of sublatitudinal strike, which are penetrated by a grate number of crack dislocations and pressed with both sides by Middle-Upper Paleozoic flinty, coaly-clay shales with intercalations of sandstones and limestones, and also porphyritic tuffs (in the south). The peculiarity of genesis of the Tyuya-Muyun deposit is that «morphology of cavities filled up by ore series is not determined by its active formation during brining of ore elements, but the latter have used in considerable degree the already prepared cavity... of karst character» (Fersman, 1928). The age of karst, according to the data of V.I. Kazanskii (1970), is Paleozoic, i.e. much older than it was supposed by the earlier researchers.

Description of the mineral and assemblage

K.A. Nenadkevich first of all has played a great role in study of material composition of ore bodies of Tyuya-Muyun; he has discovered four new minerals: turanite, alaite, tangeite, and tyuyamunite there. N.N. Smol'yaninova (1970) has made a review on history of mineralogical studies and mineralogy of the deposit. Calcite and barite are the most widespread minerals composing bodies of the karst cavities. Among vanadium minerals, tangeite, including its high-arsenic variety, and tyuyamunite are the most widely distributed; mottramite, descloizite, as well as the vanadium-bearing conichalcite occur in small amounts (Belova *et al.*, 1985). The findings of turanite and alaite are noted only with a reference on the above-mentioned work (Nenadkevich, 1909). Apropos, alaite is not formally approved for some reason by the IMA CNMMN, although its status does not raise doubts thanks to sufficient detailed study of holotype that was conducting by G.A. Annenkova with co-authors (1976).

Table 1. **Unit cell parameters of turanite**

	From data of the crystal structure refinement (Sokolova *et al.*, 2004).	Calculated from the X-ray powder data
a(Å)	5.3834(2)	5.377(6)
b(Å)	6.2736(3)	6.276(7)
c(Å)	6.8454(3)	6.833(7)
α (°)	86.169(1)	86.28(2)
β (°)	91.681(1)	91.71(3)
γ (°)	92.425(1)	92.35(2)
V(Å^3)	230.38(2)	229.8(1)
Space group	P (-1)	
Z	1	

The holotype turanite specimen of systematic collection of the Fersman Mineralogical Museum (No. 3578) and also turanite specimen of our field collections (August, 2003) were studied.

The specimen No. 3578 (4.5 x 7.5 x 5 cm in size) was collected by K.A. Nenadkevich in 1910 and recorded in the Museum in 1912. The aggregations of this type were described him as the «radiate fibrous olive-green globular concretions and kidney-shaped crusts almost exceptionally inside cavities in malachite and strongly mineralised limestone». The specimen represents a fragment of crystal crust formed predominantly by fibrous aggregates of malachite (length of needle-shaped crystals is 0.5-3 mm). In the central part of the specimen there is a cavity filled by large, up to 10 mm in diameter, spherulites of turanite, which have the characteristic saturated volborthite tint. At careful examination of the specimen, the constitution of the turanite spherulites is not radiate fibrous, but radiate lamellar; along the biggest side the length of plates is up to 5 mm. The turanite spherulites are covered by thin crust of swamp-green tangeite. This mineral is represented by thin needle-shaped crystals up to 0.1-0.2 mm in size. Apparently, the overgrowth of tangeite on turanite has the epitaxial character. Moreover, tangeite forms the separate crusts of the matted-fibrous and spherulite aggregates (1-2 mm in diameter) with a light grass green, whitish colour, overgrowing on malachite. Sometimes, in cavities one can see the transparent double-headed quartz crystals (up to 1 mm long), containing abundant inclusions of the tangeite needles. Material for the study of the crystal structure (Sokolova *et al.*, 2004) and obtaining of other properties and given below characteristics was collected from this speci-

Table 2. **X-ray powder diffraction data for turanite, Tyuya-Muyun.**

No. 3578		Guillemin (1956)		Calculated values		
$I_{meas.}$	d/n, Å $_{meas.}$	$I_{meas.}$	d/n, Å $_{meas.}$	I.	d/n, Å.	hkl
		80	7.25			
<1w	5.26			5	5.377	001
10	4.79	100	4.76	100	4.771	011
4	3.67			12	3.659	-111
7	3.47	20	3.45	30	3.484	111
3	**3.41**			15	3.414	002
2	**3.14**			11	3.127	020
3	3.07			18	3.083	012
3	2.91			9	2.9173	-102
				9	2.9166	021
2	**2.84**	20	2.88	9	2.8479	102
9	**2.69**	40	2.70	38	2.6883	200
9	**2.568**	60	2.56	39	2.5682	-1-12
8	**2.491**	30	2.47	39	2.4916	1-21
2w	2.387	10	2.37	7	2.3853	022
7	**2.289**	30	2.29	28	2.2941	211
6	**2.113**	30	2.11	24	2.1162	-103
2	**2.070**			10	2.0761	103
5	**1.971**	30	1.97	22	1.9709	-130
1	**1.918**	10	1.91	7	1.9178	130
1w	1.829			7	1.8297	-222
4w	1.741			14	1.7420	222
3w	1.615	10	1.61	11	1.6161	-114
3w	1.582	10	1.57	15	1.5826	114
5	**1.529**	20	1.53	14	1.5297	-3-12
5	**1.521**			15	1.5231	3-21
2	**1.504**			9	1.5047	-141
4	**1.490**			13	1.4894	0-33
3	**1.469**			12	1.4683	141
3	**1.397**	10	1.40	10	1.3993	-233
2	**1.309**			5	1.3108	-411
				4	1.3092	2-33
<1	1.295			3	1.2965	-2-33
				1	1.2937	-2-41
1w	1.200			3	1.2018	314
				1	1.2003	052
				1	1.1984	-341
1w	1.175			1	1.1767	-144
				3	1.1742	2-15
1w	1.146			4	1.1470	422
				1	1.1463	-431
				2	1.1450	341
1w	1.094			3	1.0941	-2-51
				1	1.0930	153
1w	1.064			2	1.0642	-325
2w	1.059			3	1.0581	-206
1w	1.053			3	1.0581	-206
				2	1.0525	-433
3w	0.986			3	0.9854	-260

Notes. *URS-50IM, FeK radiation, Mn filter, the specimen is a rubber cylinder (d=0.15 mm); RKU-114M camera; w — wide lines; reflexes used for calculation of unit cell parameters are marked by bold (analyst V.Yu. Karpenko)* men.

Among specimens collected by us on August, 2003, in dumps of the Tyuya-Muyun mine in the west part of the Mt. Radievaya, turanite was found as a part of spongy masses noted by K.A. Nenadkevich (1909) and A.E. Fersman (1928) and named «olive ore» by them.

In the compact tangeite-turanite masses, these two minerals are hardly distinguished from each other, but in cavities, turanite can be recognized at once by the tabular morphology of crystals (Fig. 1a), whereas the rod-like crystals are characteristic for tangeite (Fig. 1b). These two minerals are well distinguished in polished sections by reflectivity, which is bigger for turanite in comparison with that of tangeite. Moreover, turanite is polished much better than tangeite. The cavities in turanite-tangeite aggregates are often completely or partly filled up by calcite, rarely by the honey-yellow, brown crystals of barite. A fragment of this tangeite-turanite aggregate is shown of Figure 2.

Physical properties

Turanite has a rich olive-green colour and a vitreous lustre; it is very similar to volborthite. The mineral is transparent in thin fragments. In immersion preparations it shows a polysynthetic twinning. The width of separate individuals in twins is 0.005-0.03 mm that has complicated the selection of material for the crystal structure study (Sokolova *et al.*, 2004). In the concentrated Clerici solution (density is 4.25 g/cm^3), the mineral grains slowly submerge. The calculated density of turanite is 4.452 g/cm^3. Cleavage is perfect on (011); the mineral is brittle. The Mohs hardness is 4.5-5. The micro-indentation hardness measured with the PMT-3 instrument in a section perpendicular to (011) is VHN = 436 kg/mm^2 (10 measurements, fluctuation of values is 354-570 kg/mm^2, load 50 g, calibrated by NaCl). The hardness of turanite is the additional diagnostic characteristic distinguishing it from volborthite, which is close by surface properties, but has the lower Mohs hardness — 3.5-4, VHN = 150-220 kg/mm^2).

X-ray study

The study of crystal structure of the mineral was made on a four-circle diffractometer Bruker P4 with CCD detector APEX 4K, MoKα radiation (Sokolova *et al.*, 2004). The crystal structure

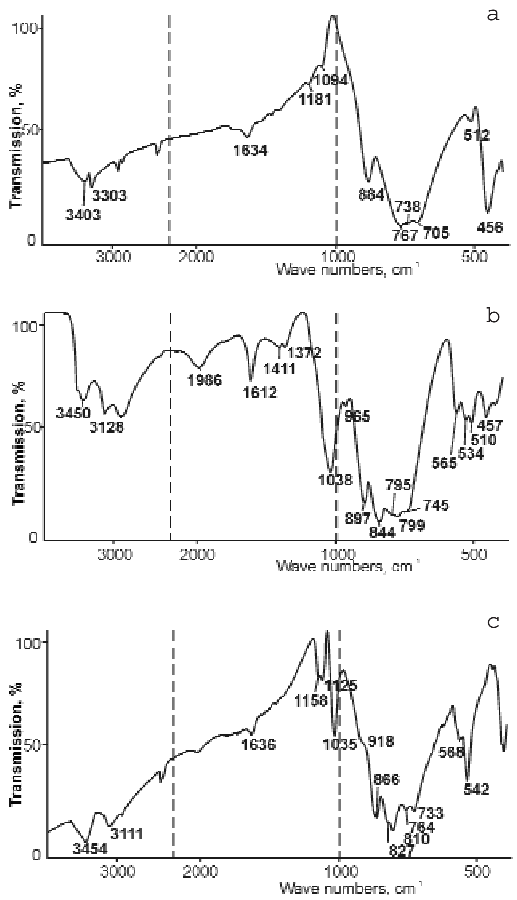


Fig. 4. The IR spectra: a) turanite, the specimen No. 3578 (FMM); b) volborthite (Upper Khodja Akhmet, Uzbekistan); c) tangeite (lab. No. 744)

was determined by a direct method and refined with the R factor equal to 2.2% for 1332 unique reflexes; space group is P(-1), the unit cell parameters are given in Table 1. The layers of the Cu octahedra are parallel to (001) and make a basis of crystal structure (Fig. 3a); they cause a perfect cleavage of the mineral. There are three Cu sites, first of which is coordinated by four (OH) groups and two O atoms; the Cu(2) and Cu(3) sites are coordinated by two (OH) groups and four O atoms respectively. Also there is a single four-coordinated V site surrounded by the O atoms. Each of the (VO_4) tetrahedra leans by three of four its vertices on the vertices of the vacant octahedra. Being located between the Cu octahedra layers, the tetrahedra form a structure of «sandwich» (Fig. 3b). The same motives are known for crystal structures of simonkolleite, cianciullite, gordaite, cornubite, and ramsbeckite (Sokolova *et al.*, 2004).

We obtained the X-ray powder pattern for

Table 3. Chemical composition of turanite and tangeite, Tyuya-Muyun (wt %).

Components	Turanite			Tangeite	
	(mean from 2 analisys)	(mean from 2 analisys)			
	1	2	3	4	5
CaO				22.59	11.29
CuO	62.94	64.81	64.60	34.32	23.65
PbO					27.96
V_2O_5	28.90	29.86	29.54	36.35	18.89
SO_3				2.49	0.67
As_2O_5					10.40
H_2O	5.85*	5.81**	5.85	3.66**	3.13**
Total	97.69	100.48	100.00	99.41	95.99

Note. *Amount of water was calculated: * by results of the crystal structure refinement; ** by the charge balance. 1-3 turanite (calculation on 2 atoms of V): 1 — large spherulites (specimen No. 3578, systematic collection of the FMM),* $Cu_{4.97}(VO_4)_{2.00}(OH)_{4.08}$; *2 — a part of the spongy tangeite-turanite aggregates (lab. No. 744, 2003),* $Cu_{4.96}(VO_4)_{2.00}(OH)_{4.08}$; *3 — ideal chemical composition,* $Cu_5(VO_4)_2(OH)_4$; *4-5 tangeite (calculation on the base of 1 atom (V+As+S): 4 — a part of the spongy aggregates with turanite (lab. No. 744),* $Ca_{0.94}Cu_{1.00}(VO_4)_{0.93}(SO_4)_{0.07}(OH)_{0.95}$; *5 — lead-arsenic tangeite the zoned-concentric kidney-shaped concretion,* $(Ca_{0.66}Pb_{0.40})_{1.06}Cu_{0.97}[(VO_4)_{0.68}(AsO_4)_{0.29}(SO_4)_{0.03}]_{1.00}(OH)_{1.09}$. *Analyses 1, 2, 4 — analyst A.A. Agakhanov; 5 — analyst P.E. Kotel'nikov*

the specimen No. 3578. The unit cell parameters calculated by the X-ray powder pattern and the interplanar distances and are given in the Tables 1 and 2 respectively. The X-ray data given by C. Guillemin (1956) correspond in whole to our data, excepting an interplanar distance d/n = 7.25 Å, which is possibly an artifact or connected with some admixture.

The turanite crystals have a tabular habit determined by a pinacoid {011}. The large crystals of turanite is not well-shaped; unfortunately, it was not possible to measure the small crystals (up to 0.05 mm) because of their size.

Chemical composition

Turanite is the second hydrous vanadate of copper after volborthite, which has been found in nature. Chemical composition of the mineral was studied with a JCXA-50A JEOL electron microprobe instrument, equipped with a LINK energy-dispersive spectrometer, at accelerating voltage 20 kV and electron microprobe current 3 nA. Standards were as follows: metallic Cu and V (Cu, V), diopside USNM 117733 (Ca), barite (S). The arsenic-lead tangeite (an. 5) was analysed with an Superprobe 733 instrument equipped with a INKA ENERGY energy-dispersive spectrometer, 20 kV, electron microprobe current 2.5 nA; standards were as follows: metallic Cu and V (Cu, V), $CaSiO_3$ (Ca), SiO_2 (Si), PbS (Pb), GaAs (As).

The calculated data was accepted for H_2O. Chemical composition of the mineral is given in Table 3. Moreover, tangeite, forming a part of the cavernous aggregates together with turanite, was analysed. A small amount of sulphur, stably presenting in different parts of the analysed tangeite, attracts attention. Arsenic tangeite with unusually high content of lead was found in one of the specimens formed by the zoned kidney-shaped aggregate. Although, in this specimen turanite was not detected, we give chemical composition of tangeite, which more completely characterizes an assemblage of vanadium minerals of Tyuya-Muyun.

IR spectra

The IR spectra of turanite and tangeite were obtained with a Nicolet IR Fourier spectrometer; a mineral specimen was pressed in the KBr tablet (Fig. 4). For comparison, the IR spectrum of volborthite obtained in identical conditions is given. On the spectra of turanite and volborthite one can see the characteristic absorption bands in a range of 450-460 cm^{-1} and 730-1100 cm^{-1}; they are connected with the stretching vibrations of the VO_4 tetrahedra. The main distinctions among them are in a range of 510-600 cm^{-1}. Probably, these distinctions are connected with a presence of the VO_4 tetrahedra jointed in diorthogroups in volborthite. In addition to the characteristic absorption bands connected with the VO_4 tetrahedra, tangeite has a small band in a range of 1120-1160 cm^{-1} that is caused by a sulphate group included in the structure. These data is quite conformed to data of the electron microprobe analysis. In volborthite, the presence of the molecular water is fixed by an intensive band of the bending vibrations δ_{H_2O} at 1612 cm^{-1}, whereas this band is not enough expressed in the tangeite and turanite spectra. A range of 3000-3500 cm^{-1} corresponds to the stretching asymmetric vibrations of the (OH) groups.

Genesis and discussion

The results of study of the holotype specimen and an examination of the additionally collected material show that turanite is indeed a quite individual mineral with the original crystal structure and chemical composition.

According to data of A.E. Fersman (1928), turanite was formed from thermal waters, which extracted vanadium from the Mesozoic coaly shales located to the south. Quartz porphyries cutting the shales were a source of copper. For all specimens we have observed the more late formation of tangeite with respect to turanite. That seems connected with solutions enrichment by calcium. It is interesting, that at the deposit is no volborthite in spite of abundance of vanadium and copper. Formation of turanite instead of volborthite is an evidence of the specific genetic conditions, which cannot occur realized in nature frequently. Since volborthite was found in the specimens from Nevada, USA, the authenticity of the turanite findings here raises doubts and necessarily demands the instrumental confirmation.

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