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NEW OCCURENCE OF NICKELALUMITE ON KARA-CHAGYR, SOUTH KIRGIZIA

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The finds of rare nickelalumite was made on occurrences of vanadium-bearing schists of Kara-Chagyr and Kara-Tangi (Batkensk Region, Kirgizia). The mineral forms radiate-fibrous segregations, spherulites up to 1–2 mm in size in assemblage with ankinovichite, volborthite, tyuyamunite, allophane. The mineral colour is from light blue, almost colourless, to dark green. The intensive green colour is due to increased content of vanadium, which enters in the mineral as isomorphous admixture (up to 6.54% V₂O₅). Refractive index of vanadium-free nickelalumite are $n_g = 1.533(2)$, $n_p = 1.524(2)$, high-vanadium nickelalumite $n = 1.575 - 1.580$ (average index). In the article there are a table of chemical compositions of nickelalumite and the diagrams of correlation dependence for pairs Ni — (sum of divalent cations), S–V, Si–V, Al–Si, Al–S. High-zinc nickelalumite is characteristic for Kara-Tangi, some analyses corresponds to zinc analogue of this mineral. The following scheme of heterovalent isomorphism is proposed: $Al^{3+} + (SO_4)^{2-} \rightleftharpoons Si^{4+} + (VO_4)^{3-}$, that is also confirmed by IR-spectroscopy data. Taking into account this scheme, the formula of nickelalumite is $(Ni, Zn, Cu^{+2})(Al, Si)_4[(SO_4)_i(VO_4)_j](OH)_{12} \cdot 3H_2O$.

The origin of this mineral is connected to low-temperature alteration of carboniferous-siliceous schists, having increased contents of nickel and zinc. The find of nickelalumite is, obviously, the second in the world.

2 tables, 11 figures, and 6 references.

Looking through the V.I. Kryzhanovskii collections of minerals from vanadium-bearing schists of Kara-Chagyr (Batkensk Region, Sought Kirgizia), which are dated by 1926 year and kept in funds of Fersman Mineralogical Museum, the authors discovered among samples, registered as kolovratite*, the light blue, sometimes whitish crusts, composing by thin needle-shaped radiate-fibrous aggregates. The instrumental diagnostic has shown the mineral, composing the crusts, is nickelalumite, $(Ni, Cu^{+2})Al_4[(SO_4)_i(NO_3)_2](OH)_{12} \cdot 3H_2O$, monoclinic system, i. e. extremely rare mineral.

Along with other representatives of this group, mbobomkulite, $(Ni, Cu^{+2})Al_4[(NO_3)_2, SO_4]_2(OH)_{12} \cdot 3H_2O$, monoclinic system, and hydro-mbobomkulite, $(Ni, Cu^{+2})Al_4(NO_3, SO_4)_2(OH)_{12} \cdot 13 - 14H_2O$, monoclinic system, it occurs only in South Africa in Mbobo Mkulu cave (Martini, 1980). In autumn 2002 we have visited the areas of carboniferous-siliceous schists outcrops in South Fergana, which are most rich in vanadium mineralization (Kara-Chagyr, Kara-Tangi), with the purpose of material collecting for data refinement on a whole number of minerals. Among minerals collected by us the nickelalu-

mite also was found. The find of this rare mineral allows making its detail study.

In spite of extremely rich vanadium and nickel mineralization, vanadium-bearing schists of Mt. Kara-Chagyr (Photo 1) (right slope of middle current of River Isfairsai, Batkensk Region, Kirgizia) remain a very little studied mineralogical object till now. First mineralogical researches on this area are concerned to work period of Radium expedition, when kolovratite (Vernadsky, 1922; Popov, 1925), volborthite (named «uzbekite») (Fersman, 1928), and also nickel-enriched asbolan-like mineral (Saukov, 1926) were described. Studying Tyuya-Mun mine, A.E. Fersman (1928) broached a geochemistry of processes, occurring of Kara-Chagyr. Unfortunately, these works limit mineralogical and geochemical investigation of Kara-Chagyr till now. The outcrops of secondary minerals on Kara-Chagyr are confined to belt of spreading of uranium-bearing carboniferous-siliceous schists, extending on several hundred kilometers along foothills of Alai range. They belong to Early Carboniferous South Fergana melange complex, which serpentinite matrix contains large blocks of Early

* Today's the status of kolovratite calls in question because the absence of accurate chemical formula and crystal structural data till now, nevertheless, there was not the discredit of the mineral. Jambor and Lachance (1962) make the X-ray data for phase, which by set of chemical elements does not contradict that be consider to kolovratite. Although, the mineral undoubtedly requires completing of study, the authors incline to opinion the kolovratite has the right on existence as independent species.

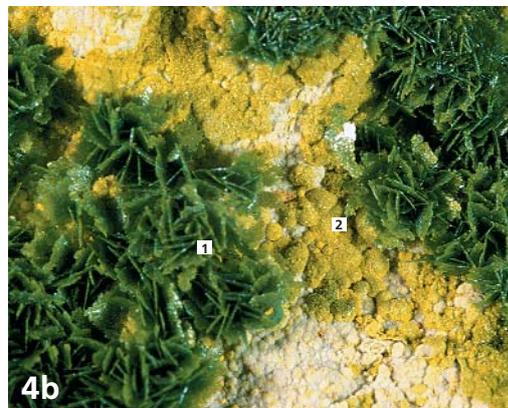
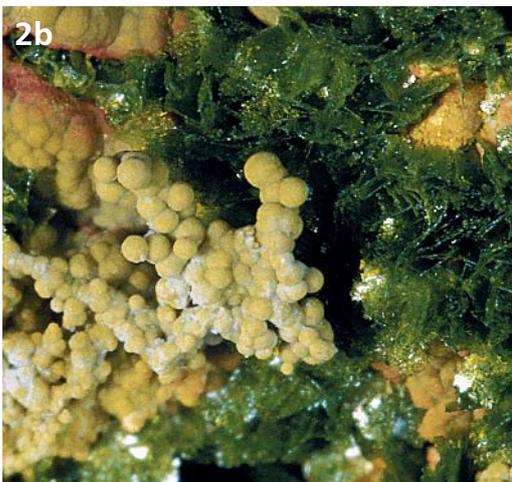
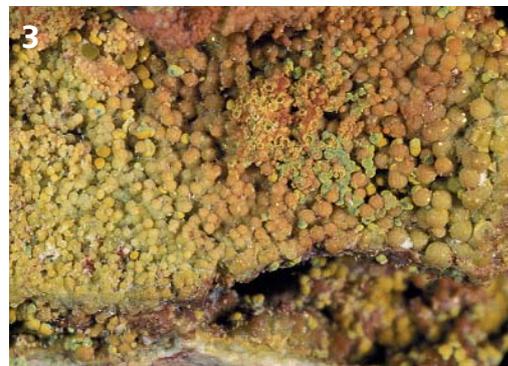


Photo 1. A typical view on vanadium-bearing shists. Kara-Chagyr deposit. Photo by V.Yu. Karpenko

Photo 2. Vanadium-bearing nickelalumite spherulites with volborthite, Kara-Chagyr.
a) № 5439 (4x6 mm)* (there is a bluish ankinovichite core on allophane in front of the picture);
b) № 5341 (3x4 mm).
Photo: Natalia A. Pekova

Photo 3. Vanadium-bearing nickelalumite spherulites, Kara-Chagyr. № 5345 (4x6 mm).
Photo: Natalia A. Pekova

Photo 4. Two generations of volborthite (dark-green sceleton tabular crystals (1) and light-green acicular ones (2)), growing upon nickelalumite spherulites. Kara-Chagyr — a) № 5339 (10x6 mm); b) № 5444 (5x3 mm). Photo: Natalia A. Pekova



* here and further size of a image size is given

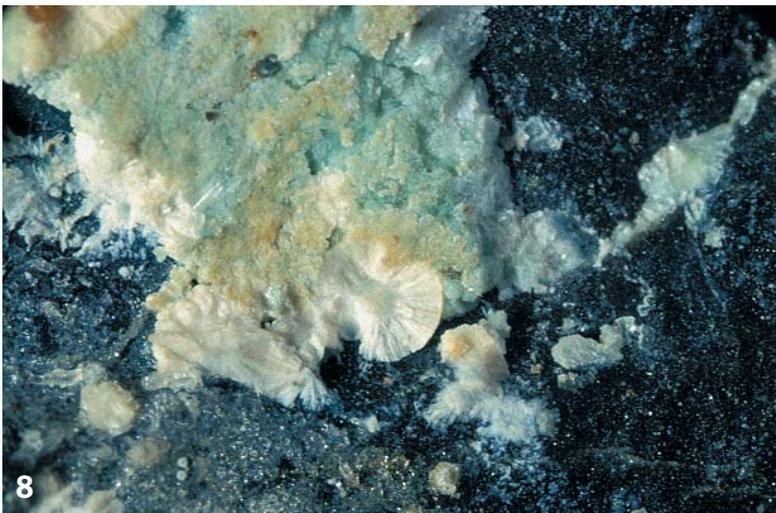


Photo 5. A small-grained ankinovichite core, grown upon nickelalumite spherulites. Yellow crystals belong to tyuyamunite and brownish core — to allophane. Kara-Chagyr. № 5448 (6x10 mm).

Photo: Natalia A. Pekova

Photo 6. Nickelalumite spherulites, covered with a core of ankinovichite acicular crystals, Kara-Chagyr. № 5445 (6x9 mm).

Photo: Natalia A. Pekova

Photo 7. Tyuyamunite tabular yellow crystals and volborthite dark-green ones, grown on ankinovichite spherulites. Kara-Chagyr. № 5443 (5x8 mm).

Photo: Natalia A. Pekova

Photo 8. A bluish core of a zincian nickelalumite. Spherulite in the center belongs to allophane pseudomorphose upon nickelalumite. Kara-Tangi. № 5360 (3x4 mm).

Photo: Natalia A. Pekova

Paleozoic carboniferous-siliceous rocks, carrying vanadium mineralization. Kara-Tangi is located at the same belt, 25 km westward from village Kadamdzhai. This is uranium deposit, exploited during 1960-th years. Unfortunately, in open press there are no publications on mineralogy of this deposit.

Occurrence

Nickelalumite on Kara-Chagyr was found in dumps and also in primary occurrence at mouth of old mine working among multi-coloured mass of nickel and vanadium minerals, developing in the cracks of quartz breccias in carboniferous-siliceous schists. In the samples this mineral looks like recently discovered nickel analogue of alvanite, ankinovichite, $(\text{Ni,Zn})\text{Al}_4(\text{VO}_3)_2(\text{OH})_{12}\cdot 2\text{H}_2\text{O}$, monoclinic system. But if ankinovichite forms crystals of good facet, then apexes of nickelalumite crystals often will block, split (Fig. 1a, 1b). The colour of nickelalumite is from light blue, almost colourless, to pistachio-coloured green. The following study has shown that deeper green colour is characteristic for vanadium-bearing minerals, and bluish, almost colourless, segregations do not practically contain vanadium. The mineral forms radiate-fibrous aggregates with length of separate fibres from 0.05 up to 0.1–0.5 mm (Fig. 1a, 1b), which is in close assemblage with ankinovichite, volborthite, allophane, tyuyamunite, rarely tangeite. As a rule, nickelalumite forms the crusts of solid spherulite aggregates of light green (Photo 2a, 2b), rich-green (Photo 3) colours. The concentric-zonal structure is observed on cross split of these aggregates. Rarely in the rock cavities it forms practically ideal spheres, growing on lamellar skeletal crystals of volborthite (Photo 4a, 4b). Spherulites sizes reach 1.5 mm. It is interesting to note the different on colour and vanadium content individuals occur together within the bounds of one small cavity.

Often crystal crust of ankinovichite of green colour with different tints and thickness up to 1.5–2 mm (Photo 5) grows on spherulite crusts of nickelalumite. Between these crusts, as a rule, there is the allophane intercalation, at the expense of that the upper crust is sufficiently easy separated. Sometimes spherulites of nickelalumite are covered by downy coating of the smallest ankinovichite crystals, which are oriented perpendicular to spherulite surface (Photo 6). In single samples the lamellar crystals of tyuyamunite grows on nickelalumite-ankinovichite spherulites (Photo 7).

At Kara-Tangi deposit nickelalumite was found in the sample from dumps of adit in the right side of the same name sai. Here the mineral forms crystal crust of light blue colour on the surface of carboniferous-siliceous schist. This crust is composed by radiate-fibrous, lamellar aggregates with individual sizes up to 1–1.5 mm. Some of nickelalumite spherulites are replaced by allophane (Photo 8). The peculiarity of nickelalumite from Kara-Tangi is increased zinc content, in single crystals zinc prevails on nickel, which corresponds to new phase, zing analogue of nickelalumite (Table 1, analyses №№ 15–16).

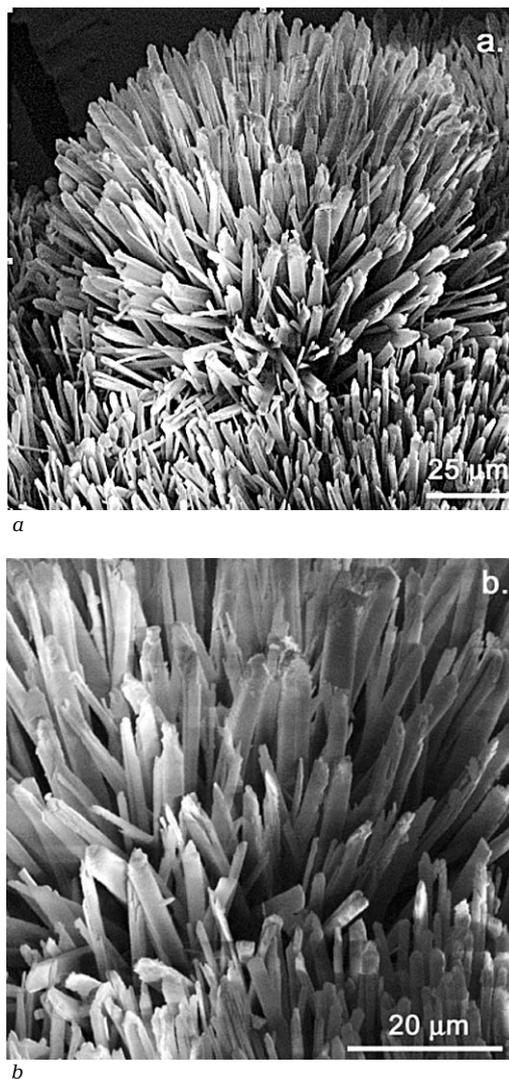


FIG. 1. Morphology of non — vanadium nickelalumite spherulites (FMM № 6794). a) A general view of spherulite; b) fragment. SEM- photo

Table 1. Chemical compositions of nickelalumite and its zinc analogue

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
№№	597/24	6794	5341	5341	5434	5439	5439	5334	5360	5360	5360	5360	Martini	theoreti	5360	5360
	(FMM)	(FMM)											(1980)	cal		
NiO	12.07	11.00	10.03	8.87	9.81	9.63	9.45	7.77	10.03	9.87	8.08	7.05	6.59	14.34	4.34	2.36
ZnO	0.66	2.04	1.15	0.34	1.92	2.40	2.05	2.25	4.83	4.88	6.24	6.64	0.00		9.45	13.02
CuO	0.00	0.12	1.10	0.31	1.63	1.90	2.44	0.95	0.22	0.1	0.52	0.72	2.35		0.95	0.06
FeO	0.02	0.00	0.00	0.00	0.24	0.08	0.00	1.80	0.03	0.29	0.33	0.02	0.00		0.41	0.20
Al ₂ O ₃	38.05	37.78	36.35	38.99	40.35	37.19	36.23	38.77	38.83	37.67	37.73	37.76	39.30	39.15	37.85	39.42
SiO ₂	0.77	0.45	1.08	0.61	0.00	3.76	2.12	1.10	0.69	0.41	0.64	0.38	8.95**		0.42	0.52
SO ₃	14.45	14.19	11.99	13.10	11.63	9.44	10.36	11.96	14.80	14.11	14.54	14.38	10.28	15.38	14.54	14.63
V ₂ O ₅	0.00	0.06	5.40	5.60	5.24	6.54	5.62	5.07	0.00	0.21	0.11	0.04	0.00		0.00	0.06
H ₂ O	31.10	31.10	31.10	31.10	31.10	31.10	31.10	31.10	31.10	31.10	31.10	31.10	28.53	31.10	31.10	31.10
Total	97.12	96.74	98.20	98.92	101.92	102.04	99.37	100.77	100.53	98.64	99.29	98.09	100.70	99.97	99.06	101.37
Formula calculated on 4 (Al + Si)																
Ni ⁺²	0.85	0.79	0.73	0.61	0.66	0.65	0.68	0.53	0.69	0.71	0.58	0.51	0.75	1.00	0.31	0.16
Zn ⁺²	0.04	0.13	0.08	0.02	0.12	0.15	0.14	0.14	0.31	0.32	0.41	0.44			0.62	0.82
Cu ⁺²	0.00	0.01	0.08	0.02	0.10	0.12	0.16	0.06	0.01	0.01	0.03	0.05	0.25		0.06	0.00
Fe ⁺²	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.13	0.00	0.02	0.02	0.00			0.03	0.01
Σ(Me⁺²)	0.89	0.93	0.89	0.65	0.90	0.93	0.98	0.86	1.01	1.06	1.04	1.00	1.00	1.00	1.02	0.99
Al ⁺³	3.93	3.96	3.90	3.95	4.00	3.68	3.81	3.91	3.94	3.96	3.94	3.97	4.00	4.00	3.96	3.96
Si ⁺⁴	0.07	0.04	0.10	0.05	0.00	0.32	0.19	0.09	0.06	0.04	0.06	0.03			0.04	0.04
(Al+Si)	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
S ⁺⁶	0.95	0.95	0.82	0.84	0.73	0.60	0.69	0.77	0.69	0.95	0.97	0.96	0.75	1.00	0.97	0.93
V ⁺⁵	0.00	0.00	0.32	0.32	0.29	0.36	0.33	0.29	0.33	0.01	0.01	0.00			0.00	0.00
(S+V)	0.95	0.95	1.14	1.16	1.02	0.96	1.02	1.06	1.02	0.96	0.98	0.96	0.75	1.00	0.97	0.93
(OH) ⁻	11.95	12.00	11.28	10.71	11.47	11.91	11.78	11.40	11.71	12.23	12.17	12.11	12.00	12.00	12.14	12.16
H ₂ O	3.12	3.23	3.81	3.56	2.99	2.20	3.37	3.17	3.08	3.15	3.12	3.19	3.00	3.00	3.15	2.75

Note:

All analyses are performed by microprobe (except № 13 — wet chemistry (Martini, 1980)). The contents of H₂O (except analysis 13) are theoretical. The content of N₂O₅ is 4.70% (0,50 apfu) for № 13 and undetermined for other samples.

1–8 — Nickelalumite, Kara-Chagyr: 1–2 — light blue needle-shaped, 3–4 — light green spherulites, 5–7 — central zone of dark-green spherulite, 8 — green spherulite. 9–12 — Nickelalumite, Kara-Tangi: light blue radiate-fibrous segregations. 13 — Nickelalumite, Mbobu Mkulu (S. Africa) (** — admixtures of opal and allophane). 14 — Nickelalumite, theoretical values. 15–16 — Zinc analogue of nickelalumite, Kara-Tangi: light blue radiate-lamellar segregations.

Chemical composition

The chemical composition of nickelalumite was studied in polished preparations on electron microprobe JXA-50A with energy-dispersive spectrometer Link (Tabl. 1). The experimental conditions were as follows: accelerating voltage 20 kV, absorbed electron current 3×10^{-9} A. The standards: microcline USNM 143966 (Si, Al), ilmenite USNM 96189 (Fe), gahnite USNM 145883 (Zn), metallic V and Cu (V, Cu), NiO (Ni), barite (S). The concentrations were calculated using ZAF-correction. Formula was recalculated on 4 atoms (Al + Si).

The samples from Kara-Chagyr and Kara-Tangi with different colour and morphology were analyzed. The wide variation of components contents in nickelalumite attracts

attention. Because of paucity of analytical data on chalcoalumite group minerals, there are no sufficient data for estimation of possible izomorphous variations within the group limits till now. The results of our analyses allow partly filling this gap. The correlation diagrams of dependence between contents of main components of the mineral demonstrate availability of isomorphism between divalent cations and also between silica, sulfur, and vanadium (Fig. 2a-2e). The isomorphism between divalent metals (mainly between nickel and zinc) brings to continuous series from zing-free nickelalumite up to its zinc analogue. Taking into account the constant presence of small amounts of copper, there is, probably, an isomorphism in threefold system nickelalumite — chalcoalumite — zinc analogue of nickelalu-

mite.

More complicated scheme of isomorphism is visible between Al, Si, S, and V. The negative dependences between pairs Al-Si and V-S, the positive trends between contents of silica and vanadium, and also aluminum and sulfur are observed. In all probability, vanadium is present as anion $(VO_4)^{3-}$, that is indirectly confirmed by IR-spectroscopy data. Thus, the following scheme of isomorphism is seems to be probable: $Al^{3+} + (SO_4)^{2-} \rightleftharpoons Si^{4+} + (VO_4)^{3-}$.

It is obvious from this equation, that excess positive charge, arising from partial replacement of aluminum by silica, can be compensated by excess negative charge, which is introduced, in our case, by anion $(VO_4)^{3-}$. Thus, taking in account this scheme of isomorphism, the ideal formula of nickelalumite from Kara-Chagyr can be record as following: $(Ni,Zn,Cu^{+2})(Al,Si)_4[(SO_4)_1,(VO_4)](OH)_{12} \cdot 3H_2O$.

Nickelalumite from Kara-Tangi is practically vanadium-free, whereas on Kara-Chagyr the content of vanadium fluctuates in wide range, up to significant vanadium variety. The characteristic distinction of nickelalumite with different chemical composition is the colour of the sample. As a rule, vanadium-free nickelalumite forms light blue, almost colourless crystals, while vanadium one has green colour of different tints, from light green to grass deep green. The central parts of some spherulites from Kara-Chagyr are enough high-vanadium (see analyses №№ 5–7, Tabl. 1), whereas the peripheral part is depleted by vanadium. Because of that there is a probability of existence of phase with predominance of $(VO_4)^{3-}$ over $(SO_4)^{2-}$, i. e. the mineral, which is vanadium analogue of nickelalumite.

Optical properties. X-ray data

Under microscope vanadium-free nickelalumite is transparent, almost colourless. Its crystals are flattened prismatic and rich in length up to 0.1 mm. Nickelalumite is optically biaxial, negative. The mineral extinction is oblique, extinction angle relatively to crystal elongation is 40° , $n_g = 1.533(2)$, $n_p = 1.524(2)$. The aggregates of vanadium-bearing nickelalumite under microscope have fine-fibrous structure; here it was possible to measure the middle index $n \sim 1.575 - 1.580$ (for sample № 5439, analyses №№ 5–6 in Tabl. 1). Nevertheless, it is evident, that the presence of vanadium leads to increasing of refractive indexes of this mineral.

X-ray data are in the Tabl. 2. It is necessary to note that most satisfactory data was per-

Table 2. X-ray powder data for nickelalumite

1		2		3		hkl
I	d/n, Å	I	d/n, Å	I	d/n, Å	
10wb	8.35	10wb	8.54	100	8.543	0 0 2
					7.877	0 1 1
3	6.61			5	6.667	1 1 0
		1wb	6.35	5	6.364	1 1 -1
				5	6.073	1 1 1
					5.431	1 1 -2
		3wb	5.00	5	5.095	1 1 2
				10	4.778	0 1 3
3wb	4.62			10	4.577	2 0 -2
9	4.27	9	4.26	60	4.267	0 0 4
				10	4.179	2 0 2
2wb	3.71					1 1 -4
5	3.30	3	3.36	2	3.332	2 2 0
4	3.16	2	3.16	5	3.177	2 2 -2
6	3.02	3	3.01	10	3.044	3 1 1
6	2.683	1wb	2.700	5	2.718	1 3 -2
				2	2.623	0 3 3
2	2.592					2 1 5
8	2.508	7	2.516	15	2.507	1 3 3
		3	2.412			2 3 2
7	2.276	8	2.282	15	2.289	1 2 6
3	2.222	1	2.210	5	2.208	-4 1 4
		<1	2.140			2 3 4, 1 4 1
2	2.067			1	2.098	2 2 6
				1	2.027	2 4 0, 3 3 3
9	1.981	9	1.993	20	1.997	2 3 5
				1	1.899	2 0 8, 0 0 9
				1	1.855	-4 0 7, 3 4 -1
3	1.824					1 3 7
3	1.811	1	1.811	5	1.81	1 4 5
4	1.740					1 4 -6, 1 5 -1
4	1.710	2	1.714	10	1.72	2 0 9
1	1.647					5 3 1, 4 4 1
3	1.556	2	1.558	1	1.56	3 1 9
6	1.480	7wb	1.479			
6	1.455	7wb	1.457			
4	1.400	1	1.397			
4	1.361					
		2	1.350			
1	1.302					
1	1.272					
1	1.241					
1	1.217	1	1.221			
4	1.189	4	1.188			
		3	1.122			

Experimental conditions (1-2): CuK α radiation, Ni filtre, RKD-57.3, the preparation is rubber post.

1 — Nickelalumite (vanadium-free), Kara-Chagyr (specimen 6794, FMM).

2 — Vanadium-bearing nickelalumite, Kara-Chagyr (specimen 5332).

3 — Nickelalumite, Mbobo Mkulu (Martini, 1980);

wb — wind band

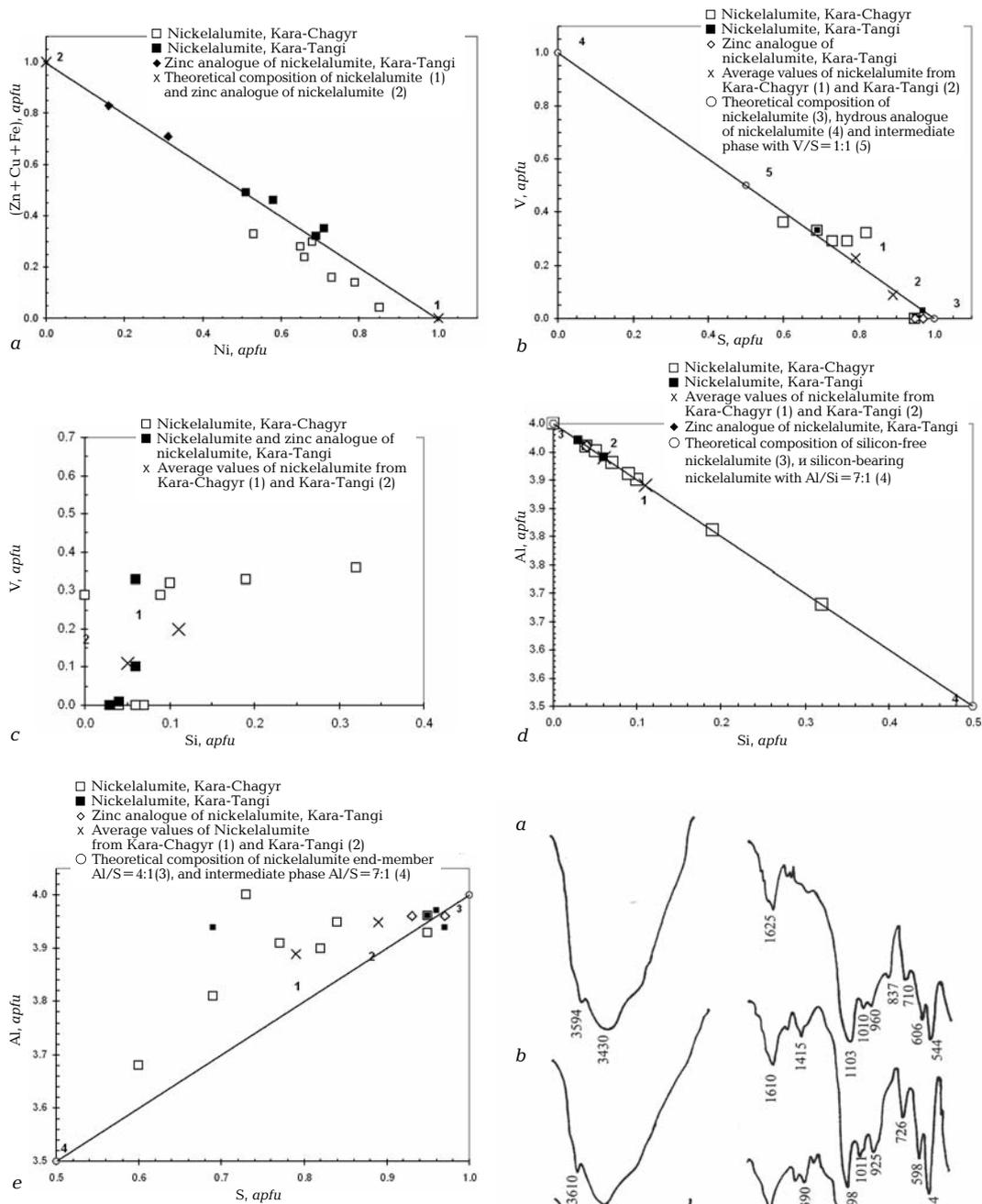
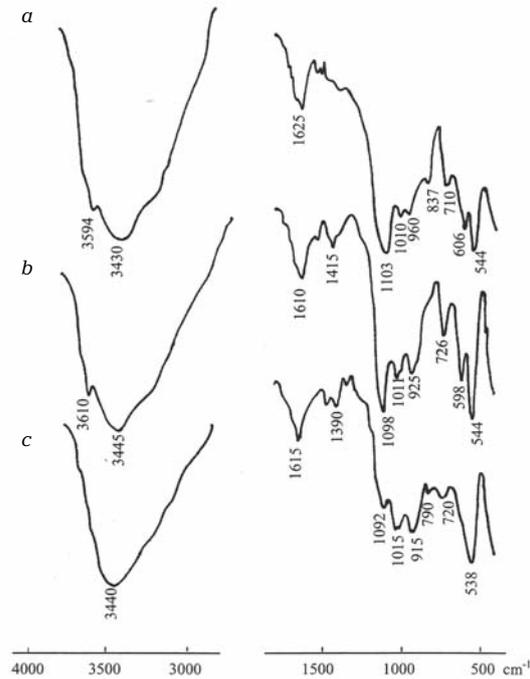


FIG. 2. Crystallochemical dependence for nickelalumite and its Zn-analogue: a) S (2-valence metals) versus Ni; b) V versus S; c) V versus Si, d) Al versus Si; e) Al versus S

FIG. 3. IR-spectra of nickelalumite and chalcoalumite: a) chalcoalumite, Grand Canyon, Az., USA, FMM № 79266; b) nickelalumite non-vanadious (light acicular xls), Kara-Chagyr, Kirgizia, FMM № 597/24; c) nickelalumite vanadious (apple-green spherulites), Kara-Chagyr, Kirgizia, № 5434



formed by photomethod (URS-50, CuK α radiation, Ni filter, camera RKD-57.3). The quality of diagram was extremely low, that is, apparently, connected to texturization of the sample during preparation.

IR-spectroscopy

IR-spectra of studied nickelalumite, and also, for comparison, chalcoalumite, are on Fig. 11a-11c. The spectrum of pure nickelalumite is very close to that of chalcoalumite, which is confirmed the structural closeness of two minerals. The bands 598–606, 1010–1011, and 1098–1103 cm^{-1} , connected to oscillations of SO_4 -tetrahedra, are characteristic. The band 1098–1103 cm^{-1} of both the pure nickelalumite, and chalcoalumite differs by enough intensity with respect to the band 1010–1015 cm^{-1} , that is peculiar to sulphates, which compositions the significant isomorphous admixtures is not observed in. At the same time for vanadium-bearing nickelalumite the intensity of the band 1092 cm^{-1} is significant decreased. This fact is known to be connecting with activation of full-symmetrical valent oscillations of SO_4 -tetrahedra that, in its turn, is caused by violation of local symmetry at the isomorphous replacement of sulphate anion by other one. Moreover, in the spectra of vanadium-bearing nickelalumite (the data for several samples was made) the appearance of small additional band in the range 750–800 cm^{-1} is observed. Very probable this band is connected to oscillations of V^{+5} in tetrahedron coordination (the same bands are characteristic for vanadates, for example, descloizite, tyuyamunite *et cetera*). Thus, IR-spectroscopy data do not contradict to our assumption about isomorphous replacement of $(\text{VO}_4)^{3-}$ and $(\text{SO}_4)^{2-}$ groups. At last, the absence of pronounced band 3590–3610 cm^{-1} in «water» area of spectre of vanadium-bearing nickelalumite indicates the structural changes, taking place in it. It is necessary to note, that on IR-spectra of nickelalumite in the range 1390–1415 cm^{-1} there is a small band, which is evidence of the present of small amount of nitrate component in the mineral. Unfortunately, we cannot yet confirm the presence of nitrogen by other methods. Microprobe analysis is unacceptable in this case, the mineral is almost on one third consists of water, that assumes its extremely unstable behaviour under the electron beam.

The verification of nitrate presence by qualitative reactions did not succeed. Vanadium is presence in our samples everywhere and prevents the reaction on nitrate-ion with

diphenyl-amin. Reaction with alkali and Deward alloy turns out insufficiently sensible. We shall note in nickelalumite from type locality there are enough large amount of $(\text{NO}_3)^-$ anion up to formation of its nitrate analogue, mbobokulite.

Genesis

Apparently, the low-temperature hydrothermal processes play a considerable part in genesis of nickelalumite from Kara-Chagyr, which was noted by A.E. Fersman (1928). The presence of such rare mineral on Kara-Tangi is evident, in all probability, of community of the processes of late mineral formation, which take place in black schist rocks of South Fergana. The origin of nickelalumite along with such minerals as ankinovichite, kolovratite, and also some unnamed nickel-zinc silicates is undoubtedly connected to increased contents of nickel and zinc in these schists. The find of nickelalumite in South Kirgizia is, evidently, the second in the world.

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