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The First Find of (Ba,V) Micas in the Urals

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(Ba,V) micas are rather rare [5]. Reports about their occurrence in the Urals are unknown to date [1, 8]. We found these micas in igneous and metamorphic rocks of the Il'menskie Gory (Ilmeny Mountains) Complex and its framework in the southern Urals.

Two biotite varieties with different Ba contents were revealed in boulders of the coarse-grained biotite–amphibole subalkaline gabbro in a serpentinite melange sheet in the Osinovyi Mys (Promontory) area on the eastern coast of Lake Greater Ishkul (Ilmeny reserve).

The moderately Ba-rich biotite occurs in the inequigranular to porphyritic holocrystalline rock (sample IK-194-5). Biotite with a higher Ba content is observed in another boulder of biotite–amphibole gabbro with distinct ophitic texture. The composition, structure, and appearance of this rock indicate its intrusive origin [3].

Euhedral biotite flakes, 1–3 mm across, occur at boundaries of plagioclase and amphibole grains (Fig. 1) and as inclusions within these minerals. The induction striation developed in some cases testifies to the synchronous crystallization of biotite, amphibole, and plagioclase. The content of biotite in the rock is less than 10%.

Despite similar bulk mineral and chemical compositions of gabbro in the aforementioned two boulders from the serpentinite melange in the Osinovyi Mys area, they differ in compositions of feldspars, amphibole, apatite, magnetite, and biotite. The biotite is characterized by sharply variable BaO contents (Table 1). In terms of other parameters, both biotites represent the Ti- and Mg-rich variety [7] with a significant role of Fe^{3+} atoms (Table 2). In the low-Ba biotite, the contents of phlogopite and annite end members are 46.7 and 28.6%, respectively; in the high-Ba biotite, 54.3 and 22.5%, respectively.

Both biotite crystals have a dark greenish color, owing to the high degree of iron oxidation. They are characterized by sharp pleochroism with a light greenish brown color along N_p and very dark greenish brown color along N_g. The absence of band splitting in the 1000–970 cm^{-1} region in the IR-spectrum of Bi-biotite (Fig. 2) also indicates that the Ba-bearing mica belongs to biotites rather than to phlogopites [5]. The crystallochemical formulas of Ba-biotites from gabbro of the Il'menskie Gory Complex were calculated using the data presented in Table 1 (based on 7 cations). The low-Ba variety (sample IK-194-5) has the following composition:

$$(K_{0.98}Ba_{0.04})_{1.02}(Mg_{1.40}Fe^{2+}_{0.81}Fe^{3+}_{0.37}Ti_{0.25}Al^{VI}_{0.14}Mn_{0.03}V_{0.01})_{3.01}(Si_{2.74}Al^{IV}_{1.26}O_{10})(OH)_{1.37}.$$

The composition of the high-Ba variety (sample IK-194-16) is as follows:

$$(K_{0.73}Ba_{0.27})_{1.0}(Mg_{1.63}Fe^{2+}_{0.54}Fe^{3+}_{0.43}Al^{VI}_{0.19}Ti_{0.19}Mn_{0.02})_{3.0}(Si_{2.50}Al^{IV}_{1.50}O_{10})(OH_{1.72}Cl_{0.04})_{1.76}.$$

The difference in the chemical compositions of the two biotite varieties is reflected in their physical properties (Table 2), particularly, in their density and microhardness. The occurrence of Ba atoms with two valent bonds in the lattice increases its strength. Therefore, biotite becomes harder and heavier with an increase in BaO contents. The microhardness of Ba-biotite is three or four times higher than that of common biotite. No chemical or optical zoning or secondary alteration is observed in crystals of Ba-biotite. Judging from unit cell parameters, the biotites belong to 1M polytype.

In gabbroic rocks, the Ba-biotites occur as rare minerals confined to subalkaline varieties. This trend is also observed in our case. It has been pointed out [4, p. 104] that high BaO contents in biotites serve as evidence for

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Table 1. Average chemical composition of (Ba,V) micas from the southern Urals, wt %

Component	Barium biotite				Vanadium biotite		Vanadium muscovite
	Urals		Canada		Urals	Spain	Urals
	1	2	3	4	5	6	7
SiO_2	35.20	31.14	36.14	33.83	38.18	35.68	46.88
YiO_2	4.28	3.22	4.09	5.96	2.20	3.70	0.83
Al_2O_3	15.30	17.92	13.42	14.51	13.86	15.84	32.42
Cr_2O_3					0.32	0.52	0.17
FeO	18.23	14.41	19.79	18.30	15.66	13.85	2.06
MnO	0.40	0.31	0.12	0.08	0.96	0.55	0.08
MgO	12.05	13.67	11.66	10.80	9.29	10.47	1.29
CaO	–	–	0.02	0.02	0.47	–	<0.14
BaO	1.37	8.52	0.93	3.52	<0.14	–	<0.14
Na_2O	–	–	0.22	0.40	0.10	0.14	0.16
K_2O	9.91	7.11	8.75	7.50	9.48	9.09	9.88
F	–	–	0.90	0.68	0.79		<0.70
V_2O_3	0.11	–			5.06	4.38	4.28
Cl	–	0.41	0.46	0.05			
H_2O^+	2.64	3.22				4.33	
H_2O^-	0.26	0.04					
Total	99.75	100.03	96.50	95.65	95.94	94.17	98.05
n	15	18	9	8	20	1	30

Note: Analyses of Uralian micas from the authors' collection were carried out on a JXA-733 microprobe at the Institute of Mineralogy, Uralian Division, RAS (E.I. Churin, analyst); *n* is number of analyses; H_2O was determined in Penfield pipes; (1, 2) micas from boulders in serpentinite melange in the Osinovyi Mys area, Lake Greater Ishkul, Ilmeny reserve, Chelyabinsk district: (1) sample IK-194-5, moderately Ba-rich biotite from biotite–amphibole, hyalophane-bearing labradorite gabbro; (2) sample IK-195-16, Ba-rich biotite from biotite–amphibole bytownite-anorthite gabbro; (3, 4) micas from subalkaline gabbro, Coldwell Complex, Ontario, Canada [10]: (3) moderately Ba-rich biotite from the Eastern Gabbro Massif, (4) Ba-rich biotite from the Western Gabbro Massif; (5, 7) micas from the Lower Silurian (?) quartzites in the contact zone of granitic pluton, 3 km northwest of the Vtoraya Klyuchevka Village (Chebarkul area, Chelyabinsk district, the southern Urals): (5) sample IK-38-4, vanadium biotite (segedinite), (7) sample IK-38-4, vanadium muscovite (roscoelite); (6) vanadium biotite from sulfide-rich interlayers in Lower Silurian quartz–feldspathic metamorphic rocks in the Prades Mountains, Catalonia, Spain [7].

high formation temperatures. According to [10], unmetamorphosed (intrusive) gabbros of the Coldwell alkaline complex in northwestern Ontario (Canada) contain biotites with moderate and high contents of Ba; the Coldwell Complex comprises several gabbroic plutons; and biotite from the Western Gabbro contains as much as 6.1 wt % BaO and 8.1% TiO_2, whereas biotite from the Eastern Gabbro contains only 0.3–1.8% BaO and 3.3–4.9% TiO_2.

In both cases, the gabbroic rocks are close in chemical composition. The occurrence of biotites with variable BaO contents is accounted for by their crystallization from the Ba-bearing intergranular liquid (biotites with moderate Ba contents) or by the influence of Ba-rich emanations from younger syenite intrusions, which were responsible for the metasomatic alteration of the solid gabbro and the formation of Ba-rich biotites [10]. Since the Coldwell Gabbro is undoubtedly an intrusive formation, it may be suggested that the biotite–amphibole gabbro from the Osinovyi Mys area in the Ilmeny Mountains are also intrusive rocks.

The magmatic origin of the Ba-biotites is supported by the development of induction surfaces related to their synchronous growth together with the adjacent amphibole, plagioclase, epidote, magnetite, and apatite crystals; by the ophitic texture of the rocks; and by the euhedral habit of many minerals. The absence of signs

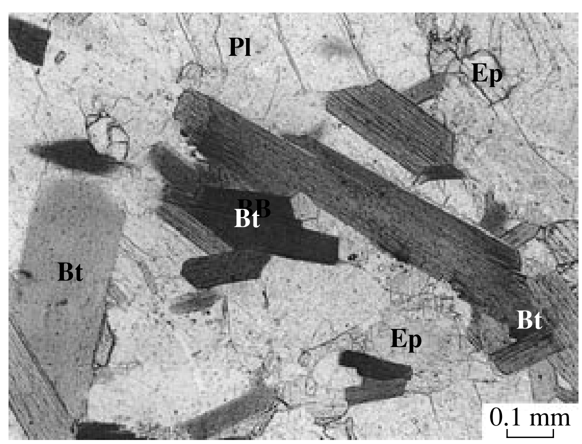

Fig. 1. Biotite–amphibole gabbro from a boulder in serpentinite melange. Photomicrograph, parallel polars. Sample IK-194-6, Osinovyi Mys, Lake Greater Ishkul, Ilmeny reserve, Chelyabinsk district, the southern Urals. (Bt) Barium biotite, (Pl) labradorite, (Ep) epidote.

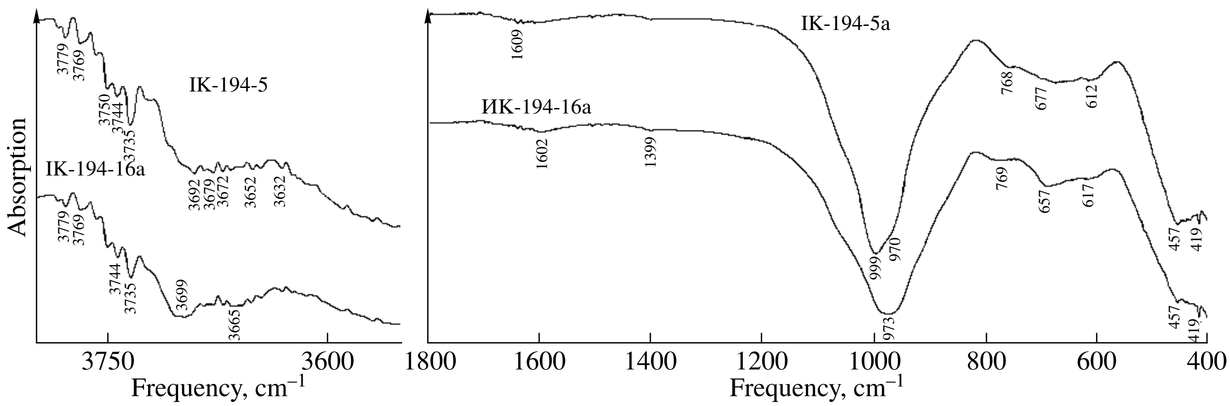

Fig. 2. IR spectra of barium biotites from biotite–amphibole gabbro. (Sample IK-194-16) BaO-rich biotite; (sample IK-194-5) moderately BaO-rich biotite. Spectra were recorded by V.E. Eremyashev on a Nexus IR-Fourier spectrometer at the Institute of Mineralogy, Uralian Division, Russian Academy of Sciences.

of reaction between minerals and the cenotypal appearance of rocks are typical features of the Osinonyi Mys gabbro. The Coldwell alkaline intrusive complex is confined to an intracontinental rift zone of Proterozoic age. By analogy, it may be suggested that the boulders of biotite–amphibole gabbro from the Osinovyi Mys area are also igneous rocks related to an ancient rift system at the margin of the East European continent that were entrained by serpentinite protrusions. The biotite–amphibole gabbro from the Osinovyi Mys area probably is a lower crustal rock of the Paleourals.

Table 2. Physical properties of barium biotites from the Ilmeny Mountains

Parameter, property	IK-194-5	IK-194-16
Density (d_{av}, g/cm^3)	2.85	3.11
Microhardness (H_{av}, kg/mm^2)	156	236
Coefficient of hardness anisotropy (K_H)	2.48	2.33
Parameters of unit cell:		
a, Å	5.34	5.32
b, Å	9.17	9.26
c, Å	10.21	10.20
β, deg	100.21	99.81
V, Å^3	497.71	495.48
n_p	1.600 ± 0.003	1.593 ± 0.003
n_m	1.652 ± 0.003	1.640 ± 0.003
n_g	1.656 ± 0.003	1.642 ± 0.003
Rel. Fe^{3+} content, %	31.84	44.51

Note: (sample IK-194-5) biotite–amphibole labradorite gabbro; (sample IK-194-16) biotite–amphibole bytownite-anorthite gabbro. Density was determined with the volumetric method in barometric pipe; microhardness was determined in polished sections with a PMT-3 microhardness tester (load 100 g); refractive indices were measured in immersion liquids; Fe^{3+} content was determined with Mössbauer spectroscopy.

We found V-rich micas in the metasedimentary rocks (quartzites) of the presumably Lower Silurian sequence in the eastern framework of the Il'menskie Gory Complex in the East Uralian Uplift. These rocks are exposed along the Miass–Vtoraya Klyuchevka highway, 3 km northwest of the Vtoraya Klyuchevka Village (Chebarkul area, Chelyabinsk district). Quartzites are exposed in the contact zone of the Klyuchevka pluton of two-mica plagiogranites. These quartzites are characterized by an abundance of black isometric grains with a silky luster, 0.5–1.5 mm in diameter. They are separated from one another by rims of white fine-grained quartz aggregate with locally developed curved flakes of graphite, small sheets of light green mica, and discrete crystals of iron sulfides. The abundant intergranular irregular vugs are filled with light yellowish white fine-grained and loose kaolinite.

The examination of thin and polished sections has shown that the black color and silky luster of quartz grains in quartzites is caused by the abundance of tiny thin (1–15 μm in diameter and 0.7–2.0 μm in thickness) isometric or hexagonal (in plan view) inclusions in cores of quartz grains. The inclusions are completely opaque in transmitted light but bright straw-colored in reflected light. They reveal a marked anisotropy and indications of cleavage along pinacoid. This nonmagnetic mineral is not dissolved in hydrofluoric acid. Its microhardness (200–400 kg/mm^2) is tens of times higher than that of the morphologically similar graphite. The XRD pattern and intense lines of Si, Ca, S, and Cl in energy-dispersive spectra allow us to suggest that this mineral could be a new mineral species. The host quartz grains are optically homogeneous. The outer, almost inclusion-free zone rims a dark core saturated with tiny inclusions and cuts off margins of inclusion-rich bands. One can see several systems of variously oriented opaque sheets within these bands. Tiny (commonly 3–15 μm) sporadic inclusions of other black

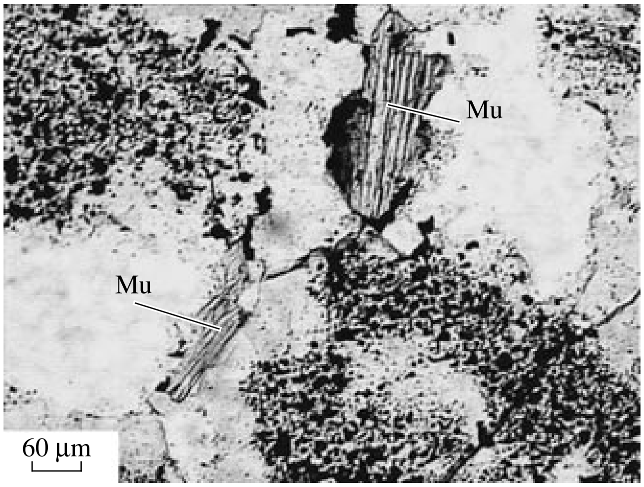

Fig. 3. Sheets of vanadium muscovite (Mu) in interstices of quartzite. Photomicrograph, parallel polars. (Sample IK-38-4) quartzite, 3 km NW of the Vtoraya Klyuchevka Village, Chebarkul area, Chelyabinsk district, the southern Urals.

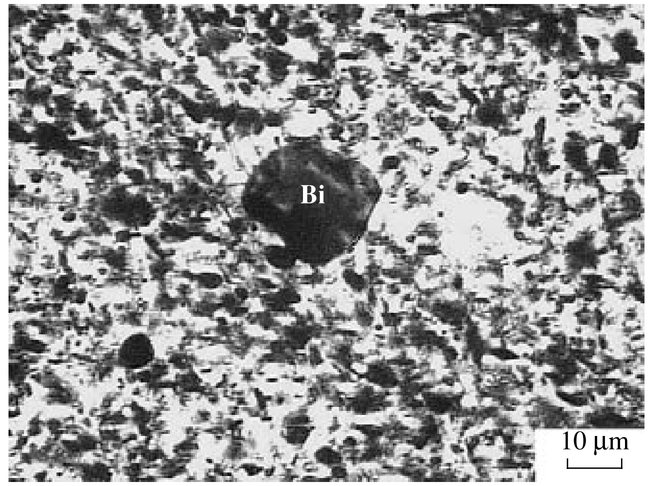

Fig. 4. Isometric sheet of vanadium biotite (Bi) in segregations of the tiny grains of unknown mineral hosted in quartz. Photomicrograph, parallel polars. (Sample IK-38-4) quartzite, 3 km NW of the Vtoraya Klyuchevka Village, Chebarkul area, Chelyabinsk district, the southern Urals.

opaque minerals are also present. Energy-dispersive spectra recorded with a REMMA-203 spectrometer indicate that the bands contain an appreciable amount of isometric grains of Fe-sphalerite, pyrite, Ni-pyrrhotite, and Mn-ilmenite; sporadic crystallites of F-apatite, pentlandite, and zircon; and opaque isometric (in plan view) V-rich grains with variable amounts of Ti and Fe [2].

We also detected high V contents in the mica flakes in the quartzites. The small light-green muscovite flakes localized between the quartz grains are characterized by slight parallel extinction and serrate and tortuous contours (Fig. 3). The crystallochemical formula (based on 6 cations) of muscovite calculated from the data presented in Table 1 appears as the following:

$$(K_{0.81}Na_{0.02})_{0.83}(Al^{VI}_{1.49}V^{3+}_{0.22}Mg_{0.12}Fe^{2+}_{0.11}Ti_{0.04})_{1.98}[(Si_{3.02}Al^{IV}_{0.98})_4O_{10}](OH)_2.$$

Based on the high V content (0.22 f.u.), the muscovite may be referred to as roscoelite (a vanadium variety) [5, 7], which had not been reported from the Urals until now [8].

The small light-brown (no larger than 25 μm) thin isometric biotite sheets are sporadically noted within dark cores of quartz grains (Fig. 4). They are oriented conformably with the general banding of rock. The chemical composition of biotite (Table 1) is recalculated into the crystallochemical formula for 7 cations:

$$(K_{0.96}Ca_{0.04}Na_{0.01})_{1.01}(Mg_{1.10}Fe^{2+}_{1.04}Al^{VI}_{0.39}V^{3+}_{0.32}Ti_{0.13}Mn_{0.06})_{2.97}[(Si_{3.02}Al^{IV}_{0.98})_4O_{10}](F_{0.20}OH)_2.$$

The high V_2O_3 contents (3.24–5.88%) in biotite merit attention. According to summary works [5, 7], the V admixture in biotite does not exceed 0.05–0.20%. The V-rich varieties had remained unknown until their discovery in the Urals in 1994. Therefore, the V-rich biotite, which was identified by us in the Urals, may be regarded as a new mineral variety. We propose to call this mineral *segedinite* in honor of Rostislav Aleksandrovich Segedin, the noted researcher of the Kazakhstan part of the Urals. One year after our publication [2], V-biotite with 4.38 wt % V_2O_3 was reported from Spain [9].

Thus, the graphite-bearing quartzite-type rocks, which were found by us in the contact zone of the Klyuchevka plagiogranitic pluton, contain at least four varieties of vanadium minerals hitherto unknown in the Urals. Two of these varieties are micas. The medium-grained quartz-rich rocks, which host the vanadium minerals, bear obvious indications of silicification. Contours of the newly formed quartz grains cut off the primary banding of rocks, which is emphasized by the linear distribution of lamellas of yet unknown mineral and segedinite flakes. The curved graphite flakes, discrete roscoelite sheets, and small sulfide grains occur in interstices between quartz grains. It is likely that these rocks are a specific type of hornfels developed after the carbonaceous–siliceous sediments in the contact zone of granitic pluton.

The V-bearing quartz–graphite hornfels at the contact with granites in Karatau, Uzbekistan have a similar metasomatic origin [5, p. 355]. The vanadium minerals are abundant in interlayers of graphite quartzites, quartzite schists, and calciphyres of the Olkhon Group in the western Baikal region and in the banded graphite-free quartz–diopside and calciphyre rocks of the Slyudyanka Group in the southern Baikal region [6]. The content of V-rich minerals is also appreciable in sulfide-rich interlayers among the Lower Silurian quartz–feldspathic schists that are metamorphosed at the contact with granitic pluton in the Prades Mountains, southwestern Catalonia, Spain. As in the Urals, the V-biotite and Fe–V oxides have been described here [9]. It is notable that the vanadium mineralization in most of the aforementioned areas is characterized by microscopic dimensions and by a confinement to the metasedimentary rocks in contact aureoles. Such a lithological–geostructural setting indicates that the quartzite sequence with vanadium minerals in the southern Urals is promising for noble metals.

REFERENCES

1. Yu. S. Kobyashev, S. N. Nikandrov, and P. M. Valizer, *Minerals of the Ilmeny Mountains* (The Ilmeny State Reserve, Miass, 2000) [in Russian].
2. V. G. Korinevsky, E. V. Korinevsky, V. A. Kotlyarov, *et al.*, Ural. Mineral. Sb., No. 12, 18 (2002).
3. V. G. Korinevsky, Dokl. Akad. Nauk **394**, 669 (2004) [Dokl. Earth Sci. **395**, 202 (2004)].
4. M. D. Krylova, V. A. Galibin, and D. P. Krylov, *Major Dark-Colored Minerals of High-Grade Metamorphic Complexes: Mineralogy, Petrology, and Geochemistry. Reference Guide* (Leningrad, Nauka, 1991) [in Russian].
5. *Minerals. Handbook* (Nauka, Moscow, 1992), Vol. 4, Issue 1 [in Russian].
6. *Mineralogy of Eastern Siberia at the Turn of the 21st Century (New and Rare Minerals)* (Intermet Engineering, Moscow, 2001) [in Russian].
7. *Nomenclature of Micas: The Final Report of Subcommittee for Micas, Commission for New Minerals and Mineral Names of the International Mineralogical Association*, Zap. Vseross. Mineral. Ob-va, No. 5, 55 (1998).
8. N. P. Yushkin, O. K. Ivanov, and V. A. Popov, *Introduction to Topomineralogy* (Nauka, Moscow, 1986) [in Russian].
9. C. Canet, P. Alfonso, J. C. Melgarejo, and S. Jorge, Canad. Mineral. **41**, 561 (2003).
10. C. S. J. Shaw and R. S. Penczak, Canad. Mineral. **34**, 967 (1996).