

## GEOCHEMISTRY

# Sodium–Strontium Mica $\text{Na}_{0.50}\text{Sr}_{0.25}\text{Al}_2(\text{Na}_{0.25}\square_{0.75})\text{Al}_{1.25}\text{Si}_{2.75}\text{O}_{10}(\text{OH})_2$ from Rubinovy Log

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Presented by Academician N.P. Yushkin October 7, 2003

Received October 10, 2003

An unusual high-Sr mica was found in 2002 during detailed mineralogical investigations of glimmerite plagioclase collection from the ruby Rubinovy Log occurrence located within Tsentral'noe chromite deposit (Raiz ultramafic massif), which is currently being mined, in the Polar Urals.

The Rubinovy Log ruby occurrence is located on the left bank of the Makar-Ruz River, which cuts across the Raiz ultramafic massif from north to south. It consists of a dunite–harzburgite rock association affected by intense metasomatism and metamorphism [4–6, 8]. According to various sources, the main lenslike body ranges in size from  $70 \times 23$  to  $30 \times 20$  m. The presently exposed small root portion of the plagioclase body ( $20 \times 7$  m) consists of the following zones (going from the outer zone to the center): albite, pargasite–chromite, corundum–chromite–pargasite–phlogopite–oligo-clase, and ruby–oligo-clase. Presumably, the gray plagioclase zone with large ruby crystals has been completely mined. The gray plagioclase with small ruby crystals and green mica occurs only in the dump along flanks of the plagioclase body and on the banks of the Rubinovy Creek. The antigorite–chlorite–talc schists in the outer contact grade into lizardite serpentinites adjacent to the weakly altered dunites. The large chromite body No. 9 of the Tsentral'noe deposit is located 150 m from the ruby-containing outcrop, and what is left of the plagioclase body is likely to be soon buried beneath wastes of the quarry.

Shcherbakova [8] has noted that phlogopite in the micaceous subzone is supplemented with intergrowths of another mica identified as fuchsite. The green mica from Rubinovy Log was mistakenly taken to be chromium mica for a long time, until our microprobe investigations showed that it is actually Na,Sr-mica similar

to paragonite in composition and fuchsite in appearance.

The green Na,Sr-mica is associated with ruby, chromite, pargasite, oligoclase, and phlogopite. It develops as fine rims around ruby in the form of overgrowth on pinacoid faces and as hexagonal prisms (Fig. 1). The overgrowth resembles the kelyphitic rim around garnet. All the rocks of the Rubinovy Log contain a significant amount of chrome spinels (up to 10%) in two varieties: large ferrochromite grains (1–3 mm) in the rocks and dust-like ferroalumochromite dissemination (50–200  $\mu\text{m}$ ) in the Na,Sr-mica and other minerals (Table 1).

The chemical composition of new strontium mica was determined on a JSM-6400 scanning electron microscope (11 analyses) equipped with EDS Link ISIS 300 (with an accelerating voltage of 20 kV, a beam current of 1 nA, and a counting time of 50 s). Certified pure metals and synthetic compounds were used as standards. Five replicate analyses were performed on a Camebax microprobe by N.N. Kononkova. Table 1 lists representative chemical analyses of Na,Sr-mica and other rock-forming minerals taken from Rubinovy Log.

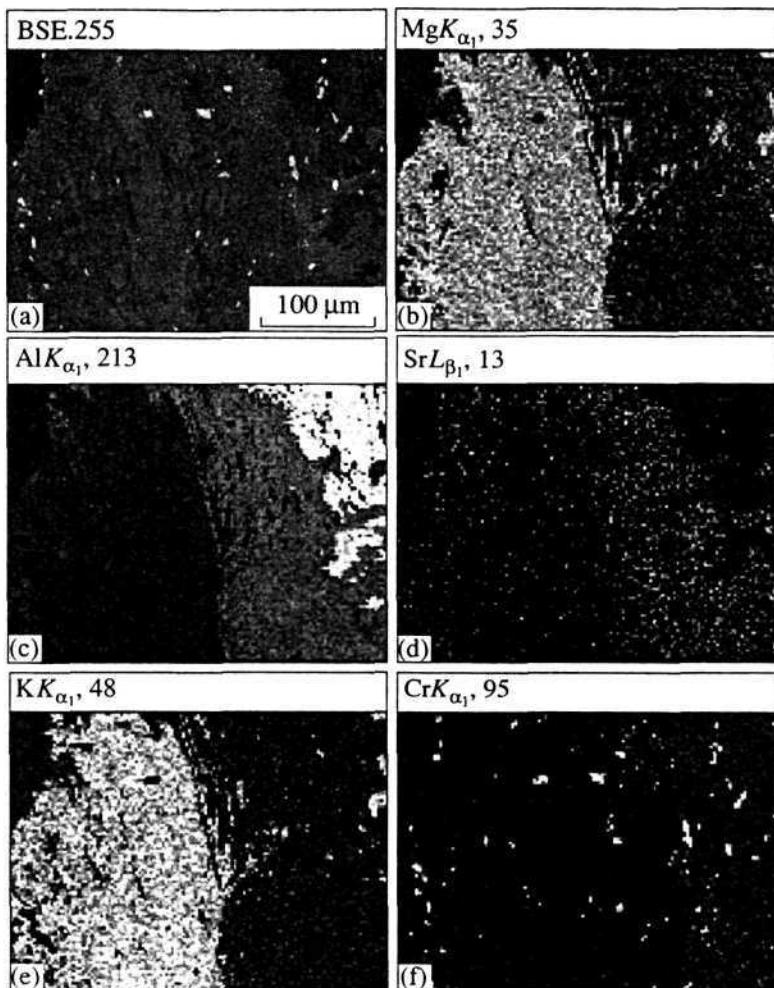
All the studied minerals of glimmerite plagioclases, except plagioclase, contain Cr, which underscores their genetic relation with ultramafic rocks. The  $\text{Cr}_2\text{O}_3$  content in minerals is as follows (wt %): ruby 3.56, green pargasitic amphibole (occasionally mistaken for actinolite) up to 1.70, phlogopite up to 1.57, and Na,Sr-mica 0.11–2.71.

The described mica has an unusually high Sr content ( $\text{SrO}$  3.06–6.02 wt %), which replaces Na in the crystal lattice. This is the first time that such a high Sr content has been found in mica. The available spectral analysis data suggest that Sr impurity in micas is generally insignificant [7]. Up to the present, the highest SrO content (1.3 wt %) has been found in paragonite from Antarctica [9]. The Sr content (6 wt %) in the studied mica is higher than the Na content, indicating that Sr is a species-forming element and that this green mica variety represents a new strontium mineral.

The deficiency of the total in mineral analyses (6–8 wt %) is most probably related to the presence of water or  $\text{OH}^-$  groups, which are not analyzed by the

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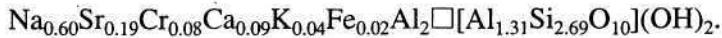
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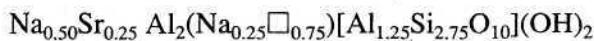
**Fig. 1.** Electron microscope images of a fragment of ruby glimmerite in the ruby, Na,Sr-mica, phlogopite, and ferroalumochromite assemblage: (a) in back-scattered electrons, (b-f) in characteristic radiation of  $MgK_{\alpha_1}$ ,  $AlK_{\alpha_1}$ ,  $SrL_{\beta_1}$ ,  $KK_{\alpha_1}$ , and  $CrK_{\alpha_1}$ , respectively. The light spots in (a) and (f) are dustlike ferroalumochromite dissemination. The light spots in (b) and (e) are phlogopite. In (c), the light spots are ruby, the gray spots are Na,Sr-mica, and the dark spots are phlogopite. The character of mineral intergrowths is seen in the sample section (replacement and corrosion of ruby by Na,Sr-mica).

microprobe method. The loss of ignition (L.O.I.) determined for the monomineral sample (50 mg) at 1000°C is 6.02 wt %. IR spectroscopy and DTA confirm the presence of OH groups in this Na,Sr-mica.

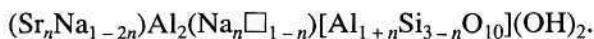
The average empirical formula calculated on the basis of (10O + 2OH) anions for 16 strontium mica samples according to [2] is



The idealized chemical formula is



or



As compared to paragonite, the new mica is significantly depleted in Na cations. Its partial substitution for Sr is compensated for by an increase in tetrahedral Al. The contents of major components in the mineral show

a narrow range of variation (wt %):  $\text{SiO}_2$  38.27–42.24;  $\text{Al}_2\text{O}_3$  39.92–43.58;  $\text{SrO}$  3.06–6.02;  $\text{Na}_2\text{O}$  3.04–6.00. The Na,Sr-mica also contains traces of  $\text{K}_2\text{O}$  (0.32–0.69),  $\text{CaO}$  (0.70–1.69),  $\text{FeO}$  (0.19–0.62), and  $\text{Cr}_2\text{O}_3$  (0.11–2.71), as well as occasional  $\text{TiO}_2$ ,  $\text{BaO}$ , and  $\text{MnO}$ .

*Structure and morphology of crystals.* The studied Na,Sr-mica is monoclinic (space group  $C_{2h}^6 - C2/c$ ,  $Z = 4$ ). Based on XRD study of a fine (0.2 mm) grain by photo method using an RKA camera, the Debye-

**Table 1.** Chemical composition and formula units of rock-forming minerals from glimmerite plagioclases (wt %)

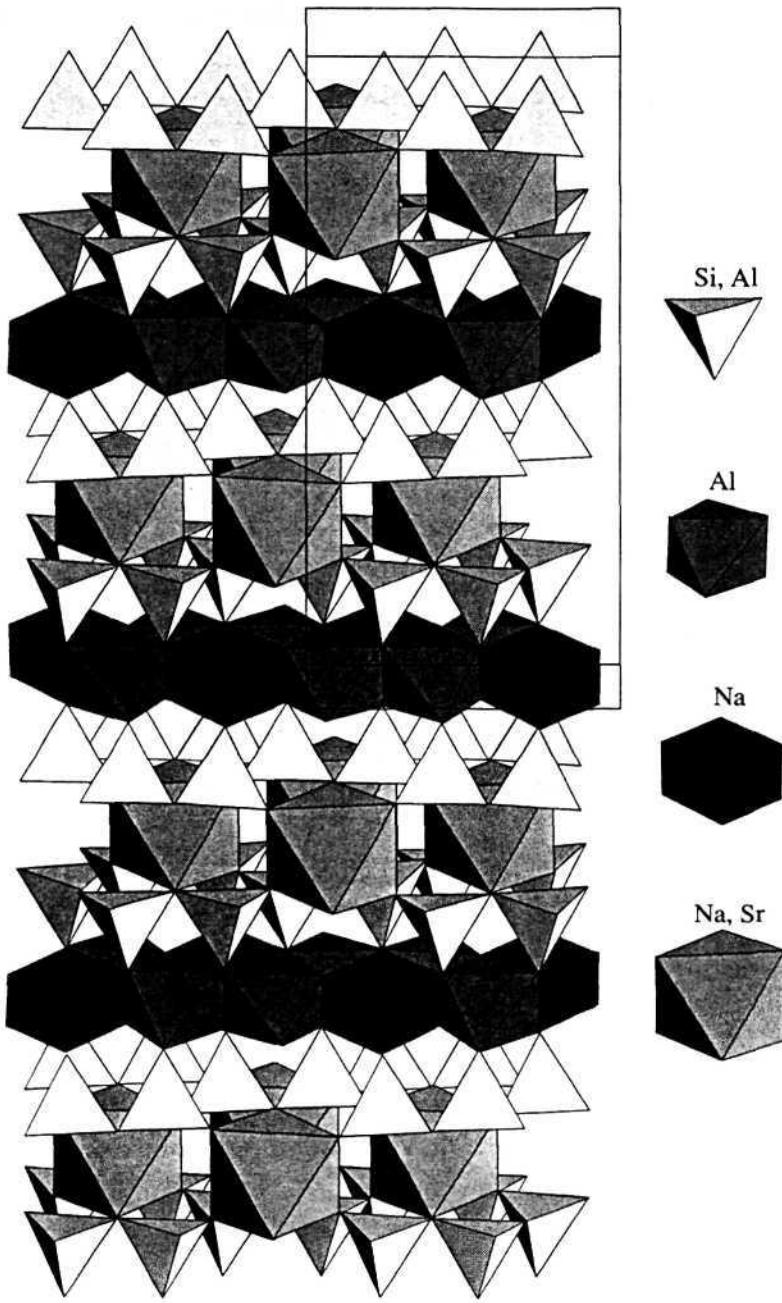
Component	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	65.57	43.28	36.70	—	—	0.12	38.62	38.27	39.74	39.24
TiO <sub>2</sub>	—	0.14	0.33	0.07	—	0.01	—	—	—	—
Al <sub>2</sub> O <sub>3</sub>	21.02	17.43	22.02	23.34	8.93	95.85	41.03	40.57	39.92	41.43
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	2.32	1.42	0.46	—	—	—	—
Cr <sub>2</sub> O <sub>3</sub>	0.02	1.70	1.94	40.89	58.11	3.56	1.19	2.71	1.58	0.79
FeO	0.02	5.25	4.21	27.12	27.32	—	0.28	0.62	0.19	0.34
MnO	—	0.07	0.04	0.49	—	—	—	—	—	—
MgO	—	15.30	19.01	5.20	3.88	—	0.12	—	—	—
CaO	5.68	11.55	0.03	—	—	—	0.76	1.32	1.08	0.70
NiO	—	0.04	—	—	0.02	—	—	—	—	—
SrO	—	—	0.01	—	—	—	5.58	6.02	5.73	5.70
BaO	—	—	1.76	—	—	—	—	—	—	—
Na <sub>2</sub> O	7.66	3.63	2.04	—	—	—	4.12	3.04	4.04	3.99
K <sub>2</sub> O	0.03	0.31	6.54	—	—	—	0.69	0.54	0.36	0.56
Total	100.00	98.70	94.68	99.43	99.68	100.00	92.39	93.09	92.64	92.72
Si <sup>4+</sup>	2.93	2.921	2.623	—	—	—	2.708	2.628	2.777	2.733
Ti <sup>4+</sup>	—	0.007	0.018	0.027	—	—	—	—	—	—
<sup>IV</sup> Al <sup>3+</sup>	1.07	1.072	1.359	7.135	2.926	0.973	1.292	1.372	1.223	1.267
<sup>VI</sup> Al <sup>3+</sup>	—	0.314	0.496	—	—	—	2.099	1.911	2.065	2.134
Fe <sup>3+</sup>	—	—	—	0.453	0.298	0.003	—	—	—	—
Cr <sup>3+</sup>	—	0.091	0.110	8.385	12.776	0.024	0.066	0.147	0.087	0.044
Fe <sup>2+</sup>	—	0.296	0.252	5.882	6.384	—	0.016	0.036	0.011	0.020
Mn <sup>2+</sup>	—	0.004	0.002	0.107	—	—	—	—	—	—
Mg <sup>2+</sup>	—	1.540	2.026	2.011	1.616	—	—	—	—	—
Ca <sup>2+</sup>	0.27	0.835	0.002	—	—	—	0.057	0.097	0.081	0.052
Ni <sup>2+</sup>	—	0.002	—	—	—	—	—	—	—	—
Sr <sup>2+</sup>	—	—	—	—	—	—	0.227	0.240	0.232	0.230
Ba <sup>2+</sup>	—	—	0.049	—	—	—	—	—	—	—
Na <sup>+</sup>	0.73	0.475	0.283	—	—	—	0.560	0.405	0.547	0.539
K <sup>+</sup>	0.002	0.027	0.811	—	—	—	0.062	0.047	0.032	0.050

Note: Minerals. (1) Oligoclase An<sub>27</sub>, (2) pargasite, (3) phlogopite, (4) ferroalumochromite, (5) ferrochromite, (6) ruby, (7–10) Na,Sr-mica.

Scherer pattern of this mineral has the diagnostic lines 9.63 (3), 4.34 (10), 3.13 (9), 2.50 (10), 2.07 (8), 1.893 (8), 1.591 (8), 1.469 (10), 1.018 (8), and 1.008 (8). It is very similar to the XRD pattern of paragonite. Single-crystal study performed on a four-circle Synthex P1 diffractometer at the Department of Crystallography (Moscow State University) indicated the unit parameters  $a = 5.161(4)$ ;  $b = 8.907(7)$ ;  $c = 19.31(2)$  Å;  $\beta = 94.83(8)^\circ$ . Since these values are close to the unit cell parameters of 2M<sub>1</sub> paragonite, this Na,Sr-mica sample can be considered to be a 2M<sub>1</sub> polytype. The crystal structure of Na,Sr-mica (Fig. 2) was refined using a SHELX97 program [12] ( $R = 0.073$ ). Its crystal structure is similar to that of other micas and consists of

three-layer TOT packages with octahedral layers sandwiched between two tetrahedral sheets of (Si,Al) tetrahedrons. The tetrahedral sheets consist of two non-equivalent tetrahedrons with nearly equivalent Si and Al distributions. Unlike purely sodic dioctahedral paragonite, the octahedral Na,Sr-mica layer has a distinct additional site partially occupied by Na atoms. Even taking into consideration this additional Na site in the O-layers, the studied mineral must be classified as dioctahedral mica, according to recommendations given by the CNMMN MMA Mica subcommittee [11]. Large interlayer octahedrons of the Na,Sr-mica contain Na, Sr, and Ca, which statistically substitute each other.

*Occurrence modes and physical properties.* The Na,Sr-mica occurs as flakes, scales, and fine scaly



**Fig. 2.** Polyhedral structure of Na,Sr-mica.

aggregates. It exhibits perfect cleavage parallel to (001), uneven fracture, and a light emerald-green color. Its hardness is greater than that of other micas. The Vickers hardness (VHN) measured by indentation of the diamond pyramid is  $217 \pm 37 \text{ kp/mm}^2$ , which corresponds to a Mohs hardness of 4. The density ranges from  $3.07 \pm 0.3 \text{ g/cm}^3$  (based on the microburette method) to  $2.99 \text{ g/cm}^3$  (based on X-ray data), which is also somewhat greater than that of paragonite.

*Optical properties.* The refractive indices of the mineral determined by the focal screening method on a PPM 1 apparatus designed by V.G. Feklichev are as

$n_g = 1.642(2)$ ,  $n_m = 1.635(2)$ ,  $n_p = 1.598(2)$ ,  $n_g - n_p = 0.044$ ,  $2V(\text{meas}) 60^\circ - 80^\circ$ , and  $2V(\text{calc}) 70^\circ$ . The  $2V$  (calc) was obtained from nomogram of G.S. Kravtsov. The mineral is optically biaxial negative, with a distinct pleochroism from pale yellow (along  $N_p$ ) to yellowish green (along  $N_g$ ). It has positive elongation and straight extinction. No luminescence was observed under UV and cathode rays. The IR spectrum of Na,Sr-mica (with bands at 488, 544, 716, 1008, 3450, and  $3625 \text{ cm}^{-1}$ ) is similar to that of paragonite [7]. Therefore, by analogy with paragonite, one can assume that the 488 and  $544 \text{ cm}^{-1}$  bands are related to Si-O-Me and Si-O

**Table 2.** Structural, optical, and physical properties of sodium micas

Characteristics	Paragonite (Near-Polar Urals [7])	Sr-paragonite (Antarctica [9])	Na,Sr-mica (Rubinovy Log)	Brammallite (Kazakhstan)
$a_0$	5.13	5.19	5.161	5.12
$b_0$	8.89	9.02	8.907	8.91
$c_0$	19.36	20.00	19.31	19.26
$\beta$	94.10	not indicated	94.83	$95^{\circ}50' \pm 20'$
Color	White	White	Light emerald-green	White with olive tint
Hardness Mohs Vickers	2.5	2–3	4 $217 \pm 37$	Soft
Density (calc), g/cm	2.82–2.90 (2.907)	2.84–2.95 (2.85)	3.07 (2.99)	Data absent
$n_g$	1.600–1.609	1.586–1.612	1.642	1.579
$n_m$	1.594–1.609	1.582–1.604	1.635	Data absent
$n_p$	1.564–1.580	1.550–1.574	1.598	1.561
$n_g - n_p$	0.028–0.038	0.035–0.042	0.044	0.018
$2V$	40–50	30–45	60–80	Large
Optical sign	(–)	(–)	(–)	(–)
Endoeffects	850, 1100	Data absent	850, 1100	670

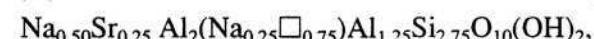
deformation vibrations; the  $1008\text{ cm}^{-1}$  band, to Si–O stretching vibrations; and the  $3450$  and  $3625\text{ cm}^{-1}$  bands, to OH<sup>–</sup> group stretching variations.

**Response to heating.** The DTA curve of Na,Sr-mica is similar to that of muscovite and paragonite and has two endothermic effects (at  $850$  and  $1100^{\circ}\text{C}$ ). The mineral shows no interaction with acids and alkalis.

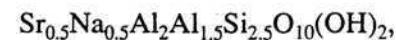
**Occurrence.** The Na,Sr-mica occurs in ruby plagioclases in association with oligoclase, pargasite, phlogopite, ferroalumochromite, ferrochromite, and chrome corundum (ruby). The K–Ar phlogopite age of plagioclases is  $320 \pm 20\text{ Ma}$ . Glimmerite plagioclase bodies are confined to pegmatoid giant-grained dunites with olivine grains as large as  $20\text{ cm}$ . The presence of hydrous and F-bearing minerals in the ruby assemblage with pegmatoid dunites indicates the participation of volatiles in the mineral formation. We believe that the ruby-bearing glimmerite plagioclases with large and even giant crystals of ruby (up to  $12\text{ cm}$ ), pargasite, and phlogopite are ultramafic pegmatites. Their formation was sponsored by volatiles and accompanied by accumulation of Ca, K, Na, Al, and Sr, which are atypical of an ultramafic system, in the final products (micas, amphiboles, and corundum).

In order to classify the discovered mineral according to mica systematics, let us consider isomorphous relationships in Na,Sr-micas during the successive substitution of Na<sup>+</sup> by Sr<sup>2+</sup> with a step of  $0.25\text{ f.u.}$  and, correspondingly, the replacement of Na<sup>+</sup> by Ca<sup>2+</sup> in Na,Ca-micas. The hypothetical mineral phases are as follows:

(A)



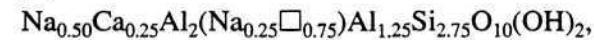
(B)



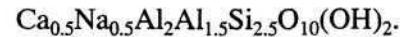
(C)



(D)



(E)



According to the recommendations of the CNMMN MMA Mica subcommittee [11], paragonite  $\text{NaAl}_2\square\text{AlSi}_3\text{O}_{10}(\text{OH})_2$  and the hypothetical phases A and D must be ascribed to dioctahedral micas, whereas hypothetical phases B and E together with end members of margarite  $\text{CaAl}_2\square\text{Al}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$  and its strontium analogue C belong to brittle micas with their own structural features. Following the same recommendations, the hypothetical mineral phases B and E should be considered trioctahedral micas, where the M site of the octahedral layers is occupied by cations ( $\geq 2.5\text{ f.u.}$ ). B and E can also be considered new minerals, where one-half of the Na cations is substituted by Sr and Ca.

Natural micas compositionally close to the hypothetical phases D and E were described as Na-margarite by Afanas'ev and Aidin'yan [1] and Koch [10]. These natural phases evidently do not belong to the margarite group and could be distinguished as independent min-

eral species based on structural study with the help of modern equipment.

According to Prof. Rieder, chairman of the CNMMN MMA subcommittee, the Na,Sr-mica described in this work can be assigned to the octa-Na variety of strontium bramallite,  $(\text{Na},\text{K})_{1-n}\text{Al}_2\Box[\text{Al}_{1-n}\text{Si}_{3+n}\text{O}_{10}](\text{OH})_2$ . However, we cannot agree with him, since the Na,Sr-mica shows an even stronger difference from bramallite than from paragonite in terms of its physical, thermal, and optical properties (Table 2). In addition, the Na,Sr-mica contains significant excess of tetrahedral Al, whereas its deficiency, as seen from the presented formulas, characterizes bramallite.

In this context, attention should be given to the Sr-bearing paragonite described by Grew *et al.* as a unique mineral with significant  $\text{Al}^{\text{IV}}$  excess (1.25 f.u.) and 1.3 wt %  $\text{SrO}$  [9]. We believe that this mineral is a high-Na variety of Na,Sr-mica, since changes in Si-O tetrahedrons have already taken place. Hence, its structure will correspond more closely to that of Na,Sr-mica than that of paragonite. It is evident that paragonite is a discrete phase with stable composition, structure, and properties. In contrast, the Na,Sr-mica shows wide variations in species-forming cations and significantly differs from paragonite and other micas in its physical properties.

Thus, the studied Na,Sr-mica differs from paragonite in structure, properties, and chemistry. It is not a variety of paragonite or other known micas. The question as to whether Na,Sr-mica is a new mineral species will remain open until new phases with a higher Sr content are discovered. However, there is no doubt that Sr must be added to the cations in site I ( $\text{Cs}$ ,  $\text{K}$ ,  $\text{Na}$ ,  $\text{NH}_4$ ) in the general mica formula  $\text{IM}_{2-3}\Box_{1-0}\text{T}_4\text{O}_{10}\text{A}_2$ . In classification of minerals, the Na,Sr-mica should be ascribed to the paragonite group of the dioctahedral mica family [3, 7, 11].

#### ACKNOWLEDGMENTS

We are grateful to T.N. Popova and G.N. Modyanova (Institute of Geology, Komi Scientific Center, Syktyvkar) for their consistent help in the research,

N.N. Kononkova (Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow) for replicate microprobe analyses, and E.L. Belokoneva (Moscow State University) for help in X-ray diffraction investigations. We are also grateful to Corresponding Member of the RAS Yu.D. Pushcharovsky for discussion of structural investigations.

This work was supported by the Russian Foundation for Basic Research (project no. 03-05-64054) and the Russian Foundation for Leading Scientific Schools (project no. NSh 2250.3003.5).

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