PURE STRONTIUM-87 ISOTOPE IN RUBIDIUM BIOTITE FROM THE UKRAINIAN SHIELD

***A.V. Andreev*[2,3], *A.A. Valter*[2]*, *N.P. Dikiy*[1], *A.N. Dovbnya*[1], *G.K. Eremenko*[2], *Yu.V. Lyashko*[1], *A.I. Pisansky*[2], *V.E. Storizhko*[2], *V.L. Uvarov*[1]**

[1] *National Science Center "Kharkov Institute of Physics and Technology", 61108, Kharkov, Ukraine*

[2] *Institute of Applied Physics NAS Ukraine, 40030, Sumy, Ukraine*

[3] *T. Shevchenko National University, 03022, Kiev, Ukraine*

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In lithium pegmatites of Shpoljano-Tashlyksky ore area (Kirovograd block of the Ukrainian shield) the biotites enriched with rubidium are distinguished. X-ray and electron-microprobe study of these minerals has shown that they attributed to low ferruginous biotites of structural modification 1M. By nuclear-physics methods the concentration of rubidium, ^{87}Rb and ^{87}Sr were defined. By X-ray-fluorescent method Sr/Rb–ratio was defined. From these data the cleanliness ^{87}Sr $\sigma\%=^{87}\mathrm{Sr}/\mathrm{Sr}_{tot}\times 100=96^{+4}_{-6}\%$ received. The natural isotopic abundance of ^{87}Sr is 7%. Rb/Sr age of the mineral is estimated as 2.14 billion years that will be coordinated with earlier results.

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1. INTRODUCTION

A pure strontium-87 isotope is formed in mineral by accumulation of the products from a β-decay of rubidium-87 according to the law [1]:

$$C_{rg} = C_{rd}\left[\exp(\frac{t\,ln2}{T_{1/2}}) - 1\right], \qquad (1)$$

where C_{rg} is the current content of a radiogenic isotope, C_{rd} is the current content of a radioactive isotope, t is the age of a mineral, $T_{1/2}$ is the the half-life period of radioactive isotope.

The accumulation of a pure isotope is promoted by geochemical and crystal-chemistry factors [2]. Earlier [2,3] we have established the isotope cleanliness of radiogenic ^{187}Os, resulting from a β-decay of ^{187}Re and present to the extent of 99.99% (while its natural abundance is 1.64%, or 1.96% [4,5]) in ancient Re-bearing molybdenites from Ukrainian ores. This fact can be due to rarity of osmium in geochemical systems, affinity of sedimentation conditions for rhenium and molybdenum from hydrotherms and durability of retention of radiogenic osmium in a molybdenite structure.

^{87}Sr formed as a result of the β-decay of ^{87}Rb has a half-life of $4.88\cdot10^{10}$ years and an isotope abundance of 7% [4,5].

The strontium sharply enriched with a radiogenic isotope, was first examined by O. Hahn et al. [6] in pollucite (Karbib, South West Africa). L.G. Arens and Z. Mattauh observed nearly pure ^{87}Sr in rubidium-containing late Proterozoic lepidolites from alkaline pegmatites of Manitoba (Canada).

Recently new varieties of ancient highly rubidic micas in Canada and on Kola peninsula have been studied [8,9], however, without reported data on radiogenic strontium.

2. Rb-BIOTITE OF THE UKRAINIAN SHIELD

We have investigated the ancient Rb-bearing biotite of the Ukrainian shield as potential mineral carrier of isotopic pure strontium-87.

In 1889-1990 in the western part of the Kirovograd block the new Shpoliano-Tashlyksky ore area (Fig.1) has been discovered. There the rare metal mineralization is connected with late Proterozoic granite pegmatites having lithium specialization [9]. In the Stankovatsko-Lipnjazhsky pegmatite field in this area, thin (2...3 cm) streaks of Rb-bearing biotite glimmerites are widely spread, tracing the contacts with amphibolites and their replaced xenolites [10].

The biotite contains increased concentrations of rare alkalis, mainly rubidium. Special studies were carried out on samples of biotite selected by G.K. Eremenko, as well as on those offered through the courtesy of V.N. Bugaenko and D.K. Voznjak.

After additional cleaning by gravitational separation and selection under microscope, the samples were subjected to microprobe analysis and XRD-study.

*Corresponding author E-mail address: avalter@iop.kiev.ua

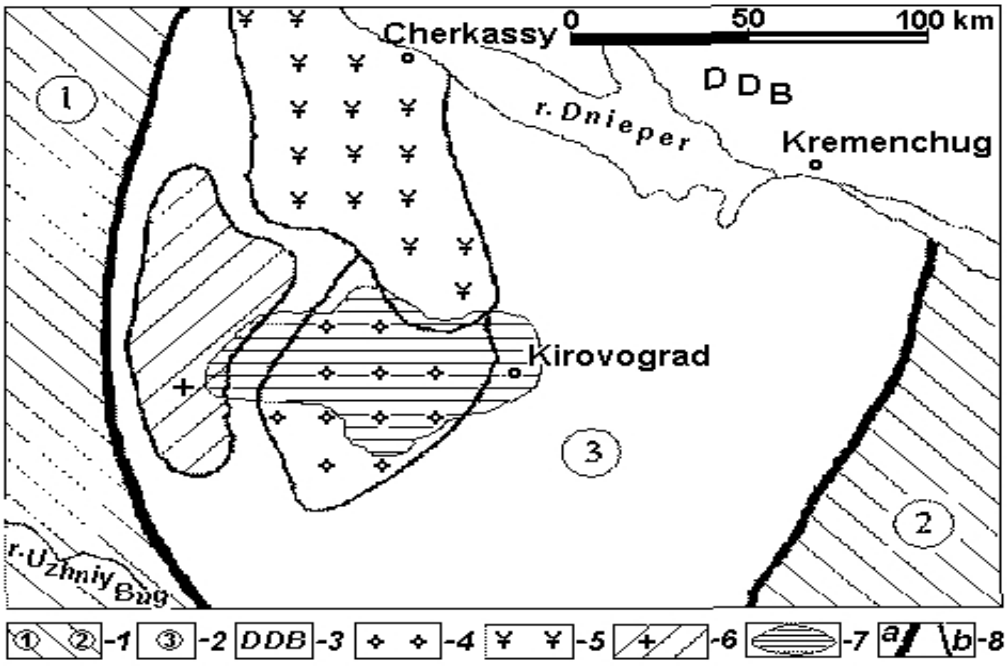

Fig.1. *Schematic diagram of the geological position of the studied rubidic biotite - the carrier of pure strontium-87 isotope.* ***1*** *Archaean blocks of the Ukrainian shield (in circles): 1 - Podolsk; 2 - Pridneprovsky.* ***2*** *Kirovograd Proterozoic block.* ***3*** *Dneprovo-Donesk basin.* ***4*** *Granitoids of the Kirovograd massive.* ***5*** *Rapakivi granites and the basic rocks of the Korsun-Novomirgorod pluton.* ***6*** *Shpoljano-Tashlyksky ore area (a cross indicates the display of Stankovatsky deposit with rubidium-containing biotites).* ***7*** *Central-Ukrainian Uranium ore area.* ***8*** *geological borders: (a) blocks borders; (b) other borders*

The factors of crystal-chemistry formulas of biotite samples have been calculated (Tabl.2) from the quantitative microanalysis data (analyst V.M. Vereshchak, Camebax SX-50 with a wave spectrometer) taking into account earlier chemical analysis [12,13].

Table 1. *Crystal chemical formulas of biotite samples investigated*

Nu.	Nu. of borehole; depth, m	Crystal chemical formula calculated for Si = 3
4	59-89; 126.0	$(Cs_{0.2}Rb_{0.15}K_{0.44}Na_{0.05})(Fe_{1.21}Mg_{1.5}Al_{0.59}Ti_{0.07})(AlSi_3O_{10})F_{0.1}OH_{1.9}$
5	72-90; 247	$(Cs_{0.02}Rb_{0.07}K_{0.87}Na_{0.06})(Fe_{0.75}Mg_{1.73}Al_{0.14}Ti_{0.08})(AlSi_3O_{10})F_{0.95}OH_{1.05}$
6	3-91; 97.5	$(Rb_{0.04}K_{0.80}Na_{0.05}Ca_{0.01})(Fe_{0.85}Mg_{1.70}Al_{0.64}Ti_{0.08})(AlSi_3O_{10})F_{0.17}OH_{1.83}$
7	33-91; 181.5	$(Rb_{0.05}K_{0.84}Na_{0.02})(Fe_{0.97}Mn_{0.02}Mg_{1.11}Al_{0.71}Ti_{0.12})(AlSi_3O_{10})F_{0.26}OH_{1.74}$
9	34-91; 113.5	$(Rb_{0.05}K_{0.99}Na_{0.02})(Fe_{1.18}Mn_{0.02}Mg_{1.29}Al_{0.7}Ti_{0.02})(AlSi_3O_{10})F_{0.25}OH_{1.75}$
10	34-91; 112-113	$(Rb_{0.05}K_{1.02}Na_{0.01})(Fe_{1.14}Mn_{0.02}Mg_{1.21}Al_{0.64}Ti_{0.13})(AlSi_3O_{10})F_{0.26}OH_{1.74}$

X-ray diffractometer patterns recorded by E.E. Grechanovskaja (DRON-2, CuK_α γ-radiation, with the speed of the counter rotation of 2°/min) (Fig.2) compared with data from [13] allow biotite to be ascribed to the ferriferous low variety and the structural modification 1M.

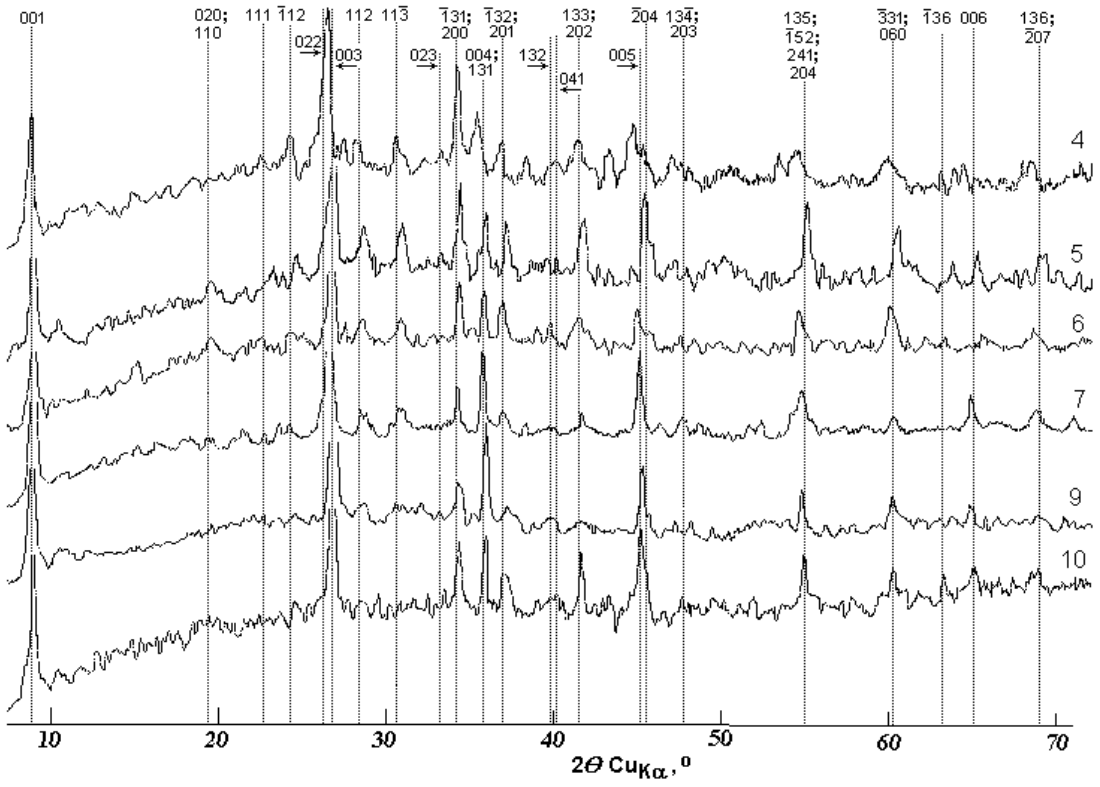

Fig.2. *X-ray diffraction pattern of biotite samples. On the right: numbers of samples; above: peak indexes for 1M modification*

3. THE INVESTIGATION OF THE RUBIDIUM-STRONTIUM ISOTOPE SYSTEM IN BIOTITE

Our goal was to determine the content and cleanliness of ^{87}Sr in ancient Rb-biotites and to obtain additional data for their isotope dating.

The natural isotope cleanliness of radiogenic ^{87}Sr in biotite does not seem to be as high as the ^{187}Os cleanliness in molybdenite. Strontium has a far greater natural occurrence, than osmium. Moreover, the attachment of strontium atoms to the biotite structure is not so strong as that of osmium in molybdenite. In interlayer spaces of the mica structure, the Sr^{2+} ion, approaching in size one-charge ions of alkali metals, can be fixed, creating a certain defect demanding indemnification of valencies, obviously according to the scheme Rb, OH → Sr, O.

This leads to a rather high average content of strontium in biotites of granitoids (0,012%), basic rocks (0,01%) and, especially, alkaline rocks (0.1%) [15], which is approximately by 9 and 10 tenths of the order greater than the probable initial content of osmium in molybdenite. It is not impossible, however, that reported in [15] average data are considerably increased at the expense of radiogenic strontium.

Measurements of the concentrations of radioactive (^{87}Rb) and radiogenic (^{87}Sr) nuclides were performed using photoactivation analysis on nuclear reactions. The irradiations of biotite samples were carried out with 10 MeV electrons from linear accelerators for ^{87m}Sr isomer excitation ($T_{1/2}$=2.805 hour) and bremsstrahlung with E_{max}=23 MeV for determination of the ^{87}Rb content ($T_{1/2}=48.8\cdot10^9$ years).

The activities of ^{87m}Sr and ^{84,86}Rb were measured with a Ge(Li)-detector ($\Delta_{1/2}$=3.2 keV for 1333 keV) and a HP Ge detector ($\Delta_{1/2}$=295 eV for 5.9 keV) using standard Rb compounds as well as $SrCO_3$ with natural and enriched ^{87}Sr isotope concentrations.

4. DETERMINATION OF ^{87}Rb

The intensity of lines 881.5 keV (^{85}Rb(γ,n)^{84}Rb) and 1077 keV (^{87}Rb(γ,n)^{86}Rb; ^{85}Rb(n,γ)^{86}Rb) were measured by Ge(Li)-detector (Fig.3) after activation of the samples and standards.

The results were normalized (measurement time, time after activation, distance from the sample to the detector, detector efficiency, sample mass) and averaged for samples (usually 4 measurements on each sample throughout 80 days after activation) and for standards. As standards RbCl and Rb_2CO_3, were used normalized to the mass of the Rb content.

The ratio of the obtained values determines the general Rb and ^{87}Rb content in the samples. For a

less intensive 1077 keV line the statistics was found twice as worse on the average and these data were neglected. The general rubidium was calculated. Errors in the determination (%) for Rb and ^{87}Rb were assumed equal, being dependent on the accuracy of measurements of the 881.5 keV line intensity.

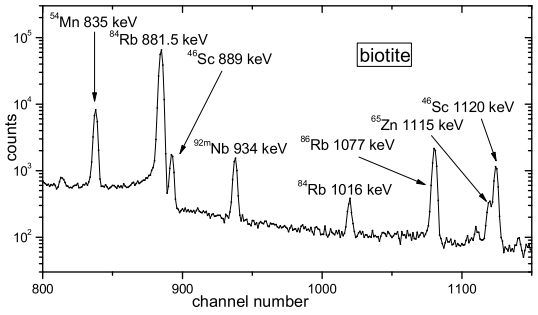

Fig.3. *A fragment of a typical γ-spectrum of biotite (sample 7, tab.1) activated with a LEA. 37 days after the activation; exposure for 4 hours*

5. DETERMINATION OF ^{87}Sr

Determination of ^{87}Sr was made using the reactions ^{87}Sr(e,e$'$)^{87m}Sr and ^{87}Sr(γ,γ')^{87m}Sr (2.803 h) $\rightarrow$ ^{87}Sr (stab); E=388.5 keV, n_i=82.1%.

For ^{87}Sr owing to much lower concentrations, than in the case of rubidium, poorer statistics of counts was used. For the most enriched Sr sample (Nu.4) measurements on ^{87}Sr were performed twice: with 11 MeV γ and 10 MeV electrons. The resulting values were practically similar indicating an insignificant error for these concentrations.

6. DETERMINATION OF THE GENERAL STRONTIUM AND CALCULATION OF THE ISOTOPE CLEANLINESS OF ^{87}Sr

To determine the general strontium the Rb/Sr-ratios were measured by X-ray-fluorescence. The determinations were conducted on separate crystals (by 20 grains with the calculated average value) by the intensity of K_α-lines with the use of an energy-dispersive X-ray spectrometer and monochromatic exciting radiation (crystal-monochromator LiF was adjusted to the K_α-line of a Mo anode of an X-ray tube).

The results for rubidium and strontium in the investigated biotite samples are summarized in Tabl.2.

As can be seen from the table, only 3 of 6 detections give acceptable values: $Sr_{tot}/^{87}Sr > 1$. These are the samples most enriched by strontium. For three other samples this relation is less than unity, i.e. is not meaningful. It would be reasonable to attribute such grouping of results to a low accuracy of the determination of ^{87}Sr and Sr/Rb-ratios in low-strontium samples. Assuming the extreme value for $Sr_{tot}/^{87}Sr$=100%, we will arrive at the following average value for 6 samples $\sigma\%=^{87}Sr/Sr_{tot}\times100=96^{+4}_{-6}\%$ against the natural ^{87}Sr prevalence of 7%.

Table.2. *Determination of Rubidium (mass %) and Strontium (ppm) in biotites*

No.	Borehole, depth,m	Chemical analysis (recalculation on oxides)	μ-probe	Total Rb (on the basis of ^{87}Rb)	Ratio Sr/Rb (on the basis of X-rays fluorescence)	Total Sr (on the basis of ^{87}Rb and X-rays fluorescence)	^{87}Sr by accelerator based technique	^{87}Sr on the basis of ^{87}Rb (assumption t=2.1·10^9 yr. for all samples)	^{87}Sr/Sr$_{tot}$ from columns 7/6 and 8/6 (in brackets)
	1	2	3	4	5	6	7	8	9
4	59-89, 126.0	2.23	2.14±0.22	2.6±0.02	0.0093 ±0.0013	244	225.5±8.8	226.5	92.4
5	72-90, 247	N/A	1.52±0.06	1.4±0.009	0.0092 ±0.0015	130.5	122.8±6.0	122.9	94.1
6	3-91, 97.5	0.80	0.61±0.04	0.82±0.005	0.089 ±0.0008	73.1	85.4±3.7	71.1	116.8 (96.2)
7	33-91, 181.5	1.16	0.87±0.01	0.9±0.006	0.0085 ±0.0006	74	96.4±3.2	83.1	130.2 (111.4)
9	34-91, 113.5	1.10	0.89±0.02	1.02±0.006	0.0092 ±0.0008	94.2	88.7±4.3	88.4	93.8
10	34-91, 112-113	N/A	0.85±0.03	0.79±0.005	0.0084 ±0.0007	66.4	85.1±3.7	68.4	128 (100.7)

7. DETERMINATION OF ISOTOPE ^{87}Rb/^{87}Sr AGE IN BIOTITES WERE STUDIED

On the graph (Fig.4) small circles and square show the ^{87}Rb–^{87}Sr values for the studied samples. Three results, referring to the richest rubidium and strontium samples (Nu. 4, 5 and 9, Tabl.1 and 2) give a straight line (1) ^{87}Sr=0.031·^{87}Rb+1 with a slope corresponding to the age of 2.14 billion years. This age correlates with the data [11] indicating a greater age of pegmatites in comparison with the enclosing granitoids (1.8-2.0 billion years).

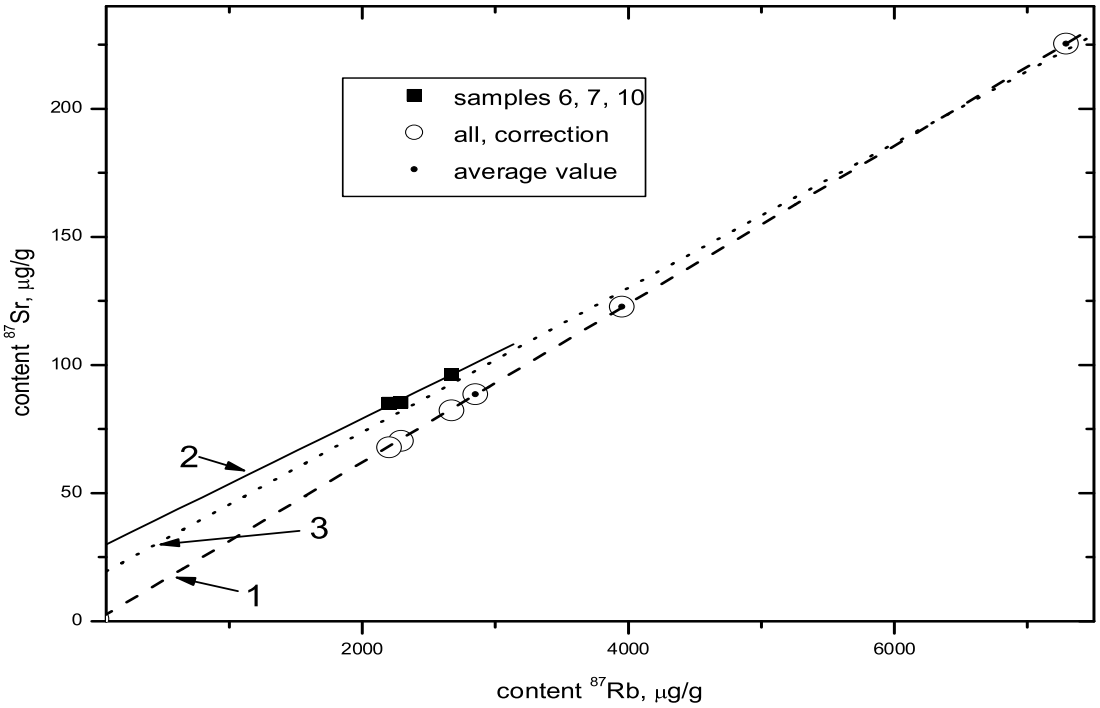

Fig.4. *^{87}Sr–^{87}Rb ratios in biotites under study (explanations in the text)*

The value of a free member corresponding to the ^{87}Sr value at the moment of mineral formation ($^{87}Sr_0$ = 1 ppm) agrees with the data on the isotope cleanliness of the samples. Assuming as a first approximation, the same parity of strontium isotopes in the mineral forming environment of the alkaline pegmatites at the moment of their crystallization, as now, we will have the average content of other strontium isotopes in three investigated samples, viz. ≈ 13 ppm, which, within the accuracy of measurement, agrees with data in tab.2 (≈ 9,7 ppm). Proceeding from this data, the value of the average isotope cleanliness $\sigma\%=^{87}Sr/Sr_{tot}\times100\approx92\%$ is in good agreement with the average determined for an individual sample.

Other three values, corresponding to rubidium-poorer samples (Nu. 6, 7 and 10) follow a straight line (2) $^{87}Sr=0.025\cdot^{87}Rb+28$ with a slope corresponding to the age t=1.76 million years. This value of the effective age is possible as a result of a far-gone granitization process. It is more difficult to explain a high value of $^{87}Sr_0$=28 ppm. Under the assumption of a normal isotope ratio of initial strontium it agrees with the general content of strontium of 400 ppm, which is in conflict with the analytical data. The explanation assuming an abnormal initial isotopic ratio of strontium in rubidic mica, contradicts the establishment of the Sr/Rb balance 1.76 billion years ago. A consistent explanation of these data can hardly be given.

The description of the positions of all 6 points by a single dependence leads to a straight line (3) $^{87}Sr=0.028\cdot^{87}Rb+17$ for which the value of the free member is also outside reasonable geological estimates.

We investigated the third possibility, viz. all 6 points follow the same dependence determined by the position of high-rubidium samples (Nu. 4, 5 and 9, Tabl.1 and 2) assuming for the same maintenance of rubidium that of ^{87}Sr, corresponding to the age of 2.14 billion years. This brought the ^{87}Sr values closer to realistic data with the exception of sample Nu.7.

Thus, it seems justified to consider the determinations of strontium and, especially of ^{87}Sr in low-maintenance Rb and Sr samples (Nu. 6, 7 and 10) to be insufficiently accurate for geochemical simulations.

8. CONCLUSIONS

1. In ores of Ukraine in the mineral carrier - a Rb-biotite - isotopic pure ^{87}Sr ($96^{+4}_{-6}\%$) was found in concentrations of 225...90 ppm.

2. From nuclear microanalysis data obtained for the $^{87}Sr/^{87}Rb$ ratio the age of formation of this biotite was estimated at $2.14\cdot10^9$ years.

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ЧИСТЫЙ ИЗОТОП СТРОНЦИЙ–87 В РУБИДИЕВОМ БИОТИТЕ УКРАИНСКОГО ЩИТА

А.В Андреев, А.А. Вальтер, Н.П. Дикий, А.Н. Довбня, Г.К. Ерёменко, Ю.В. Ляшко, А.И. Писанский, В.Е. Сторижко, В.Л. Уваров

В литиевых пегматитах Шполяно-Ташлыкского рудного района (Кировоградский блок Украинского щита) встречены биотиты, обогащённые рубидием. Рентгенографическое и электронно-микрозондовое изучение этих минералов показало, что они относятся к низкожелезистым биотитам структурной модификации 1M. Ядерно-физическими методами определены концентрации, ^{87}Rb и ^{87}Sr, рентген-флюоресцентным методом – Sr/Rb - отношение. Из этих данных получили чистоту ^{87}Sr $\sigma\%=^{87}\mathrm{Sr}/\mathrm{Sr}_{tot}\times 100=96^{+4}_{-6}\%$ по сравнению с обычной распространённостью ^{87}Sr 7%. Rb/Sr возраст минерала оценен в 2.14 миллиарда лет, что согласуется с ранее полученными результатами.

ЧИСТИЙ ІЗОТОП СТРОНЦІЙ–87 У РУБІДІЄВОМУ БІОТИТІ УКРАЇНСЬКОГО ЩИТА

А.В. Андреєв, А.А. Вальтер, М.П. Дикий, А.М. Довбня, Г.К. Єрьоменко, Ю.В. Ляшко, О.І. Писанський, В.Ю. Сторіжко, В.Л. Уваров

У літієвих пегматитах Шполяно-Ташлицького рудного району (Кіровоградський блок Українського щита) зустрінуті біотити, збагачені на рубідій. Рентгенографічне і електронно-мікрозондове вивчення цих мінералів доводить, що вони відносяться до низькозалізистих біотитів структурної модифікації 1M. Ядерно-фізичними методами визначені концентрації ^{87}Rb і ^{87}Sr, рентген-флюоресцентним методом – Sr/Rb - співвідношення. За цими даними отримали чистоту ^{87}Sr $\sigma\%=^{87}\mathrm{Sr}/\mathrm{Sr}_{tot}\times 100=96^{+4}_{-6}\%$ порівняно із звичайною розповсюдженістю ^{87}Sr 7%. Rb/Sr вік мінерала оцінений в 2.14 мільярди років, що узгоджується з результатами, що були отримані раніше.