

# DETECTION OF BERYLLIUM IN OXIDES AND SILICATES BY ELECTRON-PROBE MICROANALYSIS

V. V. Khiller

## Определение бериллия в оксидах и силикатах методом рентгеноспектрального микрозондового анализа

В. В. Хиллер

Разработана методика электронно-зондового микроанализа количественного определения содержания бериллия на примере изучения природных минералов (алюмосиликатов и оксидов). Получено количественное содержание бериллия (в совокупности с другими элементами) в изумрудах Мариинского бериллиевого месторождения и зональном мариинските-хризоберилле из хромититов Баженовского офиолитового комплекса. Все анализы минералов выполнены на электронно-зондовом микроанализаторе CAMECA SX 100 с пятью волновыми спектрометрами (ИГГ УрО РАН). Давление в камере образцов составляло  $2 \cdot 10^{-4}$  Па, в области электронной пушки  $2 \cdot 10^{-6}$  Па, в волновых спектрометрах – 7 Па. Ускоряющее напряжение 10 кВ, ток поглощенных электронов на цилиндре Фарадея (сила тока) – 100–150 нА. Диаметр пучка электронов, сфокусированных на образце, – 2 мкм, угол отбора рентгеновского излучения –  $40^\circ$ . Спектры получены на волновых спектрометрах с кристаллами-анализаторами TAP ( $2d = 25,745 \text{ \AA}$ ), LPET ( $2d = 8,75 \text{ \AA}$ ), LiF ( $2d = 4,0267 \text{ \AA}$ ) и PC3 ( $2d = 211,4 \text{ \AA}$ , специализированный кристалл для определения содержания бериллия и бора); измерения всех элементов проводились по  $K\alpha$ -линиям. Предварительно для определения положения аналитического пика и фона с двух сторон, с минимально возможными спектральными наложениями прописывались спектры на волновых спектрометрах. Полученные микрозондовые анализы минералов с количественным определением бериллия хорошо сходятся с имеющимися теоретическими составами бериллов и хризобериллов, что говорит о высокой эффективности разработанной методики. В результате постановки данной методики можно относительно быстро и надежно определять количественное содержание бериллия в природных силикатах и оксидах. Это необходимо для исследователей-геологов при изучении минералогии бериллиевых месторождений.

**Ключевые слова:** бериллий; хризоберилл; мариинскит; берилл; изумруд; электронно-зондовый микроанализ.

The author developed the technique of electron-probe microanalysis for quantitative determination of beryllium content, providing the example of studying natural minerals (aluminosilicates and oxides). This technique allowed to obtain a quantitative content of beryllium (in combination with other elements) in the emeralds of the Mariinsky beryllium deposit and in zonal mariinskite-chrysoberyl from the chromitites of the Bazhenov ophiolite complex. All analyzes of minerals were performed on a CAMECA SX 100 electron probe microanalyzer with five wave spectrometers (IGG UB RAS). The pressure in the sample chamber was  $2 \times 10^{-4}$  Pa, in the electron gun region –  $4 \times 10^{-6}$  Pa, in wave spectrometers – 7 Pa. Accelerating voltage was 10 kV, the current of absorbed electrons on the Faraday cylinder (beam current) was 100–150 nA. Diameter of the electron beam focused on the sample was 2  $\mu\text{m}$ , the angle of x-ray extraction was  $40^\circ$ . The spectra were obtained on wave spectrometers with TAP crystal analyzers ( $2d = 25.745 \text{ \AA}$ ), LPET ( $2d = 8.75 \text{ \AA}$ ), LiF ( $2d = 4.0226 \text{ \AA}$ ), and PC3 ( $2d = 211.4 \text{ \AA}$ , a specialized crystal for determining the content of beryllium and boron); the author carried out all the elements measurements along the  $K\alpha$ -lines. To determine position of the analytical peak and the background from two sides with the minimum possible spectral overlap, the author preliminarily recorded spectra on wave spectrometers. The obtained microprobe analyzes of minerals with quantitative determination of beryllium converge well with the available theoretical compositions of beryl and chrysoberyl, which indicates the high efficiency of the developed technique. By using this technique, we can relatively quickly and reliably determine the quantitative content of beryllium in natural silicates and oxides, which is an acute need for geological researchers studying the mineralogy of beryllium deposits.

**Keywords:** beryllium; chrysoberyl; mariinskite; beryl; emerald; electron-probe microanalysis.

In recent decades, the method of electron-probe microanalysis (EPMA) has been very useful for solving a wide range of issues, including those for which scientists relatively recently considered its application problematic. These include, for example, determination of the elements of the second period of periodic system in minerals [1], related to the development of instrumental and methodological base. When determining the “light” (Be, B, C, N, O, F) elements, difficulties arise [2, 3], as the characteristic X-ray emission lines of these elements are quite wide, they have long-wave X-ray radiation, low peak-to-background ratio, superposition with lines of “heavy” elements, and dependence of the integral intensity of the analytical line on the form of occurrence of the element [4–6]. Currently, the technique of electron-probe microanalysis of content of “ultra-light” beryllium element is not sufficiently developed. This is due to a number of experimental difficulties arising during the analysis: significant influence of the state of chemical bond on the shape and position of maximum of the corresponding element line, significant extent of correction for the matrix effects, necessity of using a special crystal analyzer and inclined spectrometer with ultra-thin polypro-

pylene window, absence of uniform standard samples for the determination of beryllium, etc. Due to the described problems in obtaining accurate analyzes of beryllium content, most publications provide combined or recalculated analyzes of Be-containing minerals. Thus, some researchers normalize the obtained results to a certain amount of oxygen and beryllium [5, 7, etc.], while other scientists determine beryllium using isotopic methods and “add” it to the available microprobe analyzes [8, 9, etc.]. This paper describes the technique of electron-probe microanalysis of beryllium content, on the example of studying natural minerals (aluminosilicates and oxides).

*Emerald*, a green gemstone, variety of a beryl jewelry is the mineral the author selected in 2008, during a geological excursion held at the All-Russian Scientific Conference “RMS Annual Meeting” on the dumps of the Mariinsky beryllium deposit (near Malysheva settlement, Sverdlovsk region). The author studied flakes and chips of the emerald rims from large beryl individuals composing metacrystals in phlogopite mica (Fig. 1).

All analyzes of emeralds were performed on a CAMECA SX 100 electron probe microanalyzer with five wave spectrometers. Processing of the pieces of mineral consisted of preparing them in the form of



**Figure 1.** Metacrystals of emeralds the author selected at the Mariinsky beryllium deposit. The size of the prismatic crystal is 1 cm in length.

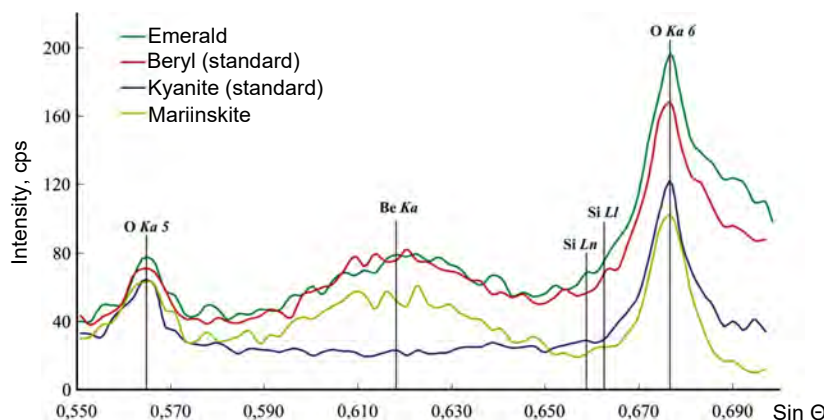


Figure 2. X-ray emission spectra in the range of Be K $\alpha$ -line for the Ural emerald, mariinskite and standard samples of beryl and Al<sub>2</sub>SiO<sub>5</sub>. For the crystal analyzer PC3 (2d = 211.4 Å), the recording range of sin  $\Theta$  is from 0.55 to 0.70, total 200 points with steps of sin  $\Theta$  = 0.00075, the recording time at each point is 2 s.

Table 1. Analytical conditions for measuring characteristic lines for emerald.

Element	Standard	Element content, wt. %	Crystal analyzer	Peak position, sin $\Theta \cdot 10^5$	Left background position, sin $\Theta \cdot 10^5$	Right background position, sin $\Theta \cdot 10^5$
Be	Beryl	5,03	PC3	61 700	-3230	4000
Na	Jadeite	11,28	TAP	46 327	-900	900
Mg	Diopside	10,78	TAP	38 478	-900	900
Al	Beryl	9,77	TAP	32 448	-750	750
Si	Beryl	30,50	TAP	27 738	-500	500
Ca	Diopside	18,37	LPET	38 387	-850	850
Ti	TiO <sub>2</sub>	59,95	LPET	31 418	-500	500
V	V	99,50	LPET	28 595	-300	300
Cr	Cr <sub>2</sub> O <sub>3</sub>	68,42	LPET	26 144	-500	500
Mn	Rhodonite	32,85	LiF	52 187	-150	250
Fe	Fe <sub>2</sub> O <sub>3</sub>	69,94	LiF	48 085	-500	500

Table 2. Results of electrone-probe microanalysis of beryl (emerald).

Analysis number	Oxide												Total
	SiO <sub>2</sub>	TiO <sub>2</sub>	V <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MnO	FeO	MgO	CaO	BeO	Na <sub>2</sub> O		
1	65,45	0,01	0,03	0,02	18,07	0,04	0,39	-	0,01	14,60	0,34	98,95	
2	63,49	0,02	0,03	0,49	14,74	0,10	0,61	2,02	0,03	14,40	1,70	97,62	
3	63,87	0,01	0,05	0,46	14,46	-	0,55	1,88	0,02	14,60	1,81	97,70	
4	63,99	-	0,05	0,45	14,31	0,01	0,67	2,06	0,03	13,90	1,86	97,34	
5	63,82	0,01	0,06	0,36	14,35	-	0,56	2,08	0,04	14,40	1,83	97,51	
6	63,76	0,01	0,04	0,32	14,79	0,04	0,45	2,05	0,03	14,40	1,69	97,58	
7	63,63	0,02	0,07	0,32	14,51	-	0,58	2,03	0,03	14,30	1,72	97,20	
Crystallochemical formulas													
1	Be <sub>3,14</sub> (Al <sub>1,91</sub> Na <sub>0,06</sub> Fe <sub>0,03</sub> ) <sub>2,00</sub> [Si <sub>5,86</sub> O <sub>18</sub> ]												
2	Be <sub>3,10</sub> (Al <sub>1,56</sub> Na <sub>0,30</sub> Mg <sub>0,27</sub> Fe <sub>0,05</sub> Cr <sub>0,03</sub> ) <sub>2,21</sub> [Si <sub>5,69</sub> O <sub>18</sub> ]												
3	Be <sub>3,13</sub> (Al <sub>1,53</sub> Na <sub>0,31</sub> Mg <sub>0,25</sub> Fe <sub>0,04</sub> Cr <sub>0,03</sub> ) <sub>2,16</sub> [Si <sub>5,71</sub> O <sub>18</sub> ]												
4	Be <sub>3,01</sub> (Al <sub>1,52</sub> Na <sub>0,33</sub> Mg <sub>0,28</sub> Fe <sub>0,05</sub> Cr <sub>0,03</sub> ) <sub>2,21</sub> [Si <sub>5,78</sub> O <sub>18</sub> ]												
5	Be <sub>3,09</sub> (Al <sub>1,52</sub> Na <sub>0,32</sub> Mg <sub>0,28</sub> Fe <sub>0,04</sub> Cr <sub>0,03</sub> ) <sub>2,19</sub> [Si <sub>5,72</sub> O <sub>18</sub> ]												
6	Be <sub>3,10</sub> (Al <sub>1,56</sub> Na <sub>0,29</sub> Mg <sub>0,28</sub> Fe <sub>0,04</sub> Cr <sub>0,02</sub> ) <sub>2,19</sub> [Si <sub>5,71</sub> O <sub>18</sub> ]												
7	Be <sub>3,09</sub> (Al <sub>1,54</sub> Na <sub>0,30</sub> Mg <sub>0,27</sub> Fe <sub>0,04</sub> Cr <sub>0,02</sub> V <sub>0,01</sub> ) <sub>2,18</sub> [Si <sub>5,73</sub> O <sub>18</sub> ]												

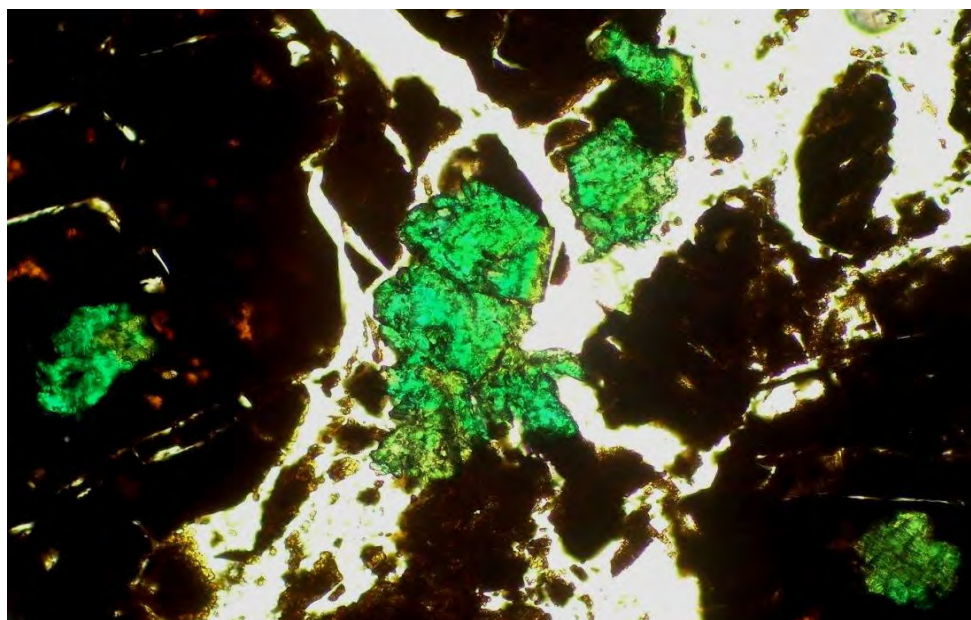
Note: № 1 – standard sample of beryl, № 2–7 – natural emerald.

a polished section, and then spraying with a layer of carbon (a thickness of about 250 Å). The accelerating voltage was 10 kV, the beam current was 150 nA, the diameter of the electron beam was 2  $\mu$ m, and the angle of x-ray extraction was 40°. The spectra were obtained on wave spectrometers with TAP crystal analyzers (2d = 25.745 Å), LPET (2d = 8.75 Å), LiF (2d = 4.0226 Å), and PC3 (2d = 211.4 Å, a specialized crystal for determining the content of beryllium and boron); the measurements of all the elements were carried out along the K $\alpha$ -lines.

The author determined position of the peak and the background for the both sides of the peak with minimum possible spectral overlaps, Fig. 2 shows X-ray emission spectra on a PC3 crystal analyzer in the range of the Be K $\alpha$ -line for the Ural emerald and standard samples of beryl and kyanite. One can see that the oxygen lines O K $\alpha$ <sub>5</sub> (sin  $\Theta$  = 0.56425), O K $\alpha$ <sub>6</sub> (sin  $\Theta$  = 0.67679) and silicon Si Ln (sin  $\Theta$  = 0.65805), Si Ll (sin  $\Theta$  = 0.66253) do not interfere with the determination of beryllium.

**Table 3. Correlation coefficients of the elements in the microanalysis of beryl (emerald).**

Oxide	BeO	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	V <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	FeO	Total
BeO	1											
Na <sub>2</sub> O	-0,44	1										
MgO	-0,44	0,99	1									
Al <sub>2</sub> O <sub>3</sub>	0,44	-1,00	-0,99	1								
SiO <sub>2</sub>	0,30	-0,94	-0,97	0,94	1							
CaO	-0,55	0,85	0,88	-0,85	-0,78	1						
TiO <sub>2</sub>	0,37	-0,01	0,07	0,00	-0,30	-0,03	1					
V <sub>2</sub> O <sub>3</sub>	-0,33	0,68	0,65	-0,71	-0,56	0,70	-0,12	1				
Cr <sub>2</sub> O <sub>3</sub>	-0,38	0,91	0,88	-0,90	-0,87	0,61	0,06	0,40	1			
MnO	0,09	-0,18	-0,09	0,21	-0,06	-0,23	0,52	-0,76	0,08	1		
FeO	-0,70	0,75	0,71	-0,75	-0,67	0,55	0,04	0,51	0,81	-0,07	1	
Total	0,57	-0,95	-0,96	0,96	0,92	-0,88	-0,04	-0,76	-0,80	0,22	-0,77	1

**Figure 3. Mariinskite grains (green) in the matrix of mica chromite. The photo size is 2 mm by the base, polished section.**

When performing the quantitative analysis, the intensity measurement time at the peak (20 s for beryllium, 10 s for the remaining elements) was twice as long as the background measurement time. The standard samples used for calibration and the position of the crystal analyzers during the recording of peak and background intensities (from both sides) of the analytical lines are in Table 1. Spectrometers counters measuring the intensity of the Na, Mg, Al, Si, Ca, Ti, and Be lines had polypropylene windows 0.2  $\mu\text{m}$  thick; spectrometers counters measuring the intensity of V, Cr, Mn, Fe – a beryllium window 25  $\mu\text{m}$  thick; detectors were gas-flow (mixture of Ar and CH<sub>4</sub>), working in auto-differential mode; the corrections we calculated using the X-PHI model; the oxygen content was determined using the microprobe software, with assumption of stoichiometric composition.

The chemical composition of the emerald in the studied samples varies within narrow limits shown in Table 2. The chromium content, which gives the bright green color to the mineral, is 0.32–0.49 wt. % Cr<sub>2</sub>O<sub>3</sub>, there also are significant amounts of sodium impurities (Na<sub>2</sub>O 1.69–1.86 wt. %), magnesium (MgO about 2 wt. %) and iron (FeO 0.45–0.67 wt. %); variations in the content of BeO from 13.9 to 14.6 wt.% (the detection limit of beryllium is about 1.4 wt.%, standard deviation is 1.3 wt. %, and peak to background ratio is 1.7). The obtained compositions of emeralds are completely satisfactorily recalculated to the crystallochemical formula of beryl (without taking into account the water, which, apparently, is present in the studied samples, within 2–3 wt. %). The author placed all impurity components, according to

the known recommendations [7, 10], in the position of aluminum, while some of the aluminum, in turn, compensates for vacancies in the position of silicon.

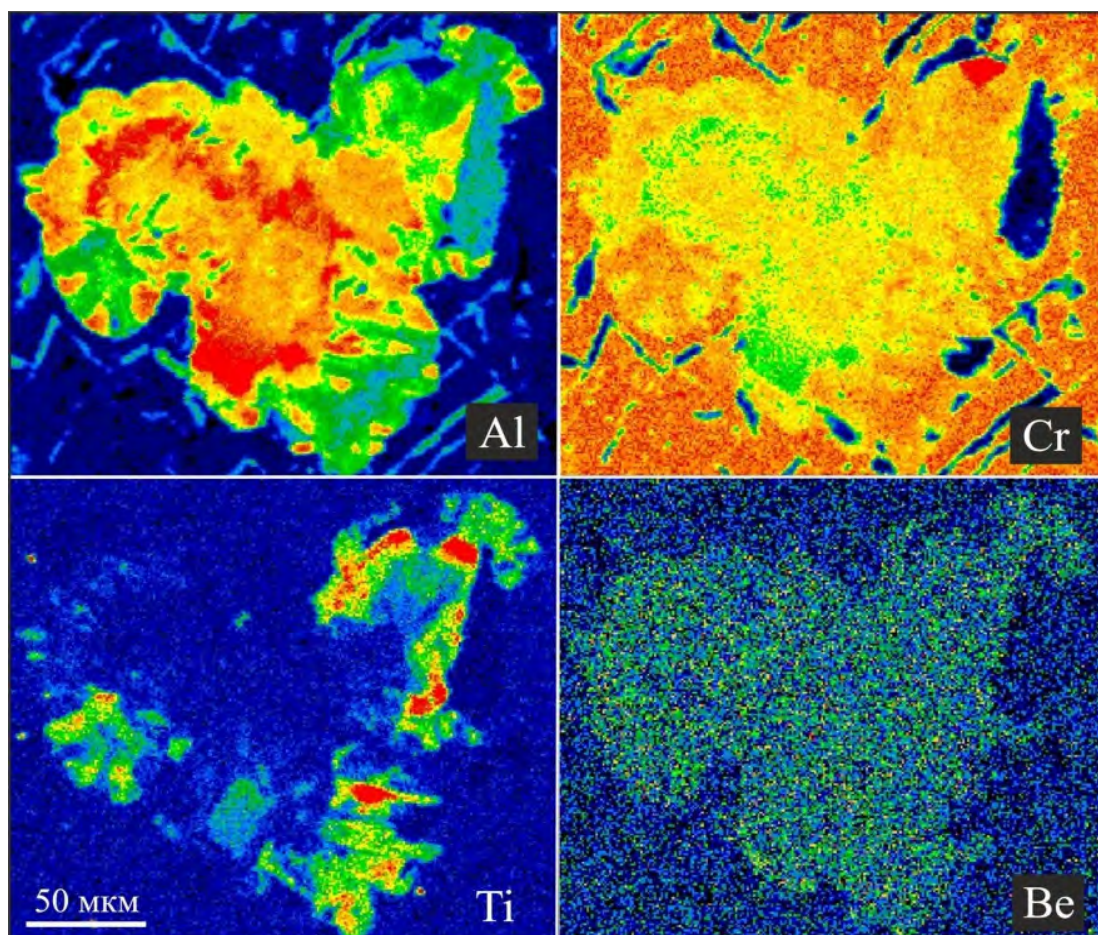
The problem of the choice of standards, as for all analytical studies, remains relevant, especially with methodological work in the field of determining light elements. The author used chemical analogs with a similar composition as standards, thus minimizing correction factors. For example, many analysts engaged in the quantitative determination of beryllium in aluminosilicates have faced a serious problem of overlapping silicon and aluminum lines over the beryllium line. We, in the presence of a specialized crystal analyzer PC3, managed to avoid such a situation, i. e. as one can see from Table 3, beryllium has an extremely low correlation with these elements, what in this case means no overlapping lines.

*Chrysoberyl–mariinskite.* To determine beryllium in a simple natural substance (oxide), the author have chosen a series of minerals of the chrysoberyl group. Recently the author participated in the discovery of a new mineral, Mariinskite, a chrome analogue of chrysoberyl [11]. It is interesting that in the same line of chrysoberyl–mariinskite there is a very rare precious stone – alexandrite, chrome-containing chrysoberyl.

The author decided to study zonal mariinskite (with an intermediate zone of folded chrysoberyl), which forms abundant fine impregnation in hydrothermally altered micaceous chromite ores within the Bazhenovsky ophiolite complex (the surroundings of Asbest

**Table 4. Analytical conditions for the measurement of characteristic lines for mariinskite.**

Element	Standard	Element content wt. %	Crystal analyzer	Peak position, $\sin \Theta \cdot 10^5$	Left background position, $\sin \Theta \cdot 10^5$	Right background position, $\sin \Theta \cdot 10^5$	Time of measurement on peak, s
Al	Corundum	52,92	TAP	32 455	-700	700	10
Ti	Rutile	59,95	LPET	31 421	-300	300	10
Fe	Cr <sub>2</sub> O <sub>3</sub>	21,89	LLiF	48 085	-500	500	10
Cr	And glass	68,42	LLiF	56 872	-500	500	10
Be	Chrysoberyl	7,00	PC3	61 629	-8500	8620	20

**Figure 4. Maps of intensity distribution of the characteristic X-ray emission of the Al K $\alpha$ , Cr K $\alpha$ , Ti K $\alpha$  and Be K $\alpha$  lines of the mariinskite grain in the matrix of micaceous chromites.**

city, Sverdlovsk region). Grain size of the minerals of the chrysoberyl group does not exceed 1 mm. They have an isometric appearance and high hardness (they protrude strongly from the chromite matrix during polishing). The minerals color is black in mass, emerald-green in clearance (Fig. 3). In addition to chromite, in association with them one can note mica (alumoseladonite, fluorophlogopite and muscovite), chromium tourmaline, fluorapatite and eskolaite [12].

The conditions for measuring the oxides of the BeAl<sub>2</sub>O<sub>4</sub>-BeCr<sub>2</sub>O<sub>4</sub> series have been partially explained in previous papers [13, 14, etc.]. All analyzes of oxides were also performed on a CAMECA SX 100 electron probe microanalyzer. The pressure in the sample chamber was  $2 \cdot 10^{-4}$  Pa, in the electron gun region  $4 \cdot 10^{-6}$  Pa, in wave spectrometers – 7 Pa. Accelerating voltage was 10 kV, current of absorbed electrons on the Faraday cylinder – 100 nA. The diameter of the beam of electrons focused on the sample was 2  $\mu$ m. Preliminarily, to determine the position ( $\sin \Theta \cdot 10^5$ ) of the peak and the background from both sides of the analytical peak, with the minimum possible spectral overlap, the author recorded spectra on wave spectrometers with TAP, LPET, LLiF and PC3 (determination of beryllium and boron) crystal analyzers. Fig. 2 shows X-ray emission spectra on the PC3 crystal ana-

lyzer in the range of Be K $\alpha$ -line for mariinskite and standard samples of beryl and kyanite. Measurements of all elements for the analysis of the mineral were along the K $\alpha$ -lines, with minimal spectral overlap during determination of the positions of peak and background levels. The author sputtered standard and test samples with carbon. The sputtering thickness on the standards was “industrial”, i. e. according to the passport 250 Å, the sputtering thickness on the section with the studied mineral was determined indirectly, by the color of the copper plate (a red-orange color identical to the sputtering on standards, also mounted on a copper shim). Standard samples: chrysoberyl – BeAl<sub>2</sub>O<sub>4</sub> from Brazil, corundum – Al<sub>2</sub>O<sub>3</sub> (synthetic, 99.9999 %), chromium oxide – Cr<sub>2</sub>O<sub>3</sub> (synthetic, > 99.99 %), rutile – TiO<sub>2</sub> (synthetic, 99.999 %), And glass – synthetic glass of andradite composition. Counter was gas-flow (gas mixture Ar-CH<sub>4</sub>), detector mode was auto-differential. One can see the conditions for measuring the lines in Table 4, with the corrections calculated according to the X-PHI model (which is better for low voltage). Based on the stoichiometry of the mineral, a microprobe software also automatically calculated oxygen level.

Chemical composition of the minerals of the chrysoberyl-mariinskite series in the studied crystals varies from aluminous

**Table 5. Results of electron-probe microanalysis of mariinskite chrysoberyl.**

Mineral	Oxide					Total
	BeO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	
Mariinskite	17,19	29,73	0,12	52,99	0,13	100,16
	15,98	17,78	0,81	65,39	0,19	100,15
	16,05	25,79	0,12	57,22	0,41	99,60
	14,81	19,01	0,77	63,98	0,26	98,83
	17,10	28,59	0,12	54,04	0,38	100,23
Chrysoberyl	17,36	37,53	0,36	44,30	0,38	99,93
	16,55	35,51	0,30	47,20	0,19	99,76
	17,78	33,84	0,14	48,21	0,40	100,37
	17,28	33,03	0,22	48,68	0,20	99,42
Crystallochemical formulas						
Mariinskite	$Be_{1,05}(Cr_{1,06}Al_{0,89})_{1,95}O_4$					
	$Be_{1,03}(Cr_{1,39}Al_{0,56}Ti_{0,02})_{1,97}O_4$					
	$Be_{1,01}(Cr_{1,19}Al_{0,80})_{1,99}O_4$					
	$Be_{0,98}(Cr_{1,35}Al_{0,62}Ti_{0,02})_{2,02}O_4$					
Chrysoberyl	$Be_{1,05}(Cr_{1,09}Al_{0,86})_{1,95}O_4$					
	$Be_{1,03}(Al_{1,09}Cr_{0,87}Ti_{0,01})_{1,97}O_4$					
	$Be_{1,00}(Al_{1,05}Cr_{0,94}Ti_{0,01})_{2,00}O_4$					
	$Be_{1,06}(Al_{0,99}Cr_{0,95})_{1,94}O_4$					
	$Be_{1,05}(Al_{0,98}Cr_{0,97})_{1,95}O_4$					

BeCr<sub>2</sub>O<sub>4</sub> to chromic BeAl<sub>2</sub>O<sub>4</sub> (Table 5); in their elemental mapping (Fig. 4), the author established a distinct zoning in distribution of aluminum (Al<sub>2</sub>O<sub>3</sub> 17.8–37.5 wt. %), chromium (Cr<sub>2</sub>O<sub>3</sub> 44.3–65.4 wt. %) and iron (FeO 1.2–2.6 wt. %). The most aluminous zones in the form of chrysoberyl create intermediate regions in BeCr<sub>2</sub>O<sub>4</sub> individuals, with variations in the BeO content from 16.4 to 22.1 wt. % (the limit of beryllium detection of is about 1 wt. %, peak to background ratio is about 2.8).

In general, the obtained microprobe analyzes of minerals with quantitative determination of beryllium coincide with the available theoretical compositions of beryls and chrysoberyls, which indicates the high efficiency of the developed technique. As a result using this technique, we can relatively quickly and reliably determine quantitative content of beryllium in natural silicates and oxides, which is an acute need for geological researchers studying the mineralogy of beryllium deposits. For example, this technique significantly facilitated the passage of our application for mariinskite in the commission for new minerals of the International Mineralogical Association.

Thereby, the author developed the technique of electron-probe microanalysis of beryllium content on example of studying natural minerals (aluminosilicates and oxides). The technique allowed to

obtain a quantitative content of beryllium (in combination with other elements) in the emeralds of the Mariinsky beryllium deposit and in the zonal mariinskite – chrysoberyl from the chromitites of the Bazhenov ophiolite complex.

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**Вера Витальевна Хиллер**

hilvervit@mail.ru

Институт геологии и геохимии

им. академика А. Н. Заварицкого УрО РАН

Россия, Екатеринбург, ул. Академика Вонсовского, 15

**Vera Vital'evna Khiller**

hilvervit@mail.ru

Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences

Ekaterinburg, Russia