

Electron probe X-ray microanalysis investigations of powder rock reference materials

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The quality of results obtained by any method of the analysis depends on availability of reference materials for comparison. It is desirable to use the certified reference materials as reference samples. The electron probe X-ray microanalysis (EPMA) was applied for studying some powder rock reference materials. All the constituent minerals have been identified. Element distributions, grain size and forms of powder rock reference materials were examined. The certified reference materials contains grains size from dust-like few microns and smaller. Small grains stick to larger ones. Most grains show irregular angular-like shape. Spherical grains are not bigger than 10 μm . Some metals were found as separate particles. The trace elements constituting accessory minerals, which are basically concentrated in the fine fraction, are inhomogeneous in small amounts of the certified reference materials. Data of these investigations are involved in certificate of the certified reference materials of svyatonossite SSv-1, subalkaline granite SG-4 and synnyrite SSn-1 (production of Vinogradov Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences, Russian Federation). These certified reference materials are used for the traditional methods of volume and bulk analyses (ICP-MS, XRF, chemical, optical spectral et al) in a wide range of environmental, geological, biological, geochemical, industrial and archaeological applications.

Keywords: electron probe X-ray microanalysis, homogeneity testing, particle size, rock reference materials

Rock reference materials (RMs) represent the fine-dispersed substance with the grain size often not over 80 μm . Their preparation commonly proceeds through the stages of (1) primary crushing of rock material by a jaw crusher to reach 5 mm grain size; (2) further processing by a rolling crusher to achieve 1 mm grain size; (3) grinding in a ball mill and subsequent homogenizing of crushed material [1, 2]. The grain-size composition of prepared rock reference material is dependent both on the procedure of RMs preparation and mineral composition of rock samples. Because mineral components have different hardness, the rate of grinding varies, even if the reference materials are processed identically. The dispersion of reference material is a critical factor in reaching the material homogeneity [3, 4]. An irregular distribution of minerals involving some trace elements can be the cause of inhomogeneous distribution of the elements in the reference material.

Mineral and grain-size compositions of rock reference materials bear important information to be correctly used. In the process of RM certification the grain-size is basically determined by dry sieving or particle size analyzer [5, 6]. Mineral composition is traditionally evaluated from petrographic descriptions of thin sections of source rocks using optical microscope.

This work was targeted to identify the shape and grain size of powder material, as well as to examine the pattern of distribution of elements and individual minerals in the certified reference materials (CRMs)

of svyatonossite, SSv-1, subalkaline granite, SG-4, and synnyrite, SSn-1 produced at the Institute of Geochemistry in Irkutsk (Russia).

Materials and methods

Equipment. The microprobe JXA8200 (JEOL Ltd, Japan) was used for executing the wavelength-dispersive electron probe X-ray microanalysis, producing X-ray maps, secondary and back scattered electron images, as well as conducting energy-dispersive observation of spectra. The device is equipped with five wavelength-dispersive spectrometers (WDS) with embedded crystals LDE1, LDE2, TAP, LDEBH, TAPH, PETJ, PETH, LiF and LiFH and energy-dispersive spectrometer (EDS) EX-84055MU (JEOL Ltd, Japan).

Study substance. Certified reference materials of svyatonossite (SSv-1), subalkaline granite (SG-4) and synnyrite (SSn-1) were prepared from aluminosilicate rocks.

Mineral composition of the CRMs was determined from optical microscope petrographic description of thin sections of source rocks - the basis of reference material. The X-ray phase analysis was employed to additionally examine CRMs of SG-4 and SSn-1. The mineral compositions determined from thin section description and X-ray phase analysis was close enough. It was feasible to identify the accessory minerals only by petrographic examination of rock thin sections. The X-ray phase analysis was not capable to locate the accessories probably because of the insufficient detection limits of the technique.

Table 1 presents the averaged mineral compositions of the CRMs. As seen from the table, the feldspar is the basic mineral of CRMs: in SSv-1 it is potash feldspar and plagioclase, and in SG-4 and SSn-1 it is potash feldspar.

When developing reference material SSv-1 the EPMA method was employed to examine thin sections of source rock with the intention to more precisely determine the mineral composition [1]. In this study EPMA has been applied to research dispersed substance of new CRMs SSn-1 and SG-4 and CRM SSv-1 for searching new information about its mineral composition.

Table 1. Mineral composition of CRMs.

Minerals	CRM		
	SSv-1	SG-4	SSn-1
	Mineral contribution, %		
Feldspar	~ 80	~ 70	~ 80
Quartz	–	~ 25	–
Amphiboles	~ 4	~ 5	–
Kalsilite and nepheline	–	–	~ 10
Pyroxene and mica	~ 11	–	~ 10
Garnet	~ 3	–	–
Accessory minerals (apatite, calcite, magnetite, orthite, grothite, zircon)	< 2	< 0.5	–

Note: Dash denotes that this mineral was not defined.

In our study the CRM substances and their fractions (I – <40 mm; II – 40 to 50 mm; III – from 50 to 60 mm; IV – from 60 to 80 mm and V – from 80 to 125 mm) were analyzed.

Table 2 lists the CRM compositions determined through interlaboratory certifications. The data are tabulated only for the elements defined by EPMA. The contents of matrix elements in these CRMs vary: granite SG-4 contains high silicon; svyatonossite SSv-1 shows higher calcium, magnesium, manganese

and iron; synnyrite SSn-1 shows very high potassium content.

Specimen preparation. Samples for analyses were prepared with the two techniques. 1. The arbitrarily chosen amount of material was poured onto the carbon double-faced adhesive tape and slightly pressed. The unfastened particles were shaken off, while the adhered particles were additionally aired to eliminate their separation in the device chamber at vacuum 10^{-6} mm of mercury. 2. The briquette sections were prepared as the particles packed with paste-polished surfaces in the epoxy resin.

In both cases the carbon layer (20-30 nm thick) was evaporated onto the sample surface to create surface electric conductivity.

Methods of investigation. The EPMA has been applied to research dispersed substance of RMs.

At first the original material (2 mg of substance over 2x2 cm area) of the three CRMs and sieved powder (5 fractions for every CRM) were initially examined with electronic microscope mode. To make the conclusions to be expanded onto all CRMs, the approaches similar to those applied to the vast areas, e.g. in geochemical mapping or environmental monitoring, were used [7, 8]. The entire surface to be analyzed was divided into sections, and each section was visualized by the electronic microscope. The arbitrarily selected sections were photographed with 40-fold magnification being minimally possible with microprobe JXA8200. Then some areas randomly selected on the sections were viewed with greater magnification. If any specific feature, e.g. shape and size of particles, detected minerals or certain elements, was repeatedly observed either on every chosen area, or on every second one or every n -area (i.e. the feature repeatedly appeared) it was supposed that this RM feature would be available with the same probability in the other parts. Considering this principle of “statistical importance” some qualitative conclusions can be made on the grain-size composition of the reference material and occurrence of some minerals in it.

Table 2. Chemical composition of CRMs.

№	Component	Certified values \pm uncertainty (P=0.95)		
		SSv-1 [3]	SG-4	SSn-1
% m/m				
1	SiO ₂	57.86 \pm 0.29	73.8 \pm 0.6	55.0 \pm 0.4
2	TiO ₂	0.78 \pm 0.04	0.25 \pm 0.01	0.091 \pm 0.006
3	Al ₂ O ₃	16.68 \pm 0.25	12.6 \pm 0.3	22.5 \pm 0.4
4	Fe ₂ O _{3 total}	5.41 \pm 0.11	3.06 \pm 0.03	1.35 \pm 0.03
5	MnO	0.14 \pm 0.01	0.052 \pm 0.003	0.0093 \pm 0.0008
6	MgO	1.25 \pm 0.07	0.079 \pm 0.014	0.18 \pm 0.02
7	CaO	6.94 \pm 0.22	0.44 \pm 0.02	0.49 \pm 0.02
8	Na ₂ O	4.51 \pm 0.22	4.13 \pm 0.14	1.19 \pm 0.08
9	K ₂ O	4.77 \pm 0.19	5.08 \pm 0.07	18.0 \pm 0.2
10	P ₂ O ₅	0.39 \pm 0.02	0.039 \pm 0.005	0.058 \pm 0.005

№	Component	Certified values \pm uncertainty (P=0.95)		
		SSv-1 [3]	SG-4	SSn-1
		$\mu\text{g}\cdot\text{g}^{-1}$		
11	As	(12)	(6.6 \pm 2.3)	(0.4)
12	Ba	69 \pm 7	123 \pm 16	2090 \pm 150
13	Ce	219 \pm 34	177 \pm 27	12.3 \pm 1.4
14	Co	8 \pm 1	0.9 \pm 0.2	1.5 \pm 0.3
15	Cr	16 \pm 2	29.4 \pm 3.4	7.9 \pm 1.2
16	Cu	5 \pm 1	10.4 \pm 1.1	3.2 \pm 0.5
17	F	820 \pm 90	1140 \pm 170	(160 \pm 80)
18	La	108 \pm 17	91 \pm 7	6.8 \pm 0.9
19	Mo	1.1 \pm 0.2	3.3 \pm 0.3	(0.38 \pm 0.9)
20	Nb	20 \pm 4	27 \pm 3	(0.3 \pm 0.1)
21	Ni	8.4 \pm 1.5	6.5 \pm 1.0	2.5 \pm 0.5
22	Pb	21 \pm 4	44 \pm 5	(1.6 \pm 0.4)
23	Rb	56 \pm 9	194 \pm 8	776 \pm 99
24	S	(170)	(150 \pm 80)	(250 \pm 70)
25	Sr	5200 \pm 400	34 \pm 7	564 \pm 56
26	Y	25 \pm 5	77 \pm 8	1.2 \pm 0.2
27	Yb	2.3 \pm 0.4	7.4 \pm 1.4	0.08 \pm 0.01
28	Zn	109 \pm 15	145 \pm 6	13 \pm 2
29	Zr	185 \pm 20	710 \pm 50	(4.0 \pm 1.1)

Note. Brackets enclose the content values provided in CRM certificates as indicative ones.

Table 3 provides the total number of the areas chosen for grain-size, element and mineral composition determination. Location and size of the areas to be studied in every CRMs were selected randomly from the entire surface. Back scattered and secondary electrons were used as analytical signals to obtain images; the element and mineral compositions were determined from X-ray spectra intensity. The

distribution of radiation intensity of the element in the assigned area was identified by fitting the wavelength-dispersive spectrometers for the line of X-ray radiation of the set area and by scanning the exciting beam of electrons over the surface. The X-ray intensity distribution images were obtained for 29 elements: F, Na, Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Mo, Ba, La, Ce, Yb and Pb.

Table 3. Number and size of surface sites of studied CRMs.

Analytical signal	Size of surface, $\mu\text{m}\times\mu\text{m}$ (\times magnification)	CRM		
		SSv-1	SG-4	SSn-1
Characteristic X-ray radiation	400 \times 400 (\times 300)	29	33	37
	120 \times 120 (\times 1000)	9	14	13
	Less then 120 \times 120 (more then \times 1000)	3	3	2
Back scattered electrons	3000 \times 3000 (\times 40)	6	7	4
	400 \times 400 (\times 300)	30	34	38
	120 \times 120 (\times 1000)	10	15	14
	Less then 120 \times 120 (more then \times 1000)	3	5	3
Secondary electrons	3000 \times 3000 (\times 40)	6	6	3
	400 \times 400 (\times 300)	30	33	37
	120 \times 120 (\times 1000)	9	13	12
	Less then 120 \times 120 (more then \times 1000)	3	4	2

The coloring on each separate pattern depends on the element content on the given area; it is proportional to the radiation intensity and varies from black (absence of an element) through blue (possible radiation background) to red (corresponds to X-ray intensity of an element with maximum concentration on a photographed site).

Results and Discussion

Grain size composition

Visualization of the entire surface by electronic

microscope mode showed that appearances of the sample surfaces are practically not distinguished from each other. Photographing the surfaces in back scattered and secondary electrons with 40 and 300 magnification verified that they are the same type for three CRMs (Fig.1). Any differences in grain size composition are not the case. It seems that grinding material of studied CRMs proceeds similarly. Material particles of all CRMs are often irregularly shaped. The minerals composing CRMs are most likely broken by grinding basically along cleavage planes.

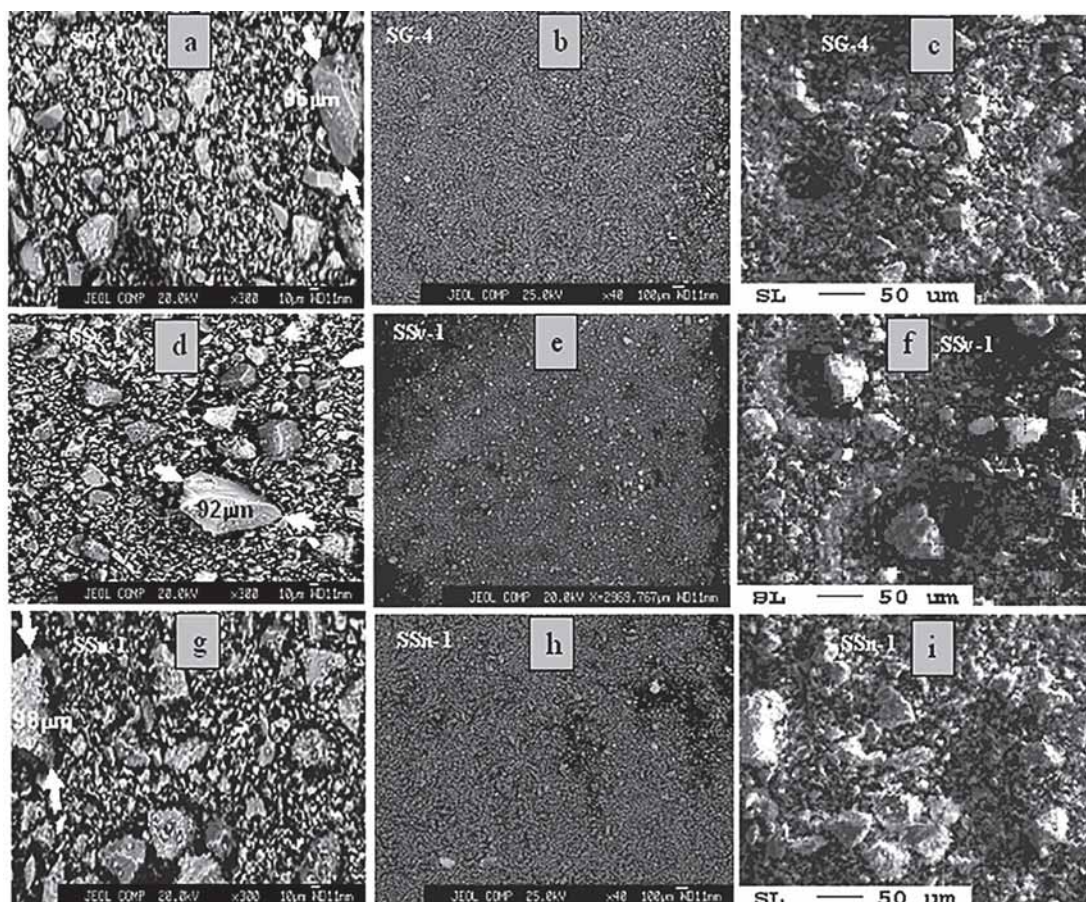


Fig.1. Substances of CRMs SG-4 (a,b,c), SSv-1 (d,e,f), SSn-1 (g,h,i). Back scattered electron images (a,b,d,e,g,h) and secondary electron images (c,f,i), magnification 40 (b,e,h) and 300 (a,c,d,f,g,i). The bottom part of each image shows the conditions of measurements: accelerating voltage (kV), magnification factor (x), scale bar (μm) and focal length (mm).

The linear sizes of grains basically do not exceed $80\ \mu\text{m}$ that satisfies the requirements of analytical methods of rock sample analysis. However, the elongated grains are found as well; their width and height are about $80\ \mu\text{m}$, while the length exceeds this value (Fig.1). Similar features were observed in each of three fractions of CRMs SG-4 and SSn-1 on the areas ($1.5\text{-}2\ \text{cm}^2$) randomly chosen on the surface section ($400\times 400\ \mu\text{m}$) (Fig.2).

On the surface images the materials of similar fractions of different CRMs look nearly identically. The shapes of grains and their distribution for similar fractions of CRMs practically do not differ, and the back scattered electron images look similarly. It character-

izes positively the process of grinding of the studied CRMs to the grains of required size.

It is also noteworthy, that when fractions are separated by dry sieving the grains larger than a mesh are available in the sieved material due to their elongated shape.

For example, the finest fraction "I" should contain only the grains $< 40\ \mu\text{m}$; nevertheless the images also display $47\ \mu\text{m}$ and $50\ \mu\text{m}$ grains (Fig.2 a,d). Fraction "II" should contain only the grains with the size ranging from $40\ \mu\text{m}$ to $50\ \mu\text{m}$; but $65\ \mu\text{m}$ and $75\ \mu\text{m}$ grains are also found (Fig.2 b,e). Fraction "III" is to contain the grains sized $50\ \mu\text{m}$ to $60\ \mu\text{m}$, but $75\ \mu\text{m}$ grains are observed as well (Fig.2 c,f).

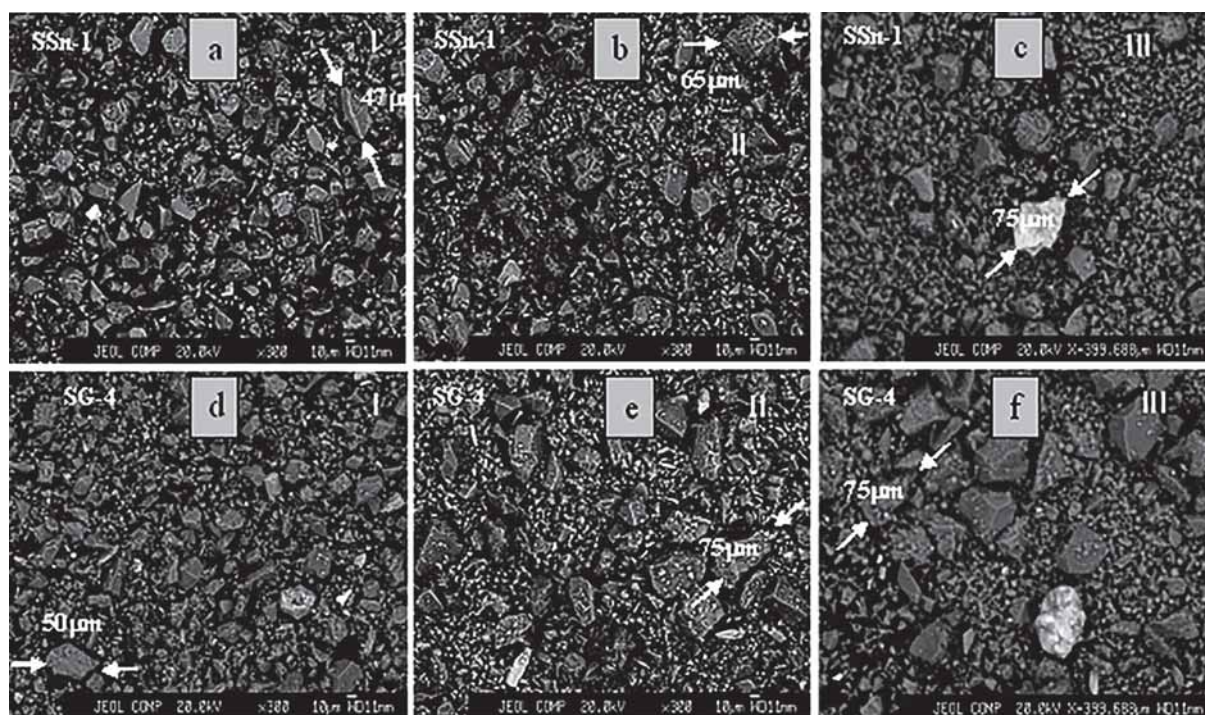


Fig.2. Back scattered electron images of fractions (I fraction includes grains $<40\ \mu\text{m}$, II fraction includes grains from 40 to $50\ \mu\text{m}$, III fraction includes grains from $50\ \mu\text{m}$ to $60\ \mu\text{m}$) for CRMs SSn-1 (a,b,c) and SG-4 (d,e,f). The bottom part of each image shows the conditions of measurements: accelerating voltage (kV), magnification factor ($\times 300$), scale bar (μm) and focal length (mm).

The fine grains stick to larger ones and remain in the sieved material. All grains, even the micron-sized ones, are covered by finer dust-like grains. Figure 3 exemplifies such grains in the CRMs SG-4 (a), SSn-1 (b) and SSv-1 (c). The back-scattered electron images of the CRMs show abundant small grains (about $1\ \mu\text{m}$) on $30\ \mu\text{m}$ grains (Fig.3 a,b,c).

The total substance of CRMs and each fraction of the CRMs contain grains of all sizes - from dust-like to larger grains corresponding to the fraction size or even larger. The grains larger than a sieve mesh are found in the final material of the RMs, for they are elongated. In the cross-section they are less than a mesh, so they penetrate vertically.

In powder CRMs there are also spherically-shaped grains (Fig.3). The diameter of these spherical grains

ranges from the tenth parts of μm up to $10\ \mu\text{m}$. It is most likely that spherical grains are formed by local overheating of rock during its grinding. The rock is locally heated up to the temperature of formation of a liquid phase, which later cools down to balls. However, they might be present in the source rock and release, when crushed.

It was found, that the fine fraction contains abundant heavy grains (brighter ones on the back scattered electron image) compared to the larger fractions. Probable explanation is that the accessory minerals containing heavy elements are usually contained in the rock as fine inclusions. These minerals seem to be resistant to grinding, and they get released at rock crushing.

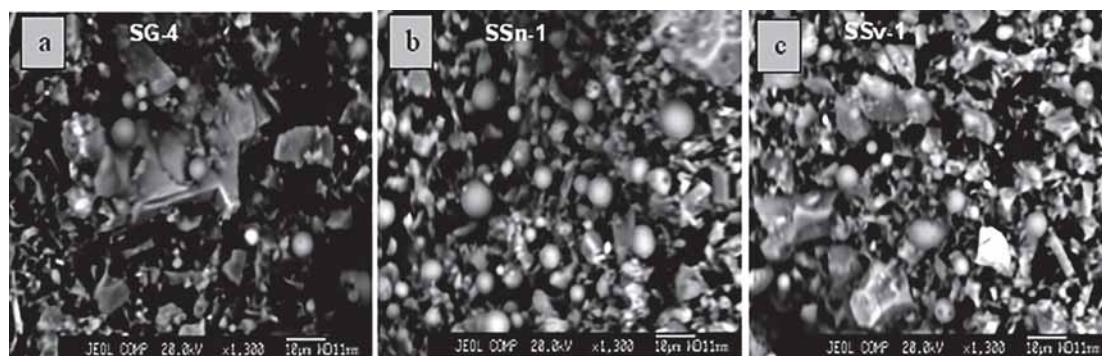


Fig.3. Back scattered electron images of ball-like grains and dust-like grains ($\times 1300$) in CRMs SG-4 (a), SSn-1 (b) and SSv-1 (c). The bottom part of each image shows the conditions of measurements: accelerating voltage (kV), magnification factor (\times), scale bar (μm) and focal length (mm).

Mineral and element composition

The X-ray distribution images show presence of elements on the surface, element locations in a certain grain or its conglomerate. On these images the minerals containing a certain element are identified. The distributions of X-ray intensity for a number of elements over randomly chosen surface of CRM are exemplified in Figure 4.

All maps of this study are performed by WDS spectrometers under next conditions: the beam current is 30 nA, dwell time is 30, accelerative voltage is 20 kV. It is well visible, that some elements (Si, K, Na, Al) are regularly distributed over all these surfaces and form large and fine silicate grains, the spherical ones included.

Iron, calcium, magnesium and manganese appear to be homogeneously distributed, in contrast to titanium and fluorine. It is evident, that titanium is irregularly distributed over the surface, and fluorine occurs just as a unique inclusion. The cobalt distribution is uncertain, as the intensity of the background radiation is comparable with the cobalt intensity line. Thus, quantitative determinations of these intensities are required. In CRMs SG-4 and SSn-1 the elements are distributed similarly to CRM SSv-1. Some of them (Si, K, Na, Al) are regularly distributed and created

the silicate grains. The iron, titanium and magnesium are found only in some minerals, though they are present in every image. Thus it is supposed that these elements are distributed homogeneously. Majority of elements: F, P, Ca, S, Cr, Cu, Zn, Y, La, Ce, Mn, Ba, Sr, Zr, Co, Nb and Ni are observed only on some maps as several inclusions, sometimes just one; or they can be absent on every map. We could determine only 25 elements out of 29 elements, e.g. As, Yb, Mo and Rb have not been determined. It can be assumed that these elements might not be available in separate inclusions at all, or their distribution in the CRMs is inhomogeneous within the substance studied. The fact is that they are contained in the main rock-forming minerals in the amount less than detection limits for EPMA, i.e. not less 0.1 m/m % (Table 2).

It is to be noted that the probability to detect accessory minerals is quite low. The detection depends on the amount of studied material, and its careful search can be exemplified by the case with niobium. The certified value of niobium in CRM SSn-1 is 0.3 ppm (Table 2). When magnified 400-fold, the inclusion about 2-3 μm was detected. In CRM SG-4 the niobium content reaches 27 ppm, but the Nb-containing inclusions sized less than a micron were detected only at magnification 1000.

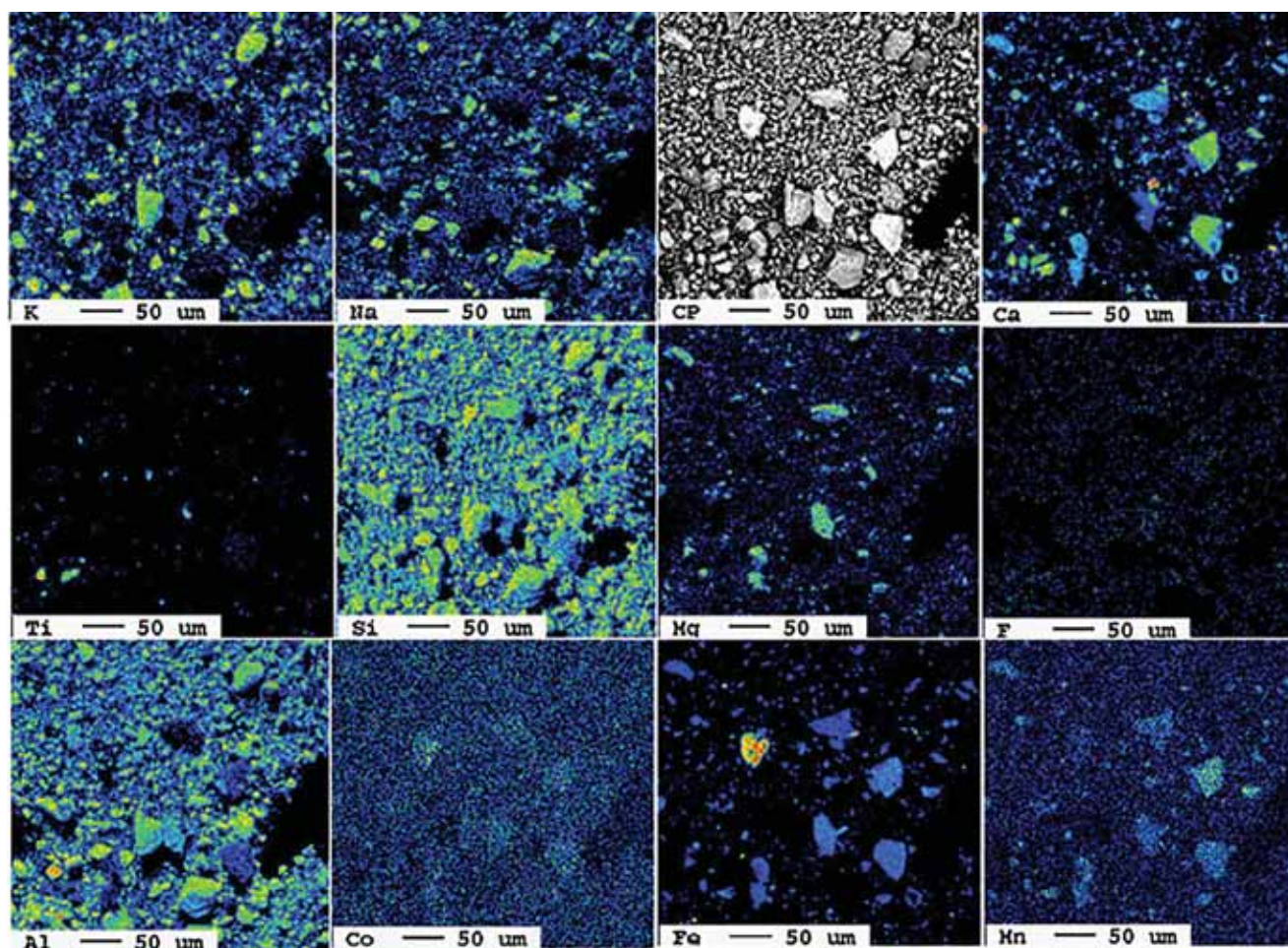


Fig.4. Back scattered electron (CP) and X-ray (for K, Na, Ca, Ti, Si, Mg, F, Al, Co, Fe, Mn) images (400 μm x 400 μm) of the CRM SSv-1.

For the elements homogeneously distributed even in a small amount of the material, the use of relatively small subsamples does not bias the results. This is contrary to the elements for which the concentrating minerals occur quite seldom. The element distribution is considered homogeneous only with abundant CRM material. Thus, the use of RMs for the elements contained in accessory minerals directly depends on the correctly chosen amount of RMs. Moreover, the required amount of the RMs should increase with decreasing the element concentration.

The abundance of the elements available in rare minerals can be defined by the amount of inclusions

available in the X-ray distribution images. For example, Figure 5 shows that calcium occurs in the compounds with fluorine in the CRM SG-4 (points 5-7 in Fig.5 c,d and points 8,9 in Fig.5 g,h) and in the other minerals (point 10 in Fig.5 g); calcium-fluorine compound occurs more frequently in CRM SG-4 (points 5-9 in Fig.5 c,g), as compared with CRM SSn-1 (point 1 in Fig.5 a,b). However, the total amount of inclusions with calcium both in CRMs SG-4 and SSn-1 is almost identical (compare Fig.5 a with Fig.5 c; Fig.5 e with Fig.5 g). CRM SG-4 contains more inclusions in combination with fluorine as compared with CRM SSn-1 (compare Fig.5 d and Fig.5 h with Fig.5 b and Fig.5 f).

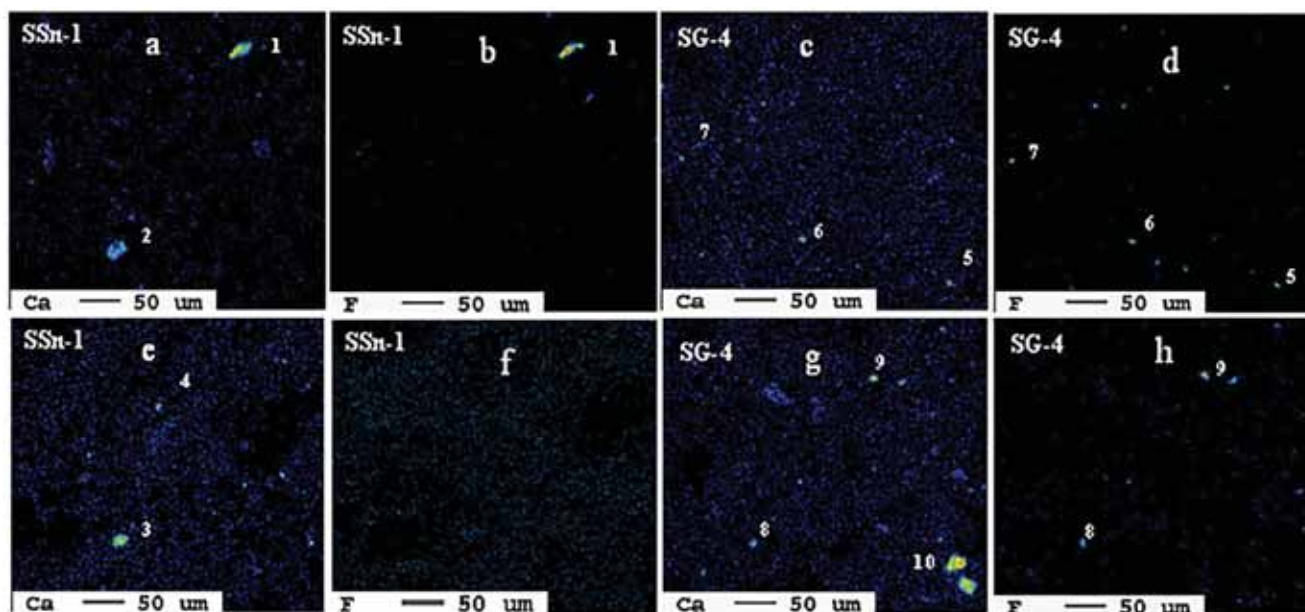


Fig.5. X-ray Ca K_{α} - (a,c,e,g) and F K_{α} - (b,d,f,h) images (400 μm x 400 μm) of CRMs SSn-1 (a,b - area 1; e,f - area 2) and SG-4 (c,d - area 1; g,h - area 2).

Considering the amount of inclusions on these images, it is supposed that fluorine content in CRM SSn-1 is significantly lower as compared with CRM SG-4, while calcium concentrations are similar. Correlation of mass fractions of fluorine and calcium oxide contents in CRMs SG-4 and SSn-1 fits the frequency of occurrence of minerals containing these elements in the images for the corresponding CRMs: calcium oxide concentrations are similar, while that of fluorine in the CRM SG-4 is one order higher than that in the CRM SSn-1 (Table 2).

Similar data are obtained for the other elements by observing the X-ray intensity distribution images and element contents (Table 2). The magnesium intensity distribution images suggest that number of inclusions containing magnesium is less in the CRM SG-4 than in the CRM SSn-1. According to RM certificates the contents of magnesium oxide in CRMs SG-4 and SSn-1 are 0.079 % and 0.18 %, respectively (Table 2). Manganese occurs in the CRM SG-4 in every second image, whereas in CRM SSn-1 it is found in every tenth image; MnO content in the CRM of SSn-1 is almost 5 times lower than the one in CRM SG-4.

The Y-containing minerals occur in CRM SG-4 more often than in CRM SSn-1: 77 ppm in CRM SG-4 and 1.2 ppm in CRM SSn-1. Similar conclusions concern cerium and lanthanum occurring from 12 to 14 times more frequently in CRM SG-4 than in the CRM SSn-1 that corresponds to their contents.

Such conclusions can be most likely made for each element, if we study a bigger amount of the material by EPMA. The EPMA studies of CRMs confirmed the occurrence of all minerals defined in CRM certifications. Besides, they revealed some accessory minerals not found before.

Numerous elements are contained in the CRMs as part of various minerals. Thus, the calcium X-ray intensity distribution image shows that calcium is present in several minerals (Fig.6 b); some of their spectra are given for CRM SG-4 in Figure 6 (d-g). Iron in all three CRMs occurs in silicate minerals - orthoclase, microcline and mica (Table 4), as well as in magnetite, ilmenite, intermetallic grains (Fig.7 d,f,e) and titanite (Fig.6 g). Titanium is included in silicate minerals (mica) (Table 4), in ilmenite, rutile (Fig.7 f,g) and titanite (Fig.6 g).

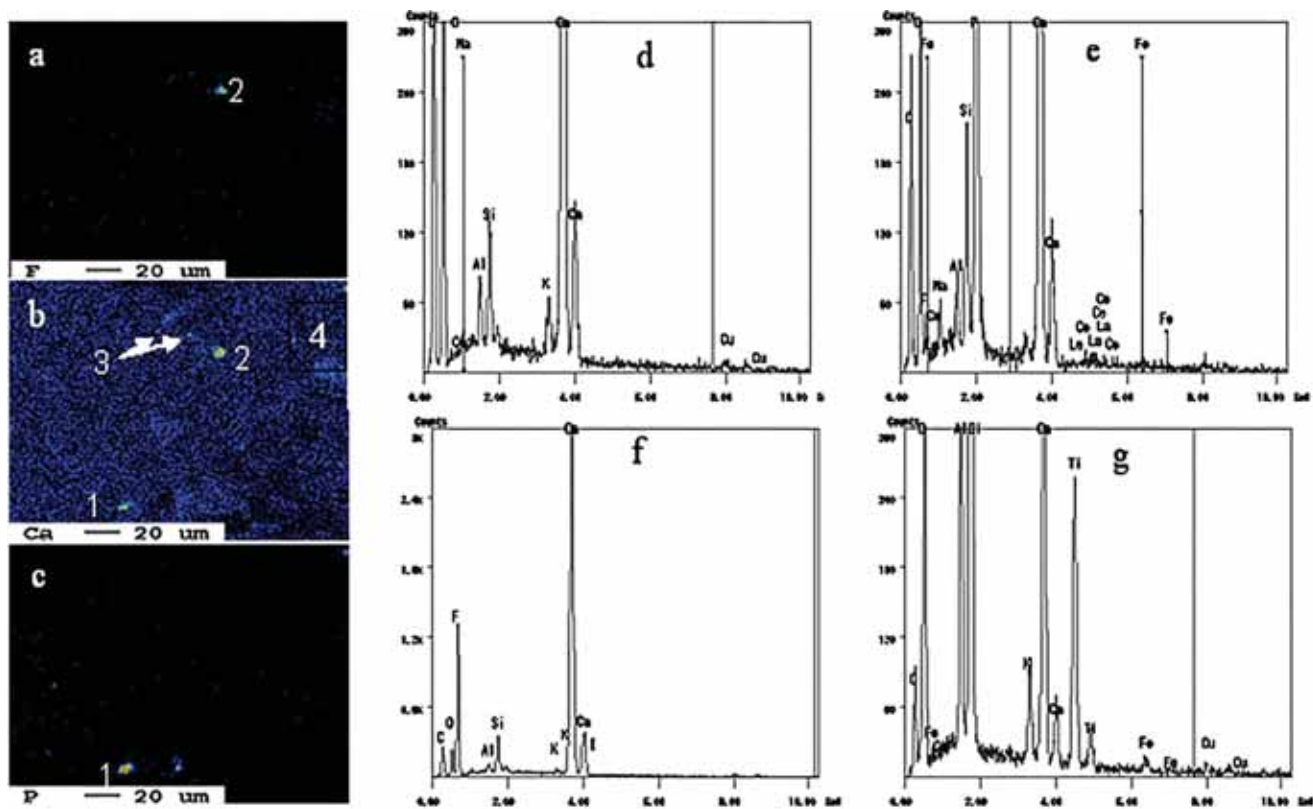


Fig.6. X-ray $F K_{\alpha}$ - (a), $Ca K_{\alpha}$ - (b), $P K_{\alpha}$ - (c) images ($120 \mu\text{m} \times 120 \mu\text{m}$) for CRM SG-4. X-ray spectra of grains containing calcium: d - calcite (b, grain 3), e - apatite (b,c, grain 1), f - fluorite (a,b, grain 2), g - titanite (b, grain 4).

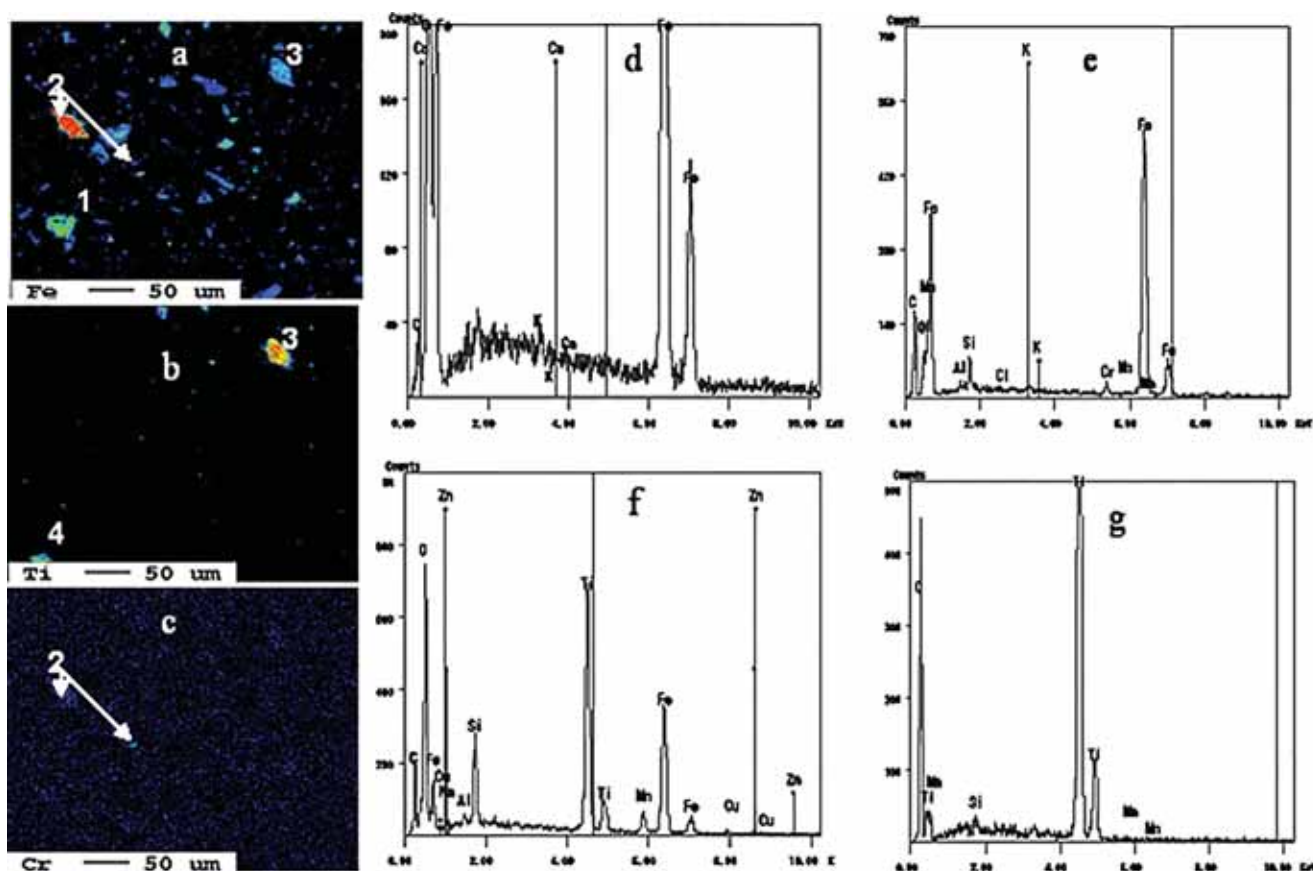


Fig.7. X-ray $Fe K_{\alpha}$ - (a), $Ti K_{\alpha}$ - (b), $Cr K_{\alpha}$ - (c) images ($400 \mu\text{m} \times 400 \mu\text{m}$) for CRM SG-4. X-ray spectra of grains containing iron and titanium: d - iron oxide (grain 1 on Fig.7 a), e - intermetallic iron (a,c, grains 2), f - titanomagnetite (a,b, grain 3), g - rutile (b, grain 4).

Table 4. The chemical composition of some discovered minerals.

CRM	Mineral	Size of grains, $\mu\text{m} \times \mu\text{m}$	Component, % m/m											Total		
			K_2O	SiO_2	Na_2O	FeO	CaO	MgO	Al_2O_3	MnO	TiO_2					
SG-4	orthoclase	20×32	16.9	63.8	0.5	–	–	–	–	–	–	18.7	–	–	–	99.9
	orthoclase	20×35	15.1	65.4	0.6	–	–	–	–	–	–	17.3	–	–	–	98.4
	microcline	26×30	8.3	67.5	3.0	0.6	–	–	–	–	–	18.7	–	–	–	98.1
	quartz	18×27	–	100.1	–	–	–	–	–	–	–	–	–	–	–	100.1
	amphibole	25×30	4.5	54.2	5.1	22.7	1.6	0.3	7.2	0.3	0.3	0.7	0.7	0.7	0.7	96.6
	amphibole	16×33	1.4	49.0	6.3	32.3	3.9	0.4	0.9	0.8	0.8	2.0	2.0	2.0	2.0	97.0
	ilmenite	4×10	–	0.9	–	43.9	–	–	–	1.4	1.4	46.9	46.9	46.9	46.9	93.1
SSn-1	mica	25×40	10.1	36.5	–	20.5	–	–	–	9.4	14.8	0.3	3.0	3.0	3.0	94.6
	mica	31×46	22.0	53.6	–	0.3	–	–	–	–	23.8	–	–	–	–	99.7
	pyroxene	18×34	–	50.4	2.1	12.7	20.6	9.3	2.9	0.4	0.6	0.6	0.6	0.6	0.6	99.0
	kalsilite	25×28	30.0	38.6	–	0.5	–	–	–	–	31.4	–	–	–	–	100.5
	goethite	6×14	0.6	1.4	–	89.4	–	–	–	–	0.4	–	–	–	–	91.8
	rutile	2×5	0.6	0.5	–	0.6	–	–	–	–	–	–	–	97.5	99.2	
	feldspathoid	12×18	22.1	53.1	–	0.3	–	–	–	–	25.1	–	–	–	–	100.6
	quartz	17×22	–	99.1	–	–	–	–	–	–	–	–	–	–	–	99.1
	orthoclase	22×31	17.2	64.9	–	–	–	–	–	–	17.9	–	–	–	–	100.0
	orthoclase	18×38	17.1	64.2	–	–	–	–	–	–	17.9	–	–	–	–	99.2
orthoclase	25×35	17.6	63.7	–	–	–	–	–	–	19.0	–	–	–	–	100.3	
SSv-1	orthoclase	28×43	16.6	63.4	0.9	–	–	–	–	–	18.9	–	–	–	–	99.8
	orthoclase	30×38	15.3	64.8	0.4	–	–	–	–	–	19.7	–	–	–	–	100.2
	pyroxene	24×36	0.5	51.4	3.2	14.2	17.8	6.9	4.3	0.5	0.2	0.2	0.2	0.2	0.2	99.0
	garnet	25×36	0.4	42.5	0.6	10.2	18.6	0.1	23.8	–	–	–	–	–	–	96.2
	amphibole	20×32	–	36.2	–	22.9	30.5	–	4.8	1.1	0.7	0.7	0.7	0.7	0.7	96.2
	amphibole	18×35	0.4	38.0	–	20.3	32.3	0.2	5.2	–	–	–	–	–	–	97.4
	titanite	8×12	0.2	33.0	–	2.2	27.3	–	3.0	–	–	–	–	–	–	97.6
	mica	28×45	9.8	35.8	–	21.7	–	9.8	13.7	0.3	2.5	2.5	2.5	2.5	2.5	93.6

Note: Dash denotes that this component was not found

Cerium, lanthanum, yttrium and calcium are parts of orthite (Fig.8 b-e), and phosphorus and calcium are parts of apatite (Fig.6 e).

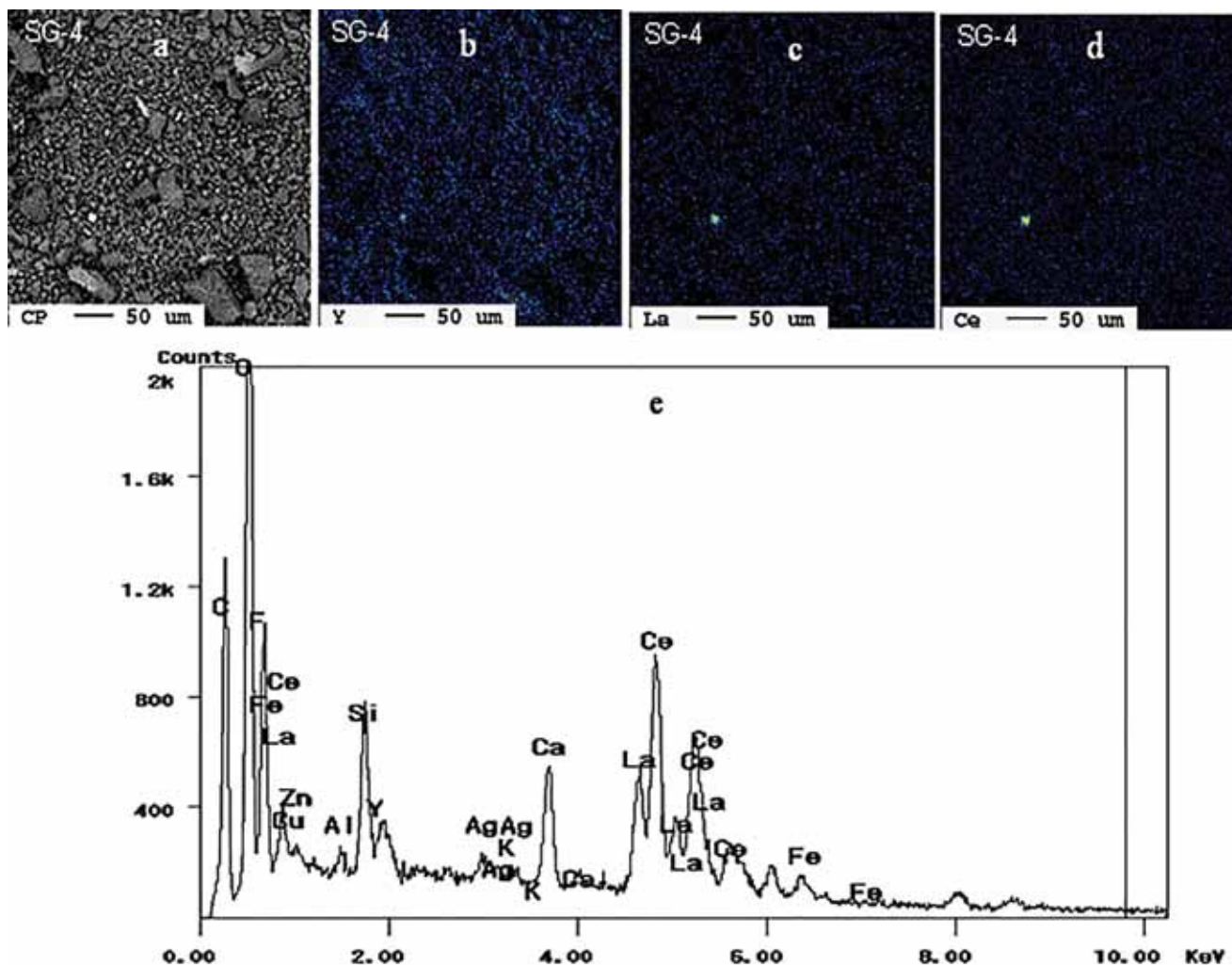


Fig.8. Back scattered electron (CP) and X-ray Y K_{α} - (b), La L_{α} - (c), Ce L_{α} - (c) images ($400 \mu\text{m} \times 400 \mu\text{m}$) for CRM SG-4. X-ray spectrum of grain containing yttrium, lanthanum and cerium (e).

Silicon, potassium, sodium, aluminium, magnesium are the main parts of different silicate minerals: orthoclase, microcline, quartz, amphibole, kalsilite, nepheline, pyroxene and mica (Table 4). The results of Table 4 were obtained by wavelength-dispersive spectrometers analyzing the CRMs prepared as polished briquetted thin sections. The area no smaller than 3 cm^2 has been analyzed for each CRM. The grains for element determinations were selected randomly.

The sizes of particles given in Table 4 confirm the conclusions obtained from distribution patterns indicating that the large fraction mainly contains silicate grains (see column "Size of grains"). Trace elements are concentrated in fine fraction and localized in accessory minerals or grains of micro size. The micron-size grains not found at the first stage of CRM

study were detected. In CRM SSv-1 this is titanite (Table 4), quartz (Fig.9 i), intermetallic iron (Fig.9 h) and high-Sr grain less than a micron (Fig.9 g); CRM SG-4 includes ilmenite (Table 4), fluorite (Fig.6 f), rutile (Fig.7 g) and intermetallic iron (Fig.7 e). In CRM SSn-1 there is nickel, tin, sphalerite, zircon, the compounds of tin with lead and copper with zinc (Fig.9 a-f), rutile (Table 4), quartz (Table 4), apatite and intermetallic iron as well.

Detection of metallic grains in rock reference materials is critical for RM preparation. To further use CRMs it is necessary to take into account that RM can be contaminated by the grains from metallic parts of grinders. However, natural intermetallic particles can be present in rocks as well. A more thorough study of RMs is required at the preliminary stage to exclude possible contamination.

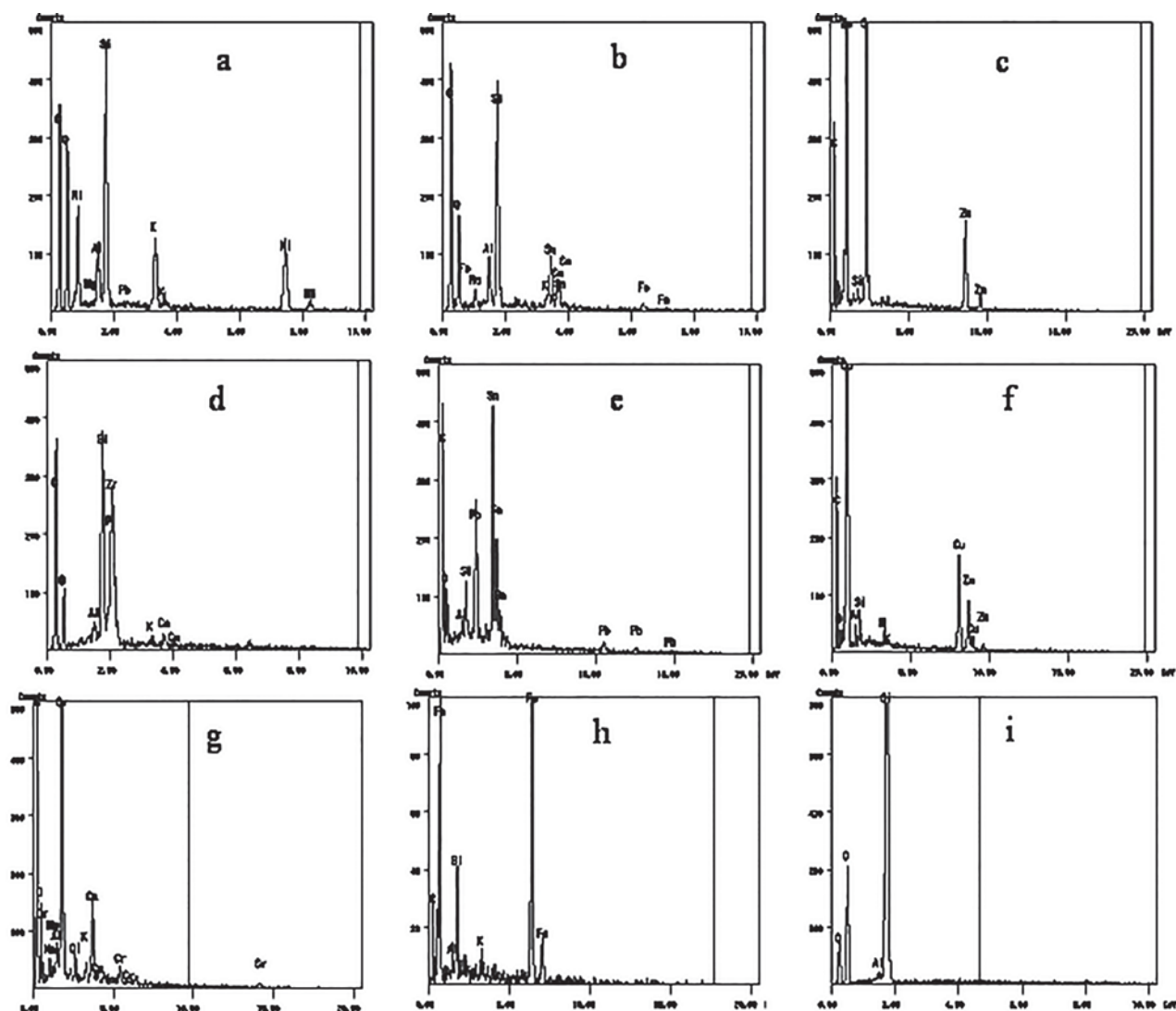


Fig.9. X-ray spectra of grains, containing high contents of some elements, from CRMs SSn-1 (a – nickel, b – tin, c – sphalerite, d – zircon, d – combination of tin and lead, e – combination of copper and zinc) and SSv-1 (f – strontium, g – iron, i – quartz).

Conclusions

1. A visual examination of the CRM surfaces studied by electronic microscope mode recognized similar surface appearances.

2. Most grains are irregularly shaped; their sizes vary from parts of microns to a sieve mesh or slightly larger. Spherical grains (not bigger than 10 μm) were also located.

3. Dry sieving is not capable to separate grains of the same size. All material fractions of CRMs contain differently-sized grains from dust-like of a few microns and smaller to the elongated ones exceeding in length a sieve mesh. Small grains stick to larger ones and cover them during sieving.

4. The finest fraction of the CRMs contains most abundant heavy grains (with higher mean atomic numbers). Some accessory minerals (e.g. magnetite, titan magnetite, orthite, apatite, rutile, titanite)

containing heavy elements are basically concentrated in the fine fraction of CRMs (<40 μm).

5. The CRM grains basically consist of silicate minerals, such as potassium feldspar, microcline, mica, etc. The major elements, e.g. silicon, aluminium, potassium, sodium, titanium, iron, magnesium involved in silicate minerals in CRMs are homogeneously distributed even over a small area of 200 to 400 μm .

6. The trace elements constituting accessory minerals are spread irregularly in small amounts of CRMs, because the concentrating minerals are distributed inhomogeneously. However, a regular occurrence of the elements in accessory minerals with a certain frequency suggests its homogenous distribution in bigger amount of CRM subsamples weighing over 2 mg.

7. The EPMA studies of CRMs confirmed the occurrence of all minerals found at the CRM certifications in rock thin sections, as well as some

accessory minerals not discovered before.

8. Iron is involved in RMs both as part of minerals and intermetallic particles. This fact should be taken into account for further CRM use, selection of proper material digestion procedure.

9. Copper, strontium, nickel and tin were found as separate particles, their size reaching a micron or some microns. Particles sized 1 μm represent the compounds of copper with zinc and tin with lead.

The information on the minerals discovered by electron probe X-ray microanalysis of CRMs SG-4 and SSn-1, certified in 2012, was included into RM certificates, section "RM description". For further use of CRM SSv-1 one should keep in mind presence of minerals not recorded in the RM certificate, e.g. ilmenite, quartz, particles with high strontium and nickel, as well as particles of intermetallic iron.

When certifying RMs, it is recommended to employ EPMA to determine their mineral composition and to make qualitative estimate of their homogeneity applying the principle of "statistic significance" described above. The up-to-date methods applied for a comprehensive analysis of the structure and RM composition are capable to provide additional information on the properties of certified reference materials which results in a more effective use of CRMs in measurement procedures.

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