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14. KONGRES GEOLOGA SRBIJE I CRNE GORE

sa međunarodnim učešćem

14th CONGRESS OF GEOLOGISTS OF SERBIA AND MONTENEGRO

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NONMETALLIC SKARN MINERALS OF THE SASA ORE FIELD

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Abstract. The paper presents the mineralogical characteristics of the non-metallic skarn minerals of the Sasa ore field. The analyses were carried out in the Institute for Crystallography in Zurich and the laboratories of the Faculty of Mining and Geology in Stip.

Key words: non-metallic, skarn, minerals, ilvaite, rhodonite, bustamite, johansenite, andradite, grossular

INTRODUCTION

Several occurrences of lead-zinc ore can be found in the vicinity of the village of Sasa. They are associated with the intrusion of granodiorite-quartzdiorite magma. The magma exerted contact metasomatic alterations to adjacent marbles and cipolines that resulted in the occurrence of contact-metasomatic, non-metallic fairly rare minerals. Based on their optical properties Baric (1961) classified them as ferrojohansenite and bustamite. The investigations of the present author determined ilvaite, rhodonite, bustamite, johansenite-ferrojohansenite, andradite, actinolite-ferroactinolite and epidote.

RESULTS

Ilvaite

The best pronounced crystals have been determined in horizon IVa, K- 1440 as rod like crystals 15 x 2 cm in size. They can be seen in horizon XVIa and K-1152, but most intensely in horizon 950, K-962.
It has indigo dark colour. It occurs in thick masses where well pronounced crystals can be seen with naked eye. They are surrounded by smaller crystals and radial aggregates. This is due to the slow crystal growth at the beginning that made possible the formation of coarse-grained crystals. Later, due to the change of the physico-chemical conditions, fine-grained crystals and radial aggregates were formed. Habit is short columnar. Planes are striated along length. The planes present are as follows: (110), (120), (010), (111), whereas (101) are less pronounced.
In thin section it is almost opaque. It exhibits clear pleochroism, dark brown to black (Z), brown (Y), yellow brown (X) (fig.1).
Chemical analyses shown in Table 1 indicate that ilvaite of Sasa contains 4.67 to 7.99% MnO.
The results of X-ray diffraction examinations correlated with literature data given by Krause (1960) yielded good match.

Rhodonite

Rhodonite is light pinkish . Its crystals are grain like and form compact masses. They possess porcelain lust. Interference colours are of first order, light grey to light yellow. Pleochroism is yellow reddish, pinkish reddish and light yellow reddish (figs. 2 and 3).
np: 1.710 to 1.720, nm: 1.715 to 1.722, ng: 1.72 to 1.732, 2V: 70 to 76°, Density 3.52 to 3.60, ng-np 0.011 to 0.012.
The rhodonite possesses perfect cleavage on (100) and (001). The angle between the two cleavages is approximately 90. Polysynthetic twins occur on (010).
The chemical composition of rhodonite is shown in Table 2.
The values obtained by X-ray diffraction examinations were correlated with those of JCPDS 13-138 and good match was found.

Bustamite

Bustamite can be found in Svinja Reka horizon IIb block 1 - south, Svinja Reka - south XII B/1 up to 2 - 3 cm rarely 5 cm in size. It is light pinkish to yellow pinkish in colour. It possesses glass brightness . In thin sections it shows highly

interference colours, hardly noticeable pleochroism, from light green grey to colourless (fig. 4 and 5). The values of the index of diffraction increase with the increase of iron contents and manganese, whereas double diffraction and the angles between optical axes remain almost constant.
np: 1.678 to 1.682, nm: 1.691 to 1.696, ng: 1.693 to 1.698, 2V: 39°, density 3.4.
There are two cleavages, one perfect on (001) and the other less pronounced on (100). The other two cleavages are not changed in thin sections. Twins can sometimes be found.
Table 2 gives the chemical composition of bustamite. The results of X-ray diffraction examinations are in good agreement with the data of JCPDS 13-175.

Johansenite

Johansentite occurs from horizon V-1700 to horizon 1126. Its crystals are fairly large and elongated along 'c' axis, and flattened along axis 'b'. They are found as columnar and radial aggregates, some tens of centimetres long. The elongated prismatic crystals are intergrown along plane (100) in common aggregates. It is olive green to green dark in colour. It can be noticed that in a crystal along the 'c' crystallographic axis the colour changes from quite bright green to dark green . This is an indicator of the change of the host medium during crystallisation.
In thin sections johansenite shows interference colours of first order. Pleochroism is bright green yellow to bright yellow (fig. 6). Well pronounced cleavage can be noticed along (110).
np/ 1.715 - 1.717, nm: 1.728 - 1.729, ng: 1.743 - 1.745, 2V: 67.68.3.
The chemical composition is shown in table 3. According to Hutton C. O. (1956), that the most common component is $MnSiO_3$, then this mineral can be called ferrojohansenite.
The results obtained by X-ray diffraction examinations are in good agreement with the data of Hutton C. O. (1956).

Actinolite

The most frequent occurrence of actinolite has been determined in horizon 1126 in the first left diameter and in the drillholes.
It has grey green to grey ashy green colour . The crystals are elongated along 'c' axis. Hairy and radial aggregates can often be found. Its lust is silky to pearly. In thin sections it shows intensive interference colour. Pleochroism is np - yellow green, nm- green, ng- light green (fig. 7). Radial structure can be seen easily.
The chemical composition is shown in table 4.
Comparison between data obtained in X-ray diffraction examinations and those of literature yielded good agreement. D values helped calculate the dimensions of electromagnetic cell. The results obtained are as follows:
Dimensions of elementary cell: a=9,845, b= 18.1468, c= 5.2517, β= 104.336°.

Garnets

Two kinds of garnets have been determined by chemical and X-ray investigations in the Sasa ore filed - andradite and grossular.

Andradite

Andradite occurs in monomineral aggregates in horizon VIII/s, III/3, XIIb/2, XIIb/3. It is dark red to waxy dark yellow . Its lust is vitreous. Microscopic analyses indicate idiomorphic cross cuts. Its crystals are unisotropic. Interference colours are grey to white grey. Pleochroism is bright yellow greenish (fig. 8). Zonar structure is clear. It possesses high relief.
Table 5 shows the chemical composition of andradite of Sasa. The values obtained by X-ray diffraction examinations were compared with card JCPDS 10-288.

Grossular

Grossular occurs in horizons VII/22, VII/22, VII/23, VIII/s, III/3, III/s, IVb/2 etc. Grossular crystals are smaller than those of andradite. They are honey yellowish in colour . They are vitreous and transparent. They seldom occur as well shaped crystals. They always occur together with bustamite. Table 5 shows the chemical composition of grossular of Sasa. The results obtained by X-ray difraction examinations were compared with card JCPDS3-801 and indicated good agreement.

Epidote

Two kinds of epidote have been distinguished. Most probably they were formed in two prolonged intervals. The first, probably formed in high temperature conditions, in temperature interval characteristic of the development of first skarn minerals. This assumption is supported by its association with rhodonite, garnets and johansenite.
The second is much more widespread and occasionally forms real epidosites.
The chemical composition of epidote is given in Table 6. It is yellow green. Its lust is oily. It occurs in xenomorphic grains. Interference colours are yellow greenish and pleochroism is bright yellow to yellow greenish.

Table 1. Chemical composition of ilvaite of Kozja Reka 950/26+10/ Sasa.

	1	2	3	4	5
SiO_2	29.85	29.75	30.24	30.50	30.06
TiO_2	-	-	-	-	-
Al_2O_3	-	-	-	-	-
Fe_2O_3	17.61	16.96	17.85	18.26	18.56
FeO	31.77	30.59	32.21	32.95	33.48
MnO	7.76	7.99	5.40	5.19	4.67
MgO	0.16	0.16	0.22	0.21	0.23
CaO	13.65	14.20	13.66	13.82	13.61
total	100.08	99.65	99.58	100.93	100.61
Si	2.04	2.06	2.08	2.07	2.05
Ti	-	-	-	-	-
Al	-	-	-	-	-
Fe^3	1.57	1.49	1.61	1.64	1.69
Fe^2	1.09	1.11	1.10	1.08	1.09
Mn	0.45	0.47	0.31	0.30	0.27
Mg	0.02	0.02	0.02	0.02	0.02
Ca	1.00	1.05	1.01	1.00	0.99

Table 2. Chemical composition of rhodonite and bustamite

	Rodonit				Bustamit		
	1	2	3	4	1	2	3
SiO_2	47.32	48.40	48.65	47.47	49.15	48.63	48.36
TiO_2	-	-	-	-	-	-	-
Al_2O_3	-	-	-	-	-	-	-
FeO	3.71	1.60	1.83	3.86	1.46	2.20	1.80
MnO	38.29	39.27	39.46	40.31	27.82	28.35	28.15
MgO	0.69	1.17	0.08	0.32	0.23	0.22	0.28
CaO	9.06	10.22	10.85	8.93	20.98	20.88	20.82
total	99.07	100.66	100.87	100.89	99.64	100.28	99.41
Si	6.04	6.08	6.08	6.00	6.06	6.00	6.01
Al	-	-	-	-	-	-	-
Ti	-	-	-	-	-	-	-
Fe	0.40	0.17	0.19	0.41	0.15	0.23	0.19
Mn	4.14	4.07	4.18	4.32	2.91	2.96	2.96
Mg	0.13	0.22	0.01	0.06	0.04	0.04	0.05
Ca	1.24	1.38	1.45	1.21	2.77	2.76	2.77

1, 2, 3, 4 rhodonite, Svinja Reka A east Sasa; 1, 2, 3 bustamite, Svinja Reka - south XII B/1 Sasa

Table 3. Chemical composition of johansenite

	1	2	3	4	5	6
SiO2	48.48	48.93	48.84	48.53	48.92	49.83
TiO2	0.34	-	-	0.04	-	-
Al2O3	-	-	-	-	-	-
FeO	9.52	10.10	9.33	10.81	11.38	10.63
MnO	19.01	18.66	18.84	17.40	16.81	16.69
MgO	0.25	0.21	0.49	0.48	0.49	0.40
CaO	22.83	22.43	22.63	22.66	22.32	22.12
total	100.52	100.33	100.13	99.92	99.92	99.67
6 (O)						
Si	1.99	2.00	2.00	1.99	2.00	2.049
Ti	0.01	-	-	0.01	-	-
T. pos	2.00	2.01	2.00	2.00	2.01	2.05
Fe^2	0.32	0.35	0.32	0.36	0.40	0.37
Mn	0.66	0.65	0.65	0.61	0.58	0.58
Mg	0.15	0.13	0.03	0.03	0.03	0.03
Ca	1.00	0.99	0.99	0.99	0.98	0.98
Na	-	-	-	-	-	-
M_1M_2	1.98	1.99	1.96	1.96	1.89	1.93

1, 2, 3, 4, 5, 6 johansenite Svinja Reka XII V/A - O south, Sasa

Table 4. Chemical composition of actinolite

	1	2	3	4	5	6
SiO2	49.13	48.71	48.70	48.85	48.81	49.48
TiO2	0.07	0.11	0.05	0.10	0.08	0.10
Al2O3	1.95	1.96	2.09	2.15	2.14	1.80
FeO	25.23	25.61	26.01	26.36	25.96	26.05
MnO	1.79	1.48	2.23	1.84	1.95	2.05
MgO	7.09	6.93	6.28	6.64	6.70	6.51
CaO	11.60	11.48	10.77	11.62	11.23	11.42
Na2O	1.09	0.93	1.23	0.64	0.70	0.51
K2O	0.12	0.08	0.08	0.11	0.08	0.11
total	98.07	97.29	97.44	98.01	97.65	98.03
Si	7.61	7.64	7.68	7.59	7.61	7.69
Al	0.36	0.36	0.32	0.40	0.37	0.31
Ti	0.01	0.01	0.01	0.01	0.01	0.01
Sum T	7.97	7.93	8.00	7.98	8.01	8.00
Fe2	3.28	3.40	3.40	3.42	3.38	3.38
Mn	0.10	0.00	0.12	0.05	0.06	0.10
Mg	1.64	1.60	1.47	1.54	1.56	1.51
Sum C	5.00	5.00	5.00	5.00	5.00	5.00
Ca	1.86	1.75	1.81	1.80	1.80	1.83
Mn	0.14	0.20	0.18	0.20	0.20	0.17
Sum B	2.00	2.00	2.00.	2.00	2.00	2.00
Ca	0.06	0.16	0.00	0.13	0.07	0.06
Na	0.33	0.28	0.36	0.19	0.21	0.15
K	0.02	0.02	0.02	0.02	0.02	0.02
Sum A	0.41	0.46	0.38	0.34	0.30	0.24

1, 2, 3, 4, 5, 6. Svinja Reka east 19^{th} 1L Sasa

Table 5. Chemical composition of andradite and grossular

	andradit					grosular		
	1	**2**	**3**	**4**	**5**	**1**	**2**	**3**
SiO_2	35.83	35.75	35.74	35.98	34.91	39.31	38.53	37.11
TiO_2	–	–	–	–	–	0.28	–	0.36
Al_2O_3	–	–	–	–	0.69	22.12	20.72	22.52
Fe_2O_3	30.60	30.60	29.86	30.34	30.40	0.54	3.11	3.23
FeO						0.42	0.42	0.42
MnO	2.95	2.96	3.38	2.81	–	0.57	0.63	0.54
MgO	0.14	0.15	0.26	–	0.58	–	0.210	–
CaO	30.79	30.56	30.72	30.84	33.20	37.16	35.52	35.31
Total	100.31	100.25	100.18	100.18	99.97	100.42	99.14	99.50
Si	3.03	3.03	3.03	3.05	2.95	2.95	2.98	2.83
Al	–	–	–	–	0.05	0.05	0.02	0.17
Tsite	3.03	3.03	3.03	3.05	3.00	3.00	3.00	3.00
Al^{vi}						1.91	1.87	1.85
Ti	–	–	–	–	–	0.02	–	0.02
Fe^{3+}	1.95	1.95	1.90	1.94	1.94	0.05	0.21	0.21
Osite	1.95	1.95	1.90	1.94	1.94	1.98	2.07	2.08
Mn	0.21	0.21	0.24	0.20	–	0.04	0.04	0.04
Mg	0.02	0.02	0.03	–	0.07	–	0.02	–
Ca	2.79	2.78	2.79	2.81	3.01	2.99	2.86	2.88
Asite	3.02	3.01	3.06	3.01	3.01	3.02	293	2.92
O	12	12	12	12	12	12	12	12

1, 2, 3, 4, 5, 6 andradite Svinja Reka XII B/3 , Sasa
1, 2, 3, grossular Svinja Reka XII B/1 , Sasa

Table 6. Chemical composition of epidote

	1	2	3	4	5	6
SiO_2	37.83	37.77	38.06	38.10	37.76	37.85
TiO_2	0.37	–	0.67	0.33	0.47	0.18
Al_2O_3	22.33	22.28	22.66	23.63	23.58	22.56
FeO	13.15	13.66	13.87	11.25	11.05	12.01
MnO	1.32	1.34	1.36	0.91	0.99	–
MgO	–	–	–	0.34	0.44	0.48
CaO	23.10	23.12	22.17	23.61	23.21	23.57
Total	98.10	98.17	98.79	98.17	98.50	98.65
Si	3.23	3.24	3.22	3.20	3.21	3.24
Al	2.24	2.19	2.26	2.34	2.36	2.28
Ti	0.03	–	0.04	0.02	0.03	0.01
Al						
Fe^2	0.94	1.00	0.98	0.79	0.72	0.86
Mn	0.10	0.10	0.10	0.06	0.07	–
Mg	–	–	–	0.04	0.06	0.06
Ca	2.11	2.16	2.01	2.13	2.12	2.16

1, 2, 3, epidote Svinja Reka IV A east, Sasa
4, 5, 6, epidote Svinja Reka, east 19 IL

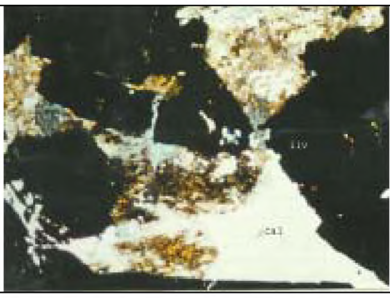

Fig. 1 Microphotograph of ilvaite black and calcite white (magn 100x)

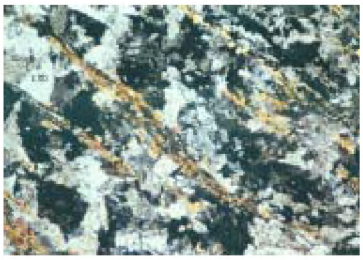

Fig.2. Microphotograph of grey blue grains of rhodonite with epidote stripes, magn. 50x N+

Fig. 3. Stripe of coarse-grained rhodonite in fine-grained rhodonite mass. Magnification 50x, N+

Fig. 4 . Microphotograph of radial Bustamite, with visible manganese oxides in the centre. Magnification 50x, N+

Fig 5 . Microphotograph of radial bustamite, magnification 50x, NII

Fig.6. Microphotograph of johansenite with clear twins, magn. 50x, N+

Fif.7. Microphotograph of actinolite magn. 50x, N+

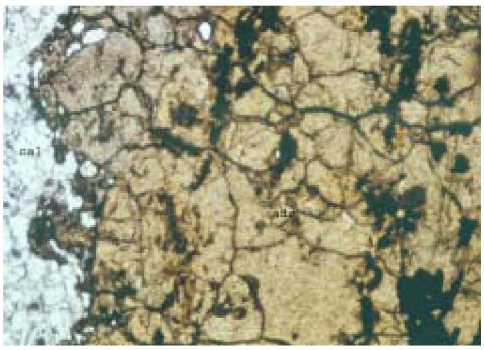

Fig.8. Microphotograph of andradite, magn. 50x IIN.

DISCUSSION AND CONCLUSION

From what has been said above the following conclusions can be made.
The investigations carried out determined some minerals such as ilvaite, rhodonite, bustamine, johansenite, actinolite, andradite, grossular and epidote. They all have some common features. They are all silicates with regard to their structure. Most often they are inosilicates (rhodonite, bustamite, johansenite, actinolite) seldom sorosilicates (ilvaite, epidote), whereas garnets are nesosilicates. Almost all are rich in Mn^{2+}.
This indicates that the solutes which performed contact metasomatic alteration were probably rich in manganese. However, it is very likely that the host rocks (quartzgraphyte schists and cipolines) were primarily enriched in this component. Examinations (Bowen et al., 1956) determined that hedenbergite was stable at temperatures lower than 965°C.
As between ferrojohansenite and hedenbergite there are many minerals in which either Fe or Mg or Mn components prevail, we can assume that stability temperature ranges to some 965°. At temperatures higher than 830°C johanenite transforms to its triclinic polyform modification - bustamite.
On the other hand however, it easily oxidises, hydrates and carbonates and commonly alters to rhodonite. The products of these alterations can be found as irregular rhodonite portions in johansenite. In that case columnar rhodonite crystals retain their earlier johansenite form, as is, partly, the case with the rhodonite of Sasa.
It should be mentioned that the medium in which rhodonite forms must be rich in manganese (Schaller, 1938).
Liebay et. al., (1959) determined that rhodonite has two polymorph modifications:
- Low temperature modification which contains some 20% $CaSiO_3$,
- High temperature modification in which the percentages of MnSiO3 and CaSiO3 are not limited.

With the Sasa rhodonite the $CaSiO_3$ content amounts to 20%. This means that it is low temperature rhodonite formed with chemical decomposition of existing johansenite. This allows for an easy reconstruction of the physico-chemical conditions in which recrystallization took place in these skarn minerals.
Johansenite formed first when the MnO content in the medium in which it formed was not very high. At 830°C johansenite transforms into triclinic modification - bustamite. Decrease in temperature and the change of the chemical composition of the medium results in the formation of rhodonite. The change of the chemical composition of the medium can be seen from the change of johansenite colour from light green to green.
At 800° C, parallel to the formation of bustamite, andradite and grossular form as well. Andradite includes excess MnO in its lattice that is residual after bustamine formation, whereas the whole amount of Al_2O_3 incorporates into grossular. After rhodonite formation the minerals still possess FeO and a less MnO.
According to experimental studies by Beran and Bittner (1974) in a medium rich in FeO, and fairly poor in MnO, but rich also in volatile components ilvaite diochially includes some 9% MnO in its lattice.
The presence of large amounts of easily volatile components and water in host medium lowers it viscosity. This allows for the formation of well formed crystals. The decrease in the amount of volatile components increases the viscosity in the medium that subsequently leads to the formation of fine-grained ilvaite aggregates.
Epidote forms at lowest temperatures as the final mineral in this sequence of contact metasomatic minerals.

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