GEOME 2 Manuscript received: May 20, 2012 Accepted: October 15, 2012

Original scientific paper

## **METAMORPHISM OF THE SKARN ROCKS FROM THE SASA ORE FIELD**

Tena Šijakova-Ivanova, Blažo Boev, Vojo Mirčovski

Faculty of Natural and Technical Sciences, "Goce Delčev" University, P.O.Box 201, MK 2000 Štip, Republic of Macedonia tena.ivanova@ugd.edu.mk

A b s t r a c t: The aim of this paper is to define the metamorphism of the skarn rocks from the Sasa ore filed. In these rocks ilvaite, rhodonite, bustamite, johansenite-ferrojohansenite, andradite, actinolite-ferroactinolite and epidote were determined. On the base of the presence minerals associations in studied rocks were determinated three facies: albite-epidote-hornfels facies; hornblende-hornfels facies; K-feldspate-cordierite-hornfels facies. The rocks studied are formed in temperature condition T 400–800°C and preassure P 1.5–2 kbar.

Key words: scarn; contact metamorphism; johansenite; rhodonite; ilvaite

### INTRODUCTION

The area comprising the Sasa ore field is made up of schistose mica granitoporphyrite, qurtz diorite-plagiogranite, quartz latites, graphite and phylliteschists, cipolines and scarns.

The scarnsoccure in a series of quartz graphite schists and cipolines.

The minerals formed during skarns stage include johansenite, augite, diopside, hedenbergite, actinolite, bustamite, rhodonite, garnets (grosular and andradite) and epidote. 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.

### **RESULTS AND DISCUSSION**

In studied rocks the following minerals were determinated: johansenite, augite, diopside, hedenbergite, actinolite, bustamite, rhodonite, garnets (grosular and andradite) and epidote.

The best pronounced crystals of ilvaite have been determined in horizon IVa, K-1440 as rod like crystals  $15 \times 2$  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 coarsegrained 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. Chemical analyses indicate that ilvaite of Sasa contains 4.67 to 7.99% MnO. (Table 1).

Rhodonite is light pinkish. Its crystals are grain like and form compact masses. They possess porcelain lust. The values obtained by X-ray diffraction examinations were correlated with those of JCPDS 13-138 and good match was found. 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. 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. Twins can sometimes be found. The results of X-ray diffraction examinations are in good agreement with the data of JCPDS 13-175.

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. 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. Twins can sometimes be found. Table 1 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 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 crystallization. In thin sections johansenite shows interference colours of the first order. Pleochroism is bright green yellow to bright yellow. According to Hutton C. O. (1956), that the most common component is MnSiO<sub>3</sub>, then this mineral can be called ferrojohansenite. Chemical composition is shown on Table 2. The results obtained by X-ray diffraction examinations are in good agreement with the data of Hutton C. O. (1956).

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. Chemical composition of actinolite is shown on Table 2. Comparison between data obtained in Xray 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,  $\beta = 104.336^{\circ}$ . Two kinds of garnets (andradite and grossular) have been determined by chemical and X-ray investigations.

Andradite occurs in monomineral aggregates in horizons 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. Zonar structure is clear. It possesses high relief. The values obtained by X-ray diffraction examinations were compared with card JCPDS 10-288. The chemical composition of andradite and grossular is given in Table 3.

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. Always occur together with bustamite. The results obtained by X-ray diffraction examinations were compared with card JCPDS3-801 and indicated good agreement.

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 the 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. 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. 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. On the Table 3 is shown the chemical composition of epidote.

On the base of the presence minerals association in studied rock swere determinated tree facies:

- albite-epidote-hornfels facies,
- hornblende-hornfelsfacies,
- K-feldspate-cordierite-hornfels facies.

Albite-epidote-hornfels facies started on 400 °C and 1–2 kbar pressure and lasts unitl 500°– 520°. Characteristic minerals which appear in these facies are: actinolite, epidote and chlorite. With increase on the temperature albite-epidote-hornfels facies. The starts of these facies are in T 520±10°C P 500 bar; 535 ± 15°C P 1000 bar; 540 ± 20°CP 2000 bar.

	Ilvaite		Rhodonite		Bustamite	
SiO <sub>2</sub>	30.06	29.75	47.32	48.40	48.63	48.36
TiO <sub>2</sub>	-	_	_	_	_	-
$Al_2O_3$	_	_	_	—	_	-
Fe <sub>2</sub> O <sub>3</sub>	18.56	16.96				
FeO	33.48	30.59	3.71	1.60	2.20	1.80
MnO	4.67	7.99	38.29	39.27	28.35	28.15
MgO	0.23	0.16	0.69	1.17	0.22	0.28
CaO	13.61	14.20	9.06	10.22	20.88	20.82
Total	100.61	99.65	99.07	100.66	100.28	99.41
Si	2.05	2.06	6.04	6.08	6.00	6.01
Ti	_	_	_	_	_	-
Al	_	_	_	_	_	-
Fe <sup>3</sup>	1.69	1.49	_	_	_	-
Fe <sup>2</sup>	1.09	1.11	0.40	0.17	0.23	0.19
Mn	0.27	0.47	4.14	4.07	2.96	2.96
Mg	0.02	0.02	0.13	0.22	0.04	0.05
Ca	0.99	1.05	1.24	1.38	2.76	2.77

## Table 1

Chemical composition of ilvaite, rhodonite and bustamite

# Table 2

Chemical composition of johansenite and actinolite

Johansenite			Actinolite						
SiO <sub>2</sub>	48.92	49.83	SiO <sub>2</sub>	49.13	48.81	48.71	48.70	48.85	
TiO <sub>2</sub>	-	-	TiO <sub>2</sub>	0.07	0.08	0.11	0.05	0.10	
$Al_2O_3$	-	_	$Al_2O_3$	1.95	2.14	1.96	2.09	2.15	
FeO	11.38	10.63	FeO	25.23	25.96	25.61	26.01	26.36	
MnO	16.81	16.69	MnO	1.79	1.95	1.48	2.23	1.84	
MgO	0.49	0.40	MgO	7.09	6.70	6.93	6.28	6.64	
CaO	22.32	22.12	CaO	11.60	11.23	11.48	10.77	11.62	
			Na <sub>2</sub> O	1.09	0.70	0.93	1.23	0.64	
			K <sub>2</sub> O	0.12	0.08	0.08	0.08	0.11	
Total	99.92	99.67	Total	98.07	97.65	97.29	97.44	98.01	
	6(O)		Si	7.61	7.61	7.64	7.68	7.59	
Si	2.00	2.049	Al	0.36	0.37	0.36	0.32	0.40	
Ti	-	-	Ti	0.01	0.01	0.01	0.01	0.01	
T. pos	2.01	2.05	Sum T	7.97	8.01	7.93	8.00	7.98	
Fe <sup>2</sup>	0.40	0.37	Fe <sub>2</sub>	3.28	3.38	3.40	3.40	3.42	
Mn	0.58	0.58	Mn	0.10	0.06	0.00	0.12	0.05	
Mg	0.03	0.03	Mg	1.64	1.56	1.60	1.47	1.54	
Ca	0.98	0.98	Sum C	5.00	5.00	5.00	5.00	5.00	
Na	-	-	Са	1.86	1.80	1.75	1.81	1.80	
$M_1M_2$	1.89	1.93	Mn	0.14	0.20	0.20	0.18	0.20	
			Sum B	2.00	2.00	2.00	2.00.	2.00	
			Ca	0.06	0.07	0.16	0.00	0.13	
			Na	0.33	0.21	0.28	0.36	0.19	
			K	0.02	0.02	0.02	0.02	0.02	
			Sum A	0.41	0.30	0.46	0.38	0.34	

ruore J	Т	a	b	1	e	3
---------	---	---	---	---	---	---

Andradite Grossular Epidote SiO<sub>2</sub> 35.98 34.91 38.53 37.11 SiO<sub>2</sub> 38.06 37.85 TiO<sub>2</sub> \_ 0.36 TiO<sub>2</sub> 0.67 0.18 0.69 20.72 22.52 22.66 22.56  $Al_2O_3$ Al<sub>2</sub>O<sub>3</sub> \_ Fe<sub>2</sub>O<sub>3</sub> 30.34 30.40 3.11 3.23 FeO 0.42 0.42 FeO 13.87 12.01 MnO 0.54 2.81 \_ 0.63 MnO 1.36 \_ MgO 0.58 0.210 MgO 0.48 \_ \_ \_ CaO 30.84 33.20 35.52 35.31 CaO 22.17 23.57 Total 100.18 99.97 99.14 99.50 Total 98.79 98.65 Si 3.05 2.95 2.98 2.83 Si 3.22 3.24 Al 0.05 0.02 0.17 Al 2.26 2.28 \_ Tsite 3.05 3.00 3.00 3.00 Al<sup>vi</sup> 1.85 1.87 0.02 Ti \_ Ti 0.04 0.01 Fe<sup>3+</sup> 1.94 1.94 0.21 0.21 Fe<sup>2</sup> 0.98 0.86 2.07 Sum O 1.94 1.94 2.08 0.04 0.04 0.20 0.10 Mn \_ Mn 0.07 0.02 0.06 Mg Mg \_ \_ 2.01 Ca 2.81 3.01 2.86 2.88 Ca 2.16 Sum A 3.01 3.01 293 2.92 12 12 12 0 12

Chemical composed of andradite, grossular and epidote

Diseappearance of chlorite, epidote and pyrophyllite is characteristic for these facies, while hornblende, anorthite, grossular-andradite, cordierite, and antophyllite appear.The characteristic minerals which suggest of these facies are grossular, andradite and actinolite.

The high temperature facies which can be determinated in these rocks is K-feldspate-cordieritehornfels facies. This facies started on  $580\pm20^{\circ}$ C *P* 500 bar;  $600\pm20^{\circ}$ C *P* 1000 bar;  $630\pm20^{\circ}$ C *P* 2000 bar, andlasts more than 800°. According (Winchler 1969) diopside, hypersthene, cordierite, grossular, biotite, anorthite, K-feldspate and other minerals are characteristic for this facies. In our case appears johansenite, bustamite, rhodonite, ilvaite, Kfeldspate, plagioclase and grossular. For assessment the temperature on which are formed scarn minerals from these deposite we will be using with literature data for stability of some minerals present in these rocks.

According Deer, Howie and Zussman (1982) anhydrous grossular in the system  $3CaO-Al_2O_3$ - $6H_2O$  is stable on  $500^{\circ}C$ , while with  $H_2O$  on  $400^{\circ}C$ . This temperature of  $500^{\circ}C$  matches with the start on the horn blende horn felsfacies wich is determinated in these rocks. Lowest temperature minerals is ilvaite who is stable on  $680^{\circ}C$ , according the experimental date of Beran, A. and Bittner, H. (1974). This temperature is approximate with the temperature of starts on the K-feldspate-cordierite hornfels facies. The highest temperature minerals in studied rocks is johansenite. 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, so we can assume that stability temperature ranges to some 965°. According Bowen et al. 1933 these minerals are stable in temperature interval 830° - 965°C. At temperatures higher than 830°C johansenite transforms to its triclinic polyform modification - bustamite. On the other hand, it easily oxidizes, 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).

Liebau et al. (1959) determined that rhodonite has two polymorph modifications:

- low temperature modification which contains some 20% CaSiO<sub>3</sub>,

 high temperature modification in which the percentages of MnSiO<sub>3</sub> and CaSiO<sub>3</sub> 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. After summarizing all the obtained results we can say that the skarn minerals from Sasa ore field were formed in the temperature interval up 400°C so to over 800°C.

On the base on present of actinolite and its chemical composition was certain pressure on which is formed the mineral association. On the contact metamorphism no major change on the pressure with the change on temperature.

Content of Na in  $M_4$  place in lattice of Ca amphiboles (Brown, 1977) is used as a barometer for low and medium temperature metamorphic rocks. For determination of P in our cause we can take diagram according Brown (1977) of contact metamorphic rocks from Sierabatolite. The date of our investigation were plot on these diagram (Fig 1). From the diagram can be seen that the points are ploted under the curve of 2 kbar or there are near it.



Fig 1 Diagram for determination of P (F. H. Brown, 1977)

## CONCLUSION

The facts presented above led us to conclude that on the base of the presence minerals association in studied rocks were determinated three facies:

- albite-epidote-hornfels facies,

### REFERENCES

- Beran A. und Bittner H., 1974: Untersuchungen zur Kristallchemie des ilvaites, TMPM *Tschermaks Min. Petr. Mitt.* 21, 11–29.
- [2] Bowen N. L., 1956: The evolution of the igneous rocks.
- [3] Brown E. H., 1977: The crossite of Ca amphibole as a guide to pressure of metamorphism. *Journal of Petrology*, Vol **18**, part 1 pp 53–72.
- [4] Deer, W. A., R. A. Howie, and J. Zussman, 1982: An Introduction to the Rock-Forming Minerals (2nd Edition), pp 31–47. England.

- hornblende-hornfels facies,

- K-feldspate-cordierite-hornfels facies.

The rocks studied formed in temperature condition  $T400^\circ$ -800°C and pressure P 1.5–2 kbar.

- [5] Hutton C. O., 1956: Manganopyrosmalite, bustamite, and feroan johansenite from Broken Hill, New South Wales, Australia, Am. Mineral. 41–58.
- [6] Liebau F., Hilmer W., Lindemann G., 1959: Über die Kristallstruktur des Rhodonites, *Acta Cryst* 12. 182.
- [7] Schaler W. T., 1938. Johansenite, a new manganese pyroxene, Am. Mineral. 23. 575.

### Резиме

### МЕТАМОРФИЗАМ НА СКАРНОВСКИТЕ КАРПИ ОД РУДНОТО ПОЛЕ САСА

#### Тена Шијакова-Иванова, Блажо Боев, Војо Мирчовски

Факулиет за йриродни и шехнички науки, Универзишет "Гоце Делчев", n. фах 201, MK 2000 Шийий, Рейублика Македонија tena.ivanova@ugd.edu.mk

Клучни зборови: скарн; контактен метаморфизам; јохансенит; родонит; илваит

Врз основа на презентираните податоци може да се заклучи дека во испитуваните карпи се одредени три фации:

- албит-епидот-хорнфелс;

хорнбленда-хорнфелс;

- К-фелдспат-кордиерит-хорнфелс.

Испитуваните карпи се формирани при температура од 400 до 800°С и притисок од 1.5 до 2 kbar.