Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia with a grant from the CEI-ES Know How Programme organize



1" INTERNATIONAL WORKSHOP ON THE PROJECT

Environmental Impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)

PROCEEDINGS

Edited by: T. Serafimovski & B. Boev Kavadarci, 10th October 2013 Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia with a grant from the CEI-ES Know How Programme organize



1st INTERNATIONAL WORKSHOP ON THE PROJECT

Environmental Impact assessment of the Kozuf metallogenic district in southern Macedonia in relation to groundwater resources, surface waters, soils and socio-economic consequences (ENIGMA)

PROCEEDINGS

Edited by: T. Serafimovski & B. Boev Kavadarci, 10th October 2013

Organizing Committee:

Prof. D-r Todor Serafimovski, *President* Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia

Prof. D-r Saša Mitrev Rector of the University "Goce Delčev"-Štip, R. Macedonia

Prof. D-r Blažo Boev Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia

D-r Josef Šimek GIS-GEOINDUSTRY, s.r.o. ("GISGEO"), Czech Republic

Prof. D-r Violeta Stefanova Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia

Doc. D-r Goran Tasev Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia

M. Sc. Ivan Boev Teaching Center-Kavadarci, University "Goce Delčev"-Štip, R. Macedonia

Scientific Committee:

Prof. D-r Todor Serafimovski, *President* Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia

D-r Josef Šimek GIS-GEOINDUSTRY, s.r.o. ("GISGEO"), Czech Republic

Prof. D-r Blažo Boev Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia

Prof. D-r Nikola Dumurdžanov Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia

Prof. D-r Trajče Stafilov Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, R. Macedonia

Prof. D-r Orce Spasovski Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia

Language: English for presentations and papers



MINERALOGY OF THE PART OF KOZUF AREA, REPUBLIC OF MACEDONIA

Tena Sijakova-Ivanova, Blazo Boev, Vojo Mircovski

¹Facutly of Natural and Technical Science, Goce Delcev University, Goce Delcev 89, MK 2000 Stip, Republic of Macedonia

Abstract

The paper presents data about mineralogical investigations of talc schist from Rzanovo deposit. Special attention in the study of talc schist was paid to the distribution of nickel in the talc and magnetite. Obtained results show that concentration of Ni in the talc is in range of 1.3-3.1%, and is a nickel phase in ore from Rzanovo deposit. Idiomorphic magnetite grains that appears in talc contents from 2.19 to 3.27% nickel.

Key words: magnetite, talc, nickel

Introduction

The Kozuf area is a large volcanic complex situated in the south of the R. Macedonia, in the marginal parts between the Republic of Macedonia and north Greece (fig.1). Geologically viewed the Kozuf area is built of several geologic formations distributed in several stratigraphic complexes.

The Kozuf area is poorly explored except of the Alsar, Rzanovo, Studena Voda, Smrdliva voda and Dudica.



Fig.1. Map of Macedonia with the position of Rzanovo

The Rzanovo deposit is situated in the north-western slopes of the central part of the Kozuf massif, near the village of Rzanovo. Specifically it is on the right side of the Porska River, close to the Macedonian - Greek border.

The geological characteristics, genesis, mineralogical composition, ore grade and reserves of the Rzanovo deposit were first reported by [1],[2].



The mineralogical composition, the sulphide parageneses in particular, were described by [3]. Also, mineralogical and geochemical investigations have been carried out and by [4],[5],[6],[7],[8],[9].

Based on knowledge available, the following lithologic rock types and ore can be distinguished: compact magnetite ore; schistose magnetite ore; oolitic hematite ore; schistose hematite ore; compact hematite ore; riebeckite schists; stilpnomelanic schists; dolomite-talc schists; talc schists; serpentinites.

On the base on previous research was concluded that mineral association on ore from Rzanovo deposit is: magnetite, hematite, talc, klinochlor, sepiolite, magnezioribekite, lizardite, dolomite, flogopite, quartz, albite, pyrite, maghemite, pyrothine, digenite and milerite.

Results and discussion

The results obtained by optical, chemical and X-ray examinations are given and discussed in the text below.

Mineralogical characteristics of talc schist

This lithological type of ore can be seen along tectonic zones and tectonic mirrors. It occurs sporadically in the Rzanovo deposit. It is greenish in colour and contains small magnetite crystals. Structure is lepidoblastic and texture is schistose. Chemical composition of talc schist by [10] is given in Table 1. Quantitative mineralogical composition of talc schist is 89% talc and 8% magnetite.

According to research [10] the talc schist is rich in magnesium and silica, whereas the iron content is relatively low compared to other ore types. The nickel content is 0.75 %. Most probably there are several generations of talc, but not each is nickeliferous. Only talc, as a product of non –metamorphic reactions is nickeliferous.

	1	2
SiO ₂	48.77	55.67
MgO	28.64	27.90
Al_2O_3	1.05	0.37
Fe ₂ O ₃	11.17	7.50
CaO	1.63	1.08
NiO	0.75	0.34
Cr_2O_3	0.36	0.31
MnO	0.26	0.11
K ₂ O	0.18	0.10
H ₂ O	0.30	0.16
LI	5.67	4.16

Table 1 Chemical composition of talc schist

Mineralogical characteristic of talc

Talc is the predominant mineral in the talc schist from Rzanovo.

Macroscopic properties

Talc is pale green mineral having pearly luster and greasy feel (Fig 2). It is extremely soft with hardness 1 and has density $2.82g/cm^3$. Streak is white. Cleavage is perfect by plane (001).



Talc crystallized monoclinic 2/m and triclinic 1 or $\overline{1}$, space group C2/c (polytype 2M₁) or P1 (polytype 1A) a=5.287Å, b=9.158Å, c=18.95Å, β =100°, Z=4(2M1) and a=5.291Å, b=9.460Å, c=5.290 Å, α =98.68°, β =119.90°, γ =85.27°. Z=2(1A) Structure is double layer Si-O tetrahedron and octahedron from cation of magnesium Si-Mg-Si.....Si-Mg-Si..... [11] analysed the crystal structure of talc by the powder method, and gave the unit cell as monoclinic with a = 5.26Å, b = 9.10Å, c = 18.81Å, and β = 80°. [12] obtained a similar result by single-crystal X-ray diffraction methods, and it became accepted that talc has a monoclinic two-layer structure (2M). [13] studied a talc from Manchuria by 114.6 mm diameter X-ray powder camera and high-angle X-ray diffractometer and reported it as having the 2M structure. However, [14] examined talc single-crystal specimens from two localities (Gouverneur-New York, and Balsam- N. Carolina) and determined their unit cells as triclinic. [15] re-examined the talc from Maryland previously studied by [12] and found that the true unit cell was triclinic (pseudo-monoclinic) with a= 5.293Å, b=9.I79Å, c = 9.496Å and α = 90.57°, β = 98.91°, γ = 90.03° space group CL. These results cast considerable doubt on the reality of monoclinic talc although it is possible that both triclinic and monoclinic poly-morphs exist[16].

Microscopic properties

In thin section talc is colourless. Optically is negative. Np 1.539-1.550, Nm 1.589-1.594, Ng-1.589-1.600. Relief is low. Talc has third order interferential colours. Depending on the intersection angle of tarnish is around $0^{\circ}-3^{\circ}$. (-) 2V $6^{\circ}-30^{\circ}$.



Fig. 2 Photography of talc

Chemical composition of talc were determined by [17] with AES-ICP in the labaratory on Faculty of Natural and Technical Science in Stip. Results are given in table 2. From the data obtained can be seen that the content of Ni is from 1.3 to 3.1%. Small part of silicium is repleaced with Al . Part of Mg in octahedral site is repleaced with Fe and Ni.



	1	2	3		
	%				
SiO ₂	60.1	60.6	59.6		
MgO	30.7	30.3	23.9		
Al_2O_3	0.04	0.1	0.1		
FeO	3.5	2.4	7.3		
NiO	1.3	1.6	3.0		
H ₂ O	4.3	4.5	4.1		
Total	99.94	99.5	99.3		
	Amount ions of	calculated on 24(O)			
Si	7.8	7.9	8.04		
Al	0.01	0.02	0.01		
Mg	5.9	5.9	4.8		
Fe	0.4	0.3	0.8		
Ni	0.1	0.2	0.3		
H ₂ O	3.6	3.9	3.9		
	n	ng/kg			
Ca	99,1	94.4	98.9		
Sr	1,5	1.7	1.3		
Ba	7,5	7.8	7.6		
Mn	954,4	942.5	963.3		
Ti	5,4	5.1	5.9		
Ti	5,4	5.1	5.9		
Р	<5	<5	<5		
Cr	252,0	250.2	258.4		
Zn	35,0	36.1	35.2		
Cu	4,6	4.2	4.4		
Pb	10,4	10.8	10.6		
Cd	6,3	6.1	6.8		
Со	66,2	65.8	64.7		
As	212,6	203.1	206.4		
Ag	0,6	0.4	0.6		
V	5,2	5.6	5.1		
Мо	<5	<5	<5		

Table 2 Chemical composition of talc from Rzanovo.

Empirical formula of talc is following :

- 1. $(Si_{7.8}Al_{0.01}Fe^{3+}_{0.19})_{8.01}$ (Mg_{5.9}, Fe_{0.21}, Ni_{0.1})_{6.2} O₂₀ (OH)₄
- 2. $(Si_{7.9}Al_{0.02}Fe^{3+}_{0.08})_{8.00}$ (Mg_{5.9}, Fe_{0.21}, Ni_{0.2})_{6.2} O₂₀ (OH)₄
- 3. $(Si_{8.0}Al_{001.})_{8.01}$ (Mg_{4.8}, Fe_{0.8}, Ni_{0.3})_{5.9} O₂₀(OH)₄

DTA and TGA investigation show that on the temperature of about 800° C not registered lost in the mass of the sample. Water in excess of 1 molecule was mostly driven of between 380° C and 500° C. This water loss was accompanied by a small endothermic heat effect, but not by any change in crystal structure or optical properties. Thermal destruction resulting in a total weight loss of about 4%. The molecule of combined water was driven between 800° C and 840° C. This water loss was accompanied by a large



endothermic heat effect and by breakdown of the talc into enstatite and amorphous silica. Inversion of the enstatite to clinoenstatite took place gradually, both phases being observed in material heated at 1200° C, and only clinoenstatite in material heated at 1300° C. The material heated at 1300° C also showed conversion of the amorphous silica to cristobalite. Thus, the final products of the thermal decomposition of talc are clinoenstatite and cristobalite.

These results match with the data by [18] which support the hypothesis on [19] that water in talc in excess of 1 molecule is not constitutional and may be held electrostatically between basal cleavage planes.



Fig3. The powder X-ray diagram of talc

On the fig.3 is given powder X-ray diagram of talc from Rzanovo. Fig.3 clearly shows three characteristic peaks of talc.

Results of X-ray examinations are in good agreement with worldwide recognized JCPDS standards no. 13-558.

Mineralogical characetristics of Magnetite

Macroscopic properties

Magnetite is black mineral. Transparency is opaque. Density is $5.2g/cm^2$. Hardness $5^{\frac{1}{2}}$ - $6^{\frac{1}{2}}$. Streak is black. Lustre is metallic. Crystal system is isometric, class m3m (4/m 3 2/m), space group *Fd3m*. Cell parameters is a = 8.397Å, Unit cell volume:V= 592.07 Å³ Z:8

Microscopic properties

Magnetite appears in individual octahedral crystal (fig. 4). In thin section magnetite is isotropic. Relief is very high. Colour in reflected light is grey with brownish tint.



ENIGMA Project (Ref. No. 1206KEP.008-12)



Fig.4 Image of idiomorphic magnetite grains in talc

Chemical composition of idiomorfic magnetite grains is given in table 3.

Table 3 Chemi	ical composition	of	idiomorphic	magnetite	grains	in talc
ruote 5 Chemi	cui composition	- UJ	iaiomorphic	magnettie	Sicuris	in inic

	1	2	
Cr_2O_3	1.93	1.88	
FeO	95.88	94.85	
NiO	2.19	3.27	
Total	100.00	100.00	
Amount ions calculated on 4(0)			
Cr	0.07	0.07	
Fe	3.81	3.77	
Ni	0.08	0.13	

Table 3 shows that the contents of nickel in idiomorphic magnetite grains is from 2.19 to 3.27%.

Examinations by [20] indicate that magnetite from Rzanovo ore deposit except in idiomorphig grains in talc, occurs and in several other forms such as: lamelle, large idiomorphic grains, magnetite grains with centres built of chromite and as a band in chromite grains.

Based on investigations carried by [20] the content of Ni in magnetite which appears as lamellae is 0.18 to 0.28%; in magnetite which appears as coarse idiomorphic grains is from 0.85 to 0.44%; in magnetite grains with centres built of chromite contents of Ni is range from 0.11 to 1.25%; in magnetiteappears as a band in chromite grains contents of Ni is 4.21%.

Results of X-ray examinations are in good agreement with worldwide recognized JCPDS standards no:19-0629



Conclusion

Based on investigations carried out it can be inferred that the talc schist can be seen along tectonic zones and tectonic mirrors. It occurs sporadically in the Rzanovo deposit. It is greenish in colour and contains small magnetite crystals. Structure is lepidoblastic and texture is schistose. The nickel content in talc schist is 0.75 %. Dominant minerals in the talc schist are talc and magnetite. Both minerals are relativy enriched with Ni. Content of nickel in talc is in the range 1.3-3.0% and is a nickel phase in ore from Rzanovo deposit. The content of nickel in magnetite grains is much higher ranging from 2.19 to 3.27%.

References

[1]Иванов Т., 1959: Николоносно гвожђе код Ржанова на Кожуфу (НР. Македонија)

Зборник радова 3 Конгрес геолога Југославије, Будва, 2, 249-264.

[2] Иванов Т., 1960: Николоносна железна руда на планини Кожуф код села Ржаново. Трудови на геолошкиот завод Скопје СВ. 7. Стр. 199-223.

[3]Grafenauer, Strmole, 1966: Zlog in milleralna sestava niklonosnih zelezovih rud Rzanova. Rudarsko-metalurski zbor nik, 1, 51-62.

[4] Maksimovic, Z, 1981: NickeL-bearing phlogopile from the nickel-iron deposit Studena Voda (Macedonia). Godisnjak Jugoslavcnskog centra za kristalografiju. Vol. 16. Zagreb.

[5] Boev, B., 1982: Metamorfizam na rudnata serija R`anovo-Studena voda mag. teza., Rudarskogeoloski fakultet Belgrad, 93 str.

[6] Boev, B., Stojanov, R., 1985: Metamorphisam of Ni-Fe ores from Rzanovo-Studena voda and the Zone Almopias, Geologica Macedonica, T.1

[7] Boev,B., Serafimovski, T., 1992: Sostav na nekoi od glavnite mineralni fazi vo produktite od predredukcijata na niklonosnite rudi od naogalisteto R`anovo-Makedonija 24 Sovetuvanje na rudarite i metalurzite, Bor, 1992.

[8] Boev, B., Lepitkova, S., 1994; Kvantitativna mineraloska analiza na ruda od zeleznoniklonosnoto naogaliste Rzanovo, 24 Oktomvrisko sovetuvanje, Bor.

[9]Boev, B., Serafimovski, T., 1995:Metalogenetic features of the Fe-Ni lateritic deposits in the Vardar zone, Republic of Macedonia Second National Simposium" Metalogeny of Bulgaria, Sofija, 1995.

[10]Boev, B., Jankovic, S., 1996: Naogalista na nikel i niklonosno zelezo vo Vardarskata zona so poseben osvrt na rudnata serija Rzanovo-Studena voda

[11] Gruner. J. W., 1934, Crystal structures of talc and pyrophyllite: Zeitschr. Krist., 88 A, p. 412-419.

[12]Hendricks (S. B.), 1938. Ibid. 99, 264 74.

[13]Stemple (I. S.) and Brindley (G. W.), I960. J. Am. Ceram

[14]Ross (M.), Smith (W. L.), and Ashton (W. H.), 1968. Am. Mineral. 53, 75I-69.

[15]Rayner (J. S.) and Brown (G.), 1973. Clays and Clay Miner. 21, 103-I4.

[16]Akizuki, M., and Zussman, J: 1978: The unit cell of talc 2MINERALOGICAL MAGAZINE, MARCH 1978, VOL. 4 2, PP. 107=10

[17]Tena Sijakova, Vesna Paneva, G. Bogoeva- Gaceva, Ilinka Donova 2008, Mineraloskohemiski karakteristiki na talkot od naogalisteto Rzanovo Zbornik na trudovi, Prv Kongres na geolozite na Makedonija, Ohrid.

[18] Ewell, R. H., Bunting, E. N., and Geller, R. F., 1935, Thermal decomposition of talc: [U.S.] Natl. Bur. Standards Jour. Research, 15, p. 551-556.

[19]Foshag, W. F., and Wherry, E. T., 1922, Notes on the composition of talc:Am. Mineralogist, v. 7, p.167-171.

[20] Boev, Blazo and Sijakova-Ivanova, Tena (1998) Mineralogy of the magnetites in the Rzanovo Fe-Ni deposit, Republic of Macedonia. Geologica Macedonica, 12. pp. 51-56.



ENIGMA Project (Ref. No. 1206KEP.008-12)