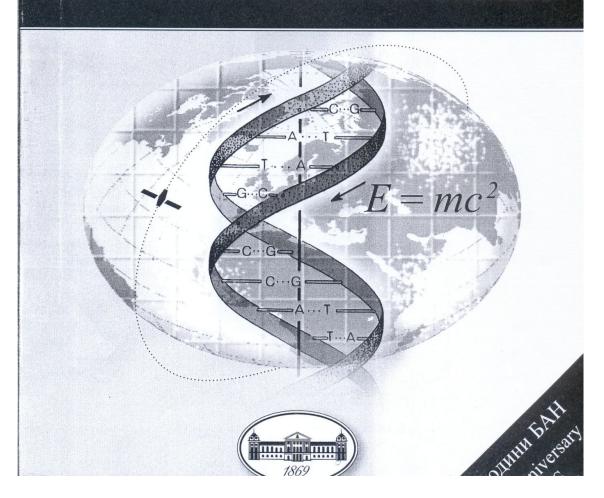
ДОКЛАДИ НА БЪЛГАРСКАТА АКАДЕМИЯ НА НАУКИТЕ

# COMPTES RENDUS

DE L' ACADEMIE BULGARE DES SCIENCES



#### РЕДАКЦИОННА КОЛЕГИЯ

Тодор Николов (главен редактор), Петя Василева, Васил Големански, Петър Кендеров, Дечко Павлов, Илия Пашев, Олга Полякова-Кръстева, Петър Попиванов, Васил Сгурев

# COMITÉ DE RÉDACTION / EDITORIAL COMMITTEE

Todor Nikolov (editor-in-chief), Vassil Golemansky, Petar Kenderov, Ilia Pashev, Dechko Pavlov, Olga Poljakova-Krusteva, Petar Popivanov, Vassil Sgurev, Petia Vassileva

#### РЕДАКЦИОНЕН СЪВЕТ

Жорес Алферов (Русия), Курт Биндер (Германия), Панайот Бончев (България), Джонатан М. Боруайн (Канада), Карло Долиони (Италия), Фридрих Ерендорфер (Австрия), Ячко Иванов (България), Люсиен Диего Лод (Белгия), Владимир Овчаров (България), Стойчо Панчев (България), Мария Папазова (България), Никола Съботинов (България), Таруат Тадрос (Англия), Цветан Цветков (България), Божидар Чурчич (Сърбия)

# CONSEIL DE RÉDACTION / ADVISORY BOARD

Zhores Alferov (Russia), Kurt Binder (Germany), Panayot Bonchev (Bulgaria), Jonathan M. Borwein (Canada), Carlo Doglioni (Italy), Friedrich Ehrendorfer (Austria), Yachko Ivanov (Bulgaria), Lucien Diego Lod (Belgium), Vladimir Ovcharov (Bulgaria), Maria Papasova (Bulgaria), Stoycho Panchev (Bulgaria), Nikola Sabotinov (Bulgaria), Tharwat Tadros (England), Tsvetan Tsvetkov (Bulgaria), Bojidar Curcic (Serbia)

Редактор Р. Радославова Rédacteur R. Radoslavova

Section of Mathematics is indexed and reviewed in Zentralblatt für Mathematik, Germany

"Journal Citation Reports 2008", published by Thomson Reuters, reports that the current Impact Factor for 2007 of "Comptes rendus de l'Académie bulgare des Sciences" is 0.106

"Comptes rendus de l'Académie bulgare des Sciences" is indexed in SCOPUS

Основано през 1948 г. от академик Г. Наджаков Fondée en 1948 par G. Nadjakov, membre de l'Académie

- © Българска академия на науките, 2009
- © Bulgarian Academy of Sciences, 2009

Prof. Marin Drinov Academic Publishing House Acad. Georgi Bonchev Str., bl. 6 1113 Sofia, Bulgaria Published in January, 2009 www.baspress. com

## Доклади на Българската академия на науките Comptes rendus de l'Académie bulgare des Sciences

Tome 62, No 1, 2009

#### CONTENTS

#### **MATHEMATICS**

- 2. Vesselin Drensky, Jie-Tai Yu. Dimension of Automorphisms with Fixed Degree for Free Algebras of Nielsen Schreier Varieties . . . . . . . . . . . . p.9
- 3. Vladimir P. Kostov. A Realization Theorem about the Schur-Szegö Composition for Entire Functions . . . . . . p.17
- 4. Toshko Boev. A Solution-Formula to Interface Electrostatics of Gas-Liquids p.23

#### PHYSICS

#### BIOLOGY

- 7. Gergana Deevska, Ilia Bankov, Mariana Nikolova-Karakashian. Acid Sphingomyelinase Activity Regulates de novo Sphingolipid Synthesis in Liver through a Negative Feedback Mechanism . . . . . p.49
- 8. Maria Dimitrova, Zhana Mitrovska, Veneta Kapchina-Toteva, Evgeniya Dimova, Stephka Chankova. Testing of Polluted Air Samples for Genotoxic Potential Using Chlamydomonas reinhardtii . . p.57

9. Kalina Racheva, Angel Vassilev. Human S-Cone Vision. Effect of Stimulus Duration on the Increment and Decrement Thresholds . . . . . . . . . p.63

#### GEOLOGY

- 10. Vojo Mirčovski, Orce Spasovski. Metamorphism of the Glaucophane and Magnesioriebeckite-Bearing Metamorphic Rocks in the Gostivar Vodno Zone, North-Western Macedonia . . . . . . . . p.69
- 12. Athanas Chatalov. Primary and Secondary Fenestral Porosity in Middle Triassic Subtidal Grainstones from the Belogradchik Strip, NW Bulgaria. Implications for Unconformity-Related Diagenesis . . . p.85

#### SPACE RESEARCH

13. Atanas Atanassov. An Analytical Method for Calculating the Satellite Bow Shock/Magnetopause Interception Positions and Times . . . . . . . . . . p.97

#### **MEDICINE**

14. Krasimir Dragoev, Maria Sredkova, Svetlana Pachkova, Valentina Edreva, Valentina Popova, Hristina Hitkova, Sashka Mihaylova. Species Distribution and Susceptibility to Antimicrobials among Clinical Isolates of Shigella species . . . . . p.105

15. Georgi I. Milchev. Stem Cells for Tissue Repair p.111 16. Dimitar E. Itzev, Kamen G. Usunoff, Negrin N. Negrev, Radomir G. Radomirov. Histo- and Immunohistochemical Investigation of the Innervation of Rat Recto-Anal Region p.123 17. Dimitar Kadiysky, Maya Svetoslavova. Aplication of Tomato Lectin				
	p.D. Prince of No. of the Control of			

## Доклади на Българската академия на науките Comptes rendus de l'Académie bulgare des Sciences

Tome 62, No 1, 2009

**GEOLOGIE** 

Pétrologie

# METAMORPHISM OF THE GLAUCOPHANE- AND MAGNESIORIEBECKITE-BEARING METAMORPHIC ROCKS IN THE GOSTIVAR – VODNO ZONE, NORTH-WESTERN MACEDONIA

Vojo Mirčovski, Orce Spasovski

(Submitted by Corresponding Member I. Zagorchev on November 14, 2008)

#### Abstract

Mineral assemblages discovered in the glaucophane- and magnesiorie beckite-bearing metamorphic rocks of Gostivar – Vodno zone allow to distinguish three metamorphic phases. The first-phase metamorphism is progressive and corresponds to conditions of the lowest temperature part of the greenschist facies at P from 2 to 4 bar and T of about 350 °C. The second metamorphic phase formed the sodic amphiboles glaucophane and magnesiorie beckite in a paragenesis with phengite and epidote – minerals that are indicators of epidote-blue schist facies. To determine the P – T conditions of metamorphism in the phase, the chemical composition of sodic amphiboles and phengite were used with application of several geothermobarometers that yielded P from 6 to 9 Kbar and T of about  $400 \pm 20$  °C. The third phase is a retrograde one in which glaucophane grade into actinolite, chlorite and albite mineral parageneses characteristic of the lowest temperature part of the greenschsist facies.

Phengites from two samples of glaucophane- and magnesiorie beckite-bearing metamorphic rocks were dated by the K/Ar method. They yielded an age of  $137\pm8$  to  $153\pm9$  Ma interpreted as the age of high-pressure metamorphism that corresponds to the Late Jurassic.

**Key words:** metamorphism, sodic amphiboles, glaucophane, epidote blueschists facies, Vodno, Gostivar

Introduction. The Gostivar-Vodno zone (GVZ) is an elongated belt spatially located in the north-northwestern margin between two large geotectonic units – the Pelagonian massif (PM) and the Western Macedonia zone (WMZ). The zone begins south of Gostivar and continues to north-east ending up to Mt. Vodno south of Skopje (Fig. 1).

Data about the presence of the sodic amphiboles bearing metamorphic rocks in the WMZ and Mt. Vodno have been reported by a number of authors like:

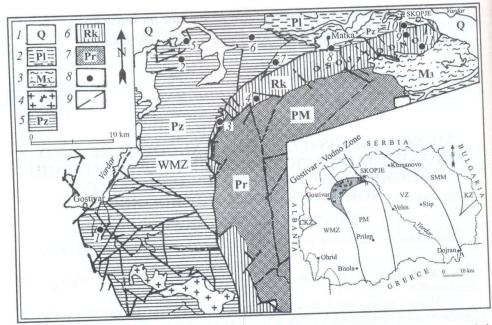


Fig. 1. Geological map of the Gostivar-Vodno zone (according to the Geological Map of the Republic of Macedonia 1:100 000) with location of the Gostivar-Vodno zone and the locations of sodic amphiboles bearing metamorphic rocks. 1 – Quaternary; 2 – Pliocene: pebbles, sands and sandy clays; 3 – Miocene: sands, marls, marly clays and conglomerates; 4 – Palaeozoic granites; 5 – Palaeozoic; 6 – Riphean-Cambrian; 7 – Precambrian; 8 – Sodic amphiboles bearing metamorphic rocks localities (1. Sušica, 2. Gorna Lešnica, 3. Sedlarevo, 4. Lukovica, 5. Zelino – Strimnica, 6. Grupcin, 7. Merovo, 8. Matka, 9. Sredno Vodno, 10. Nerezi, 11. Sopište); 9 – Fault structures, WMZ – Western Macedonian zone, PM – Pelagonian massif. Geotectonic schetch of the regional setting of Macedonia after Arsovski (1997). WMZ – Western Macedonian Zone, PM – Pelagonian massif, VZ – Vardar zone, SMM – Serbo Macedonian Massif, CKZ – Krasta zone, KZ – Kraištide zone

NIKITIN and KLEMEN [1], DUMURDŽANOV and RIEDAR [2], MAJER and LUGOVIĆ [3], MIRČOVSKI, BOEV and SPASOVSKI [4] and some others.

The sodic amphiboles bearing metamorphic rocks of the area have not been studied in detail from the point of metamorphism, except for the Sušica locality south of Gostivar [4]. This is the first attempt to define the degrees of metamorphism and the metamorphic evolution.

The geological setting of the Gostivar – Vodno zone. Based on the regional geotectonic setting of Macedonia the GV zone is part of the WMZ [<sup>5</sup>] (Fig. 1). The Riphean Cambrian and Old Palaeozoic metamorphic rocks are the most widespread rock types. Less common are Young Palaeozoic granitoids, Mesozoic terrigenous and carbonate sediments and the Neogene-Quaternary sediments [<sup>6</sup>] (Fig. 1). Sodic amphiboles can be found in the Riphean – Cambrian and Palaeozoic metamorphic complex most often in the greenschist series but seldom in cipolines.

Petrographic features of the sodic amphiboles bearing metamorphic rocks. Glaucophane – epidote schists of the Riphean – Cambrian metamorphic complex have been studied (all abbreviations of minerals are after Kretz, 1983) in which the Gln + Ep + Cal + Phg + Chl + Ab + Qtz + Grt mineral association was determined (Plate 1, a, b), as well as glaucophane-phengite cipolines of the mineral association: Gln + Phg + Chl + Ab + Cal+ Qtz (Plate 1, c, d).

Of the Palaeozoic metamorphic complex studies were carried out on magnezioriebeckite phengite schists (Plate 1, e) of mineral associations: Mg-Rbk +

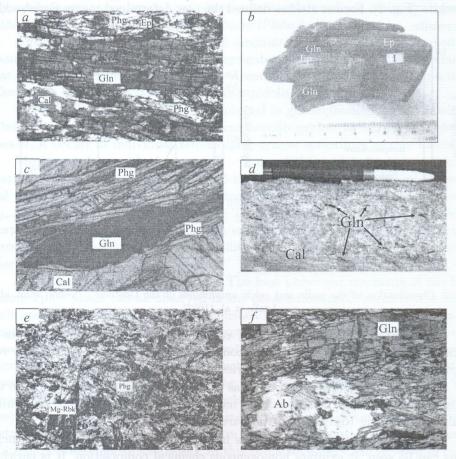


Plate 1. a) Riphean – Cambrian metamorphic complex, locality Sredno Vodno: Gln – Ep schists NII, elongated Gln prismatic crystals; b) Mesoscopic sample of Gln – Ep schist, corrugated Gln bands alternating Ep bands; c) Gln – Phg cipoline NII, Gln crystals; d) Mesoscopic sample of Gln – Phg cipoline with Gln crystals 2 cm in size. Palaeozoic metamorphic complex, locality Sušica near Gostivar: e) Mg – Rbk – Phg schist with Mg-Rbk acicular crystals and small Phg sheets NII; f) Gln – Ab – Chl – Ep schists NII; Ab-porphyroblast with inclusions of fine grains of Ep, Gln, and Ttn and Gln prismatic crystals, Gorna Lešnica locality

Phg + Qtz; and glaucophane - albite - chlorite - epidote schists, of mineral associations: Gln + Ab + Chl + Ep + Phg + Qtz + Cal + Ttn (Plate 1, f).

Sodic amphiboles. Sodic amphiboles occur as elongated rod-like or acicular 2 cm long crystals (Plate 1, b, d). They also occur as smaller acicular crystals that macroscopically can hardly be noticed. They have been oriented only along  $S_2$  foliation exhibiting clear lineation. Occasionally, crystals have been affected by retrograde metamorphism and grade into chlorite and actinolite along fissures. According to the classification of Leake et al. [7], the sodic amphiboles of the Gostivar – Vodno zone have been determined as glaucophane and magnesioriebeckite (Fig. 2). Former studies defined the now determined magnesioriebeckite as crossite.

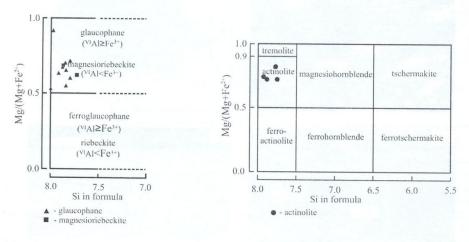


Fig. 2. Classification of the sodic and calcic amphiboles of the Gostivar – Vodno zone, after Leake et al. (1997)

Actinolite. Actinolite is not very common. It occurs in acicular shapes as primary and as irregular shapes, as secondary mineral when it developed by retrograde metamorphism at the peripheries of glaucophane crystals.

White mica. White mica occurs as laminated accumulations parallel to the schistosity or as bands, occasionally as individual sheets. All sheets of white mica analysed according to its composition are phengite.

*Garnet.* Garnet seldom occurs as individual fine grains in which no inclusions can be seen. It exhibits homogeneous chemical composition. It is enriched in spessartine (Sps 49.00-49.37%, mol, Alm 32.50%, Grs 16.90-17.24% and Pyr 0.78-1.50% mol).

**Albite.** Albite occurs in almost all rocks examined. Most often it is encountered as porphyroblasts hosting other minerals (Plate 1, f). Porphyroblasts are 0.5 to 1.5 mm in size. Two albite types can be distinguished under a microscope.

The first type is quite visible in schists where inclusions into albite grains are oriented discordant to the main foliation  $S_2$ . The second albite type is most visible in rocks that contain glaucophane. In such rocks albite porphyroblasts include fine glaucophane grains, epidote and titanite, the inclusions being concordant to  $S_2$  folliation. Albite component amounts from 99.5 to 99.8%.

**Epidote.** Epidote is the prevailing mineral in the glaucophane-epidote schists, occurring in other rock types either in lower amounts or as individual grains. Most often it occurs as fine alotriomorphic to hypidiomorphic grains (Plate 1, a). It seldom occurs as prismatic elongated hypidiomorphic porphyroblasts. Occasionally, epidote occurs as bands that alternate with glaucophane concentrations as is the case with glaucophane-epidote schists (Plate 1, b).

Chlorite. Chlorite occurs in small amounts in almost all rocks studied. It occurs as individual sheets or leaf-like aggregates, most often with the white micas that accompany S<sub>2</sub> foliation in rocks. According to the chemical composition chlorite has been defined as brunsvingite-rapidolite.

Calcite. Calcite is the prevailing mineral in glaucophane-phengite cipolines (Plate 1, c, d) occurring as elongated xenomorphic grains. In other rock types, if present, it occurs as individual xenomorphic grains, sometimes as thin bands.

Metamorphic evolution and P-T conditions of the sodic amphiboles bearing metamorphic rocks in the GVZ has been determined based on the mineral parageneses observed. Three metamorphic phases have been distinguished:  $M_1, M_2, M_3$  (Fig. 3). Estimations of P-T conditions for the distinguished metamorphic phases was done according to empirical and experimental geothermobarometers and based on the P-T stability of individual indicative metamorphic minerals.

First metamorphic phase  $M_1$ . The best preserved remnants of the first metamorphic phase can be observed in the parametamorphic rocks rich in phyllosilicates. The phase has been distinguished based on minerals mainly oriented along  $S_1$  foliation appearing as a remnant between the younger  $S_2$  foliation and based on the inclusion in individual porphyroblasts oriented to  $S_2$  strike. The  $S_1$  remnant foliation most probably is synchronous with the first  $D_1$  deformation phase since older microstructures in the rocks studied could not be seen. The mineral paragenesis of the  $M_1$  phase includes  $Chl + Ep \pm Act \pm Grt$  (spessartine)  $+ Ab \pm Cal + Qtz + Ttn$ . The mineral paragenesis distinguished indicates metamorphism in the lowest temperature part of the greenschists facies (quartz-albite-muscovite-chlorite subfacies). In this subfacies garnet can develop in rocks rich in manganese, and spesartine stability at P of 2 to 3 bar amounts to 400 °C [8]. The greenschist facies according to PLYUSNINA [9], for P of 2 to 4 bar is stable at T from 350 to 430 °C. It can be inferred that the mineral paragenesis of  $M_1$  phase developed at T of about 350 °C and P from 2 to 4 Kbar.

The second metamorphic phase  $M_2$ . The second metamorphic phase was distinguished based on well preserved  $S_2$  foliation that cuts the  $S_1$  foliation. The

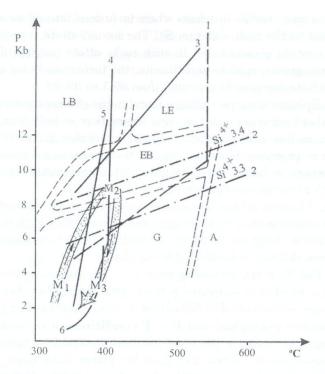


Fig. 3. Metamorphic evolution of the sodic amphibole bearing metamorphic rocks of the Gostivar – Vodno zone (stippled arrow). Approximate stability fields of metamorphic facies (after Schliedstedt, 1990): LE – Low temperature eclogite, LB – Lawsonite blueschist, EB – Epidote blueschist, G – Greenschist, A – Amphibolite facies. Reactions: 1. Glaucophane stability (after Maresh, 1977) 2. Si <sup>4+</sup> data (Massone, 1981) 3. Ab = Jd + Qtz (after Holland, 1984). 4. Lws + Ab = 2 Czo + Pg + 2 Qtz +5.6 H2O (after Franz & Althaus, 1977) 5. Pmp + Chl + Qtz = Ep + Act (after Nitsch, 1971). 6. Spessartine stability (Hsu, 1968)

indicative metamorphic minerals formed during  $M_2$  phase: glaucophane, magnesioriebeckite, phengite and epidote are formed along the  $S_2$  foliation. Under a microscope traces of the phase can be seen easily in all rock types examined. The most probable reactions which formed glaucophane are: 1. Chl + Ab  $\pm$  Act = Gln + H<sub>2</sub>O; 2. Chl + Ab + Act + Fe oxide = Gln + Ep + Mu + Qtz + H<sub>2</sub>O.

The glaucophane formation according to reaction 1 has also been suggested by Winkler [ $^{10}$ ], and according to reaction 2 by Brown [ $^{11}$ ]. The glaucophane and epidote mineral paragenesis is characteristic of the epidote-blueschist facies [ $^{12}$ ]. Estimation of the P - T conditions has been done based on the chemical composition of glaucophane, magnesioriebeckite and phengite. P from 6 to 9 Kbar were determined according to phengite with the Massone barometer [ $^{13}$ ]. According to Brown geobarometer [ $^{11}$ ], based on the chemical composition of

glaucophane, P higher than 7 Kbar is obtained. The absence of jadeite in the rocks of GVZ that may occur associated with glaucophane indicates that P was not higher than 10 to 12 Kbar [ $^{14}$ ]. Glaucophane is stable at T from 400 to 500 °C [ $^{15}$ ] for the determined P amounting from 6 to 9 Kbar. The absence of lawsonite associated with glaucophane indicates that T were lower than 390 to 400 °C at P from 5 to 7 Kbar since in these P – T conditions lawsonite is no longer stable and grades to epidote [ $^{16}$ ]. According to Evans the transition of lawsonite blueschists to epidote blueschists at P of 9 Kbar is done at T of some 390 °C, whereas at the same P the transition of the greenschist facies to facies of epidote blueschists occurs at T of 450 °C. From the said above it can be inferred that the second metamorphic phase took place at T from 400  $\pm$  20 °C and P from 6 to 9 Kbar.

Third metamorphic phase  $(M_3)$ . The phase is characterised by significant decrease in P and lower T when the rocks of the GVZ were affected by retrograde metamorphism. The most significant traces of retrograde metamorphism have been found with glaucophane in which they grade to chlorite, albite and actinolite according to the reaction  $Gln + H_2O = Chl + Ab + Act$ . The Chl + Act + Ab retrograde mineral paragenesis is characteristic of the greenschist facies. According to the data of Marech [ $^{15}$ ], glaucophane is no more stable at pressures lower than 4 Kbar and T lower than 350 °C which points out that the metamorphic phase  $M_3$  took place at T of about 350 °C and P lower than 4 Kbar.

Age of metamorphism. Two samples with large flakes of phengite and large crystals of sodium amphiboles were selected for isotopic analysis by the K/Ar method. One sample is from the glaucophane-phengite cipolines from Vodno locality, and the other is from the glaucophane-phengite-chlorite schists from Nerezi locality.

Isotopic ages on both samples were determined on phengite, by M. I. Karpenko, V. V. Ivanenko and V. A. Lebedev at the Laboratory for Isotopic Geochemistry and Geochronology in the IGEM Institute of the Russian Academy of Science, Moscow. For the time of crystallization of the phengite from the glaucophane-phengite cipolines, the age determined was  $153 \pm 9$  Ma (million years), and from the glaucophane-phengite-chlorite schists –  $137 \pm 8$  Ma, which corresponds to the Late Jurassic.

Estimates for the blocking temperature of muscovite are in the range from  $350\,^{\circ}\text{C}$  to about  $420\,^{\circ}\text{C}$  depending on the grain size and cooling rate [ $^{17,\ 18}$ ]. These blocking temperatures are near to the peak of the metamorphic temperature of the  $M_2$  phase, so that the obtained isotopic age could be regarded as age of the high-pressure metamorphism.

Conclusion. The sodic amphiboles bearing metamorphic rocks of the GVZ were metamorphosed during polyphase regional metamorphism in three metamorphic phases. The first and the third metamorphic phase took place in conditions of the lowest temperature part of the greenschist facies at T of about 350 °C and P from 2 to 4 Kbar. The second phase that formed glaucophane and magnesior-

iebeckite took place in conditions of epidote-blueschist facies at T of about 400  $\pm$  20 °C and P from 6 to 9 Kbar.

Isotopic analyses carried out by K/Ar method of two phengite samples determined the age of  $137 \pm 8$  to  $153 \pm 9$  Ma that corresponds to the Late Jurassic.

The geotectonic position of the sodic amphiboles bearing metamorphic rocks of the Gostivar–Vodno Zone on the contact between West Macedonia Zone and the Pelagonian Massif points out that they were formed in conditions of high pressures and low temperatures due to tectonic processes of subduction, collision and thrusting between these two geotectonic units during Late Jurassic times.

#### REFERENCES

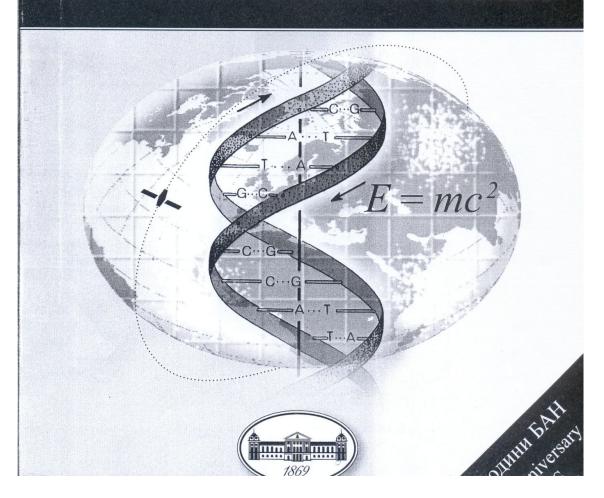
- NIKITIN V., R. KLEMEN. N. Jb. Min. Geol. Pal., Abh., Beih, B, 74, 1938, No 1, 36-49.
- [2] DUMURDZANOV N., M. RIEDER. Geologica Macedonica, T-4, 1989, No 1, 151-160.
- [3] MAJER V., B. LUGOVIČ. Hrvatske akad. Znan. i umjet., 1991, No 25, 103–129.
- [4] MIRČOVSKI V., B. BOEV, O. SPASOVSKI. Pancardi. Abstr. Sopr. Hung., 2001, 346.
- [5] ARSOVSKI M. Tectonics of Macedonia. Štip, 1997, 306 p. (in Macedonian).
- [6] DUMURDJANOV N. Geologica Macedonica, **T-3**, 1987–1988, No 1, 57–79.
- [7] LEAKE B. E. et al. The Canad. Mineral., 35, 1997, 219–246.
- [8] Hsu L. C. J. Petrol., 9, 1968, 40–83.
- [9] PLIUSNINA L. P. Experiment in the solution of modern problems of geology: experimental study of the equilibrium in metabasites, geothermometry, Moscow, Nauka, 1986, 174–183 (in Russian).
- [10] WINKLER G. F. Petrogenesis of metamorphic rocks. Fifth Edition. New York-Heidelberg-Berlin, Springer-Verlag, 1979, 176 p.
- [11] Brown E. H. J. Petrol., 18, 1977, No 1, 53-72.
- [12] EVANS B. W. Lithos, **25**, 1990, 3–23.
- [13] MASSONE H., J. Phengite Eine experimentelle Untersuchung ihres Druch-Temperatur-Verhaltens in System K<sub>2</sub>O-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. Diss. Univ. Bochum, 1981, 211 p.
- [14] MARUYAMA S., J. G. LIOU. J. Metam. Geol., 5, 1987, 529–552.
- <sup>[15]</sup> Maresch W. V. Tectonophysics, 43, 1977, 109–125.
- <sup>[16]</sup> Brothers R. N. Contrib. Mineral. Petrol., 46, 1974, 109–127.
- [17] ROBBINS G. A. Radiogenic argon diffusion in muscovite under hydrothermal condition, Unpubl. MSc Thesis, Rown University. 1972, 65-66.
- [18] VAN BLANCKENBURG F., M. I. VILLA, H. BAUR, G. MORTEANI, H. R. STEIGER. Contr. Miner. Petrol., 101, 1982, 1–11.

"Goce Delčev" University — Štip
Faculty of Mining, Geology and Polytechnic
Goce Delčev 89, 2000 Štip, R. Macedonia
e-mail: vojo.mircovski@ugd.edu.mk
e-mail: orce.spasovski@ ugd.edu.mk

ДОКЛАДИ НА БЪЛГАРСКАТА АКАДЕМИЯ НА НАУКИТЕ

# COMPTES RENDUS

DE L' ACADEMIE BULGARE DES SCIENCES



#### РЕДАКЦИОННА КОЛЕГИЯ

Тодор Николов (главен редактор), Петя Василева, Васил Големански, Петър Кендеров, Дечко Павлов, Илия Пашев, Олга Полякова-Кръстева, Петър Попиванов, Васил Сгурев

# COMITÉ DE RÉDACTION / EDITORIAL COMMITTEE

Todor Nikolov (editor-in-chief), Vassil Golemansky, Petar Kenderov, Ilia Pashev, Dechko Pavlov, Olga Poljakova-Krusteva, Petar Popivanov, Vassil Sgurev, Petia Vassileva

#### РЕДАКЦИОНЕН СЪВЕТ

Жорес Алферов (Русия), Курт Биндер (Германия), Панайот Бончев (България), Джонатан М. Боруайн (Канада), Карло Долиони (Италия), Фридрих Ерендорфер (Австрия), Ячко Иванов (България), Люсиен Диего Лод (Белгия), Владимир Овчаров (България), Стойчо Панчев (България), Мария Папазова (България), Никола Съботинов (България), Таруат Тадрос (Англия), Цветан Цветков (България), Божидар Чурчич (Сърбия)

# CONSEIL DE RÉDACTION / ADVISORY BOARD

Zhores Alferov (Russia), Kurt Binder (Germany), Panayot Bonchev (Bulgaria), Jonathan M. Borwein (Canada), Carlo Doglioni (Italy), Friedrich Ehrendorfer (Austria), Yachko Ivanov (Bulgaria), Lucien Diego Lod (Belgium), Vladimir Ovcharov (Bulgaria), Maria Papasova (Bulgaria), Stoycho Panchev (Bulgaria), Nikola Sabotinov (Bulgaria), Tharwat Tadros (England), Tsvetan Tsvetkov (Bulgaria), Bojidar Curcic (Serbia)

Редактор Р. Радославова Rédacteur R. Radoslavova

Section of Mathematics is indexed and reviewed in Zentralblatt für Mathematik, Germany

"Journal Citation Reports 2008", published by Thomson Reuters, reports that the current Impact Factor for 2007 of "Comptes rendus de l'Académie bulgare des Sciences" is 0.106

"Comptes rendus de l'Académie bulgare des Sciences" is indexed in SCOPUS

Основано през 1948 г. от академик Г. Наджаков Fondée en 1948 par G. Nadjakov, membre de l'Académie

- © Българска академия на науките, 2009
- © Bulgarian Academy of Sciences, 2009

Prof. Marin Drinov Academic Publishing House Acad. Georgi Bonchev Str., bl. 6 1113 Sofia, Bulgaria Published in January, 2009 www.baspress. com

### Доклади на Българската академия на науките Comptes rendus de l'Académie bulgare des Sciences

Tome 62, No 1, 2009

#### CONTENTS

#### **MATHEMATICS**

- 1. Alexander Arhangel'skii. On a Convergence Property . . . . . . . . p.5
- 2. Vesselin Drensky, Jie-Tai Yu. Dimension of Automorphisms with Fixed Degree for Free Algebras of Nielsen Schreier Varieties . . . . . . . . . . . . p.9
- 3. Vladimir P. Kostov. A Realization Theorem about the Schur-Szegö Composition for Entire Functions . . . . . . p.17
- 4. Toshko Boev. A Solution-Formula to Interface Electrostatics of Gas-Liquids p.23

#### **PHYSICS**

#### BIOLOGY

- 7. Gergana Deevska, Ilia Bankov, Mariana Nikolova-Karakashian. Acid Sphingomyelinase Activity Regulates de novo Sphingolipid Synthesis in Liver through a Negative Feedback Mechanism . . . . . p.49
- 8. Maria Dimitrova, Zhana Mitrovska, Veneta Kapchina-Toteva, Evgeniya Dimova, Stephka Chankova. Testing of Polluted Air Samples for Genotoxic Potential Using Chlamydomonas reinhardtii . . p.57

9. Kalina Racheva, Angel Vassilev. Human S-Cone Vision. Effect of Stimulus Duration on the Increment and Decrement Thresholds . . . . . . . . . p.63

#### GEOLOGY

- 10. Vojo Mirčovski, Orce Spasovski. Metamorphism of the Glaucophane- and Magnesioriebeckite-Bearing Metamorphic Rocks in the Gostivar Vodno Zone, North-Western Macedonia . . . . . . . . p.69
- 12. Athanas Chatalov. Primary and Secondary Fenestral Porosity in Middle Triassic Subtidal Grainstones from the Belogradchik Strip, NW Bulgaria. Implications for Unconformity-Related Diagenesis . . . p.85

#### SPACE RESEARCH

13. Atanas Atanassov. An Analytical Method for Calculating the Satellite Bow Shock/Magnetopause Interception Positions and Times . . . . . . . . . . p.97

#### **MEDICINE**

14. Krasimir Dragoev, Maria Sredkova, Svetlana Pachkova, Valentina Edreva, Valentina Popova, Hristina Hitkova, Sashka Mihaylova. Species Distribution and Susceptibility to Antimicrobials among Clinical Isolates of Shigella species . . . . . p.105

15. Georgi I. Milchev. Stem Cells for Tissue Repair	(TL)-Immunohistochemistry in Hamster Brain p.131  AGRARIAN SCIENCES  18. Nadka Naidenova, Roumiana Vassilevska-Ivanova. Supaeromaculata, a Pea Phenotype with Leaflet Dentation and Insecatus Leaves p.135			
	*			

## Доклади на Българската академия на науките Comptes rendus de l'Académie bulgare des Sciences

Tome 62, No 1, 2009

*GEOLOGIE* 

Minéralogie et géochimie

# NEW DATA ON THE MINERALOGY AND GEOCHEMISTRY OF THE STRELCI MOLYBDENUM ORE DEPOSIT, WESTERN MACEDONIA

Orce Spasovski, Vojo Mirčovski

(Submitted by Corresponding Member I. Zagorchev on November 14, 2008)

#### Abstract

The paper presents the results of the latest studies carried out on the Strelci molybdenite deposit situated in the western part of Macedonia. Investigations included microscope and electronic microprobe that offered new understanding on the mineral composition and the paragenetic relationships of the main ore minerals and data on the chemical composition of molybdenite. Analyses carried out with electronic microprobe indicate that it is pure molybdenite whose chemical composition is close to the theoretical one [1]. Very small amounts of Cu, Fe, Se were also found as admixtures. The investigations contributed to the understanding of the endogenous alterations and on the origin of the deposit.

**Key words:** deposit, Strelci, mineral composition, molybdenite, pyrite, skarn, hornfels, alkali metasomatosis

Introduction. The Strelei molybdenite deposit is situated in the vicinity of the village bearing the same name, 6 km north-east of Kičevo (Fig. 1). The deposit has been known since 1905. The earliest investigations were carried out in 1959 [2]. Aeromagnetic investigations in the area were carried out in 1960 [3] and the geological map was compiled in 1966 [4]. Systematic studies started in 1966, and with some interruptions, were completed in 1972. They included detailed geological mapping, metals prospecting, joint electric and magnetic measurements as well as drillings. Geological, geophysical and geochemical activities were carried out [5–8], and Popović and Antonović [9] made petrologic examinations.

Geological setting. Within the phyllitoid rocks, which are widespread in western Macedonia, on a confined area of about 1 km<sup>2</sup>, various magmatic rocks

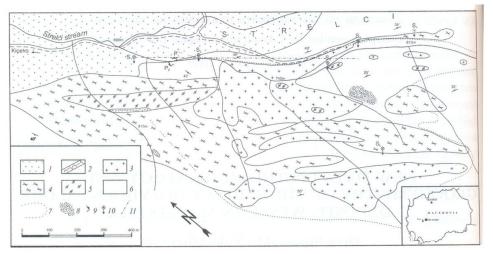


Fig. 1. Geological map of molybdenite ore deposit Strelci. 1 – Alluvial and terrace deposits; 2 – Quartz vein; 3 – Granitoid rocks; 4 – Metamorphosed rhyolite porphyre; 5 – Gabbroid rocks; 6 – Sericite-chlorite schists; 7 – Limit of mineralization and alteration processes; 8 – Skarn (mostly with magnetite and pyrite); 9 – Adit; 10 – Inclined drill hole; 11 – Axis of block-diagram (Fig. 2)

of complex relationships, multiple alterations and ore mineralisation have been revealed (Fig. 1). The rocks were affected by orogenic movements and are intensely deformed and schistified. Alterations of variable intensity developed over the magmatic rocks. Such alterations make identification of primary rock characteristics fairly difficult. Continuous transitions from sericite-chlorite, actinolite-chlorite schists, amphibolite and gabbros were revealed, although they had been regarded as various sedimentary and magmatic rocks. Rhyolites are very schistose so that under a microscope they can be distinguished only by the presence of their typical volcanic quartz. Granitoid rocks had also been occasionally and intensely schistified and their contacts cannot be seen easily due to the metasomatic processes. Large amount of biotite has developed due to the metasomatic alterations not only on the contact with granites but within all rocks including gabbroids.

Sericite-chlorite schists are built up of variable amounts of sericite, chlorite and quartz. Muscovite and feldspars are less common. Actinolite-sericite rocks can only be found in thin sections. They have occasionally been enriched in quartz and grade into quartzite schists.

Gabbroid rocks include a series of rocks such as saussuritized gabbro to amphibolite and actinolite-sericite schists that intruded earlier clastic sedimentary rocks. Later, they underwent intense deformation and recrystallisation processes. The rock most similar to gabbro contains sericitised basic plagioclase, pale green amphibole (often chloritised), uralite (developed over pyroxene), ore minerals,

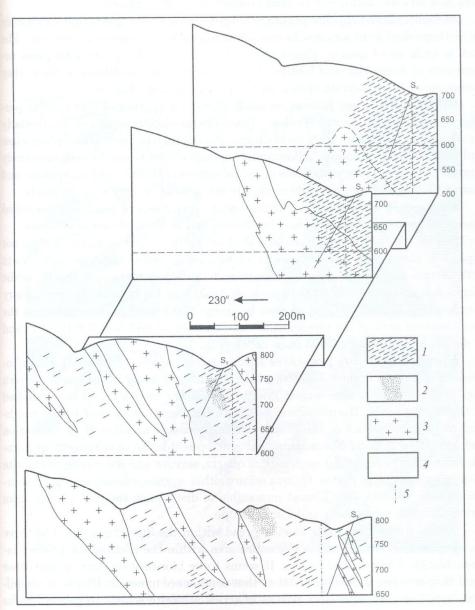


Fig. 2. Block-diagram of the molybdenite ore deposit Strelci. 1 – Mineralization, 2 – Skarn, 3 – Granitoid rocks, 4 – Crystalline schists and other rocks, 5 – Axis of block-diagram

sphene, leucoxene and apatite. Actinolite schists are built up of actinolite, epidote and sericite, and occur as final product of metamorphism.

Metamorphosed rhyolite porphyry is light cream to pale green that can hardly be distinguished from sericite-chlorite schist during microscopic observations. The rock is built up of quartz, plagioclase and potassium feldspar with frequent occurrences of muscovite and biotite. Apart from the sericite-chlorite schists, they occupy most of the terrain shown on the geological map (Fig. 1).

Granitoid rocks are present as small intrusions of granites and granite porphyry of light grey to greenish colour. The rocks are slightly schistose, particularly on the contact. They are built up of quartz, potassium feldspars, acidic plagioclase and muscovite. Occasionally, idiomorphic crystals of biotite can be seen in entirely altered rocks. Secondary minerals occur as sericite, chlorite, seldom epidote and quartz. Zircon, sphene and seldom apatite are present as accessory minerals.

Endogenic alterations. The endogenic alterations of the rocks described consist of formation of skarns and hornfelses, and in alkaline metasomatosis.

Skarns (skarn-like rocks) are indicated by a mineral paragenesis which is not typical of skarn, but consists mostly of magnetite, pyrite, epidote and quartz with certain amount of garnet, chlorite and calcite. Potassium feldspar, acidic plagioclase and seldom biotite are present. Apatite and sphene occur as accessory components. The mineral paragenesis occurs at two places: on the surface in the south-eastern part of the terrain at the same height of drill hole S-6 (Fig. 1) and in drill hole S-3 from 52 to 63 m in depth (Fig. 2).

Hornfels-forming processes affected schists relatively unevenly within intrusions of granite bodies. The largest hornfels masses occur in the south-western part of the deposit where largest granite masses are intruded and now exposed at the higher levels. Hornfels processes have not been determined in the north-eastern peripheral part of the granites. The process is manifested as silification and formation of band-like texture that made possible the development of hornfels built up of fine-grained aggregate of quartz, sericite and muscovite or chlorite with large amount of pyrite. Quartz occurs either as fine-grained aggregate accumulation or veinlets. It is almost impossible to distinguish the rock clearly from sericite-chlorite schist even under microscope.

Alkali metasomatosis is widespread within the Strelci granite. The three major minerals that prevail in the entire area within the alkalisation process include biotite, feldspar and quartz. It seems to be biotitisation, but on the other hand they are quartz-feldspar veinlets that contain ore minerals. Biotite is ubiquitous, within granite and large parties of sericite-chlorite schists to gabroid rocks where it is less present. Microscopically feldspatisation can be seen mostly as quartz-feldspar veins and 1 to 2 cm thick veinlets that penetrate schistose parties on the contact with granite. Feldspar is pink. Microcline, some pertite and twinned plagioclase have been found under the microscope. Biotitisation of a sericite-chlorite schist has been determined in a vein. Apart from these minerals,



Fig. 3 a, b. Occurrence mode of some ore minerals in the Strelci deposit and location of spots analysed. a) Mo – flaky molybdenite, Ru – allotriomorphic grain-like rutile, b) Mo – flaky molybdenite aggregate

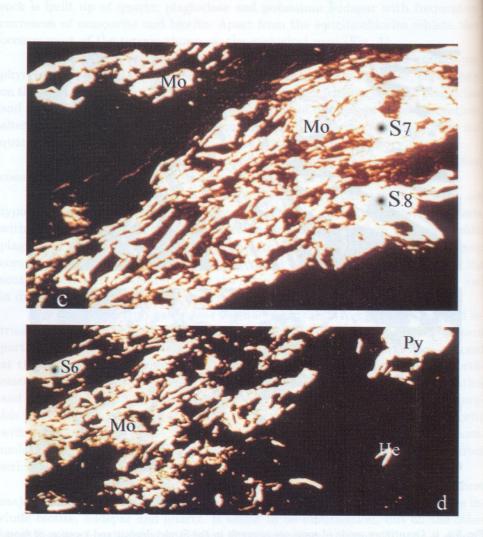


Fig. 3 c, d. Occurrence mode of some ore minerals in the Strelci deposit and location of spots analysed. c) Mo-elongated flaky molybdenite aggregate, d) Mo-flaky molybdenite, Py-allotriomorphic grain-like pyrite, He-platy hematite

calcite and pyrite also occur in the veins and veinlets along with molybdenite. Individual feldspar and quartz grains occur on the contact with granite. Quartz-feldspar veins and veinlets are most common in the northern part of the area, in the deeper parties with schists close to the contact with granites that can be seen best in drill hole S-2.

Apart from quartz and feldspar, quartz veins and molybdenised veinlets have been determined. They were formed during the same cycle with the quartz-feldspar veins and veinlets, the only difference being that they do not contain feldspar. In the northern peripheral part of the granite, on the contact with gabbro and rhyolite, a 2 to 3 m thick quartz vein has been found with significant amount of pyrite in which molybdenite was not determined.

Mineral composition and mineral paragenesis. The ore mineralization in the Strelci molybdenite deposit consists almost exclusively of molybdenite. Molybdenite occurs as individual grains (Fig. 3) and nests of irregular shape or as fine veinlets and coatings. Mechanical coatings are also characteristic of molybdenite that make it easy to be noticed when it is in minor concentrations.

The chemical composition of molybdenite was determined with electronic microprobe. The results are given in Table 1.

Examinations were carried out at the laboratory of electronic microanalysis at the Geological Institute in Bratislava with JEOL 733 SUPERPROBE and in EDS system.

The table shows that the molybdenite is pure (Mo contents being from 53.58 to 58.21%). Small amounts of Cu (from 0.42 to 0.61%, Fe (from 0.14 to 0.16%), Se (from 0.30 to 0.35%) and Te (from 0.12 to 0.13%) occur as admixtures.

T a b l e 1 Quantitative X-ray spectral analyses of molybdenite of Strelci (%)

Element	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8
Diement	D-1	15-2	5-5	5-4	2-0	5-0	5-1	5-0
S	41.95	45.52	43.30	41.36	44.82	44.15	42.82	42.35
Fe	0.00	0.00	0.10	0.00	0.00	0.00	0.10	0.11
Cu	0.00	0.48	0.60	0.42	0.56	0.00	0.55	0.41
Mo	57.31	53.10	55.70	58.21	54.10	55.31	56.20	57.13
Te	0.12	0.00	0.00	0.00	0.00	0.10	0.00	0.00
Se	0.33	0.00	0.30	0.00	0.00	0.31	0.32	0.00
Total	99.70	99.10	100.00	99.99	99.48	99.87	99.99	100.00

Figure 3 shows the position of the mineralised spots and the occurrence mode of molybdenite. It shows also the flaky molybdenite aggregate, allotriomorphic grain-like rutile, allotriomorphic grain-like pyrite and platy hematite.

The most common mineral is pyrite. It occurs in association with molybdenite. However, the paragenetic relations are undistinct. Magnetite and rutile also occur in the same heterogene relationships. Chalcopyrite is rarely observed, sphalerite being quite rare, as well. During microscopic studies antimonite, associated with homogeneous pyrite, has been determined 98 m in depth in drill hole S-1. Molybdenum ochre often occurs in the adits.

Molybdenite occurs in all rocks, in hornfels schists, in garnet and along the contacts with hornfels schists. Molybdenum distribution is uneven (Fig. 2). The highest contents, fairly evenly distributed, have been discovered in the northern-most part of the area. The even distribution most probably extends as far as drill hole S-2 where molybdenum concentrations are very low. In the drill holes that follow mineralisation does not occur in regular patterns and the mean molybdenum content is as that in drill hole S-2.

The area of S-1 drill hole with the adits is the most promising part regarding molybdenum amounts. In a 20 m interval in drill hole S-1, the mean molybdenum content amounts to 0.08%. Renium content amounting to  $25~\rm g/t$  was found in the molybdenum concentrate of adit P-1 with 30% molybdenum.

Based on investigations carried out so far it can be inferred that the mineralised zone may extend under the Quaternary cover at least 300 m from the adit towards S-3. Since drill hole S-1 has not reached the depth of the mineralised zone, investigations and drillings to depth should continue. It can also be inferred that mineralisation occurs in the upper parts of the granite mass dipping towards north-west.

Different mineral parageneses have been determined for the skarns: magnetite and pyrite with non-metallic minerals mentioned earlier. Chalcopyrite, hematite and martite seldom occur. Pyrrhotite and pyrite inclusions also seldom occurs. Low amounts of molybdenite have been found. Feldspar also occurs, although it is well known that it is not a part of this paragenesis.

Chemical analysis indicated increased amounts of copper (much higher than those of molybdenite), unlike the other portions outside the skarn parties where molybdenum amounts are much higher than those of copper. It has also been determined that copper and molybdenum contents in the entire region studied are almost the same and below economic categories except for molybdenum in some areas.

Two mineral parageneses related to different phases of formation can be distinguished in the Strelci site. The skarn mineral paragenesis present as pyrite, magnetite and chalcopyrite with epidote, garnet and quartz as accompanying minerals, is initially formed. The second mineral paragenesis includes molybdenite as a unique mineral with frequent pyrite occurrence, whereas quartz, feldspar, calcite and rutile occur as accompanying non-ore minerals.

The Strelci molybdenum deposit is one of the most important deposits in Western Macedonia. Its composition is similar to the Mačkatica and Climax de-

posits that belong to the high temperature hydrothermal deposits or quartzmolybdenum stockwork-impregnation deposits.

Conclusion. Based on the above evidence, it can be inferred that in the granitoid belt in Western Macedonia multiple intrusion of granitoid rocks took place during Early and Late Palaeozoic and Middle Mesozoic times. Granite intrusion was accompanied by release of easy evaporable components consisting of alkalis and heavy metals (Mo, Cu, Pb, Zn).

Molybdenum mineralization is related to small intrusions. Various structural varieties occur within the granites, and a wide halo of contact metasomatic and other alterations is traced.

The granites in the vicinity of Strelci are probably of Carboniferous age. Alkali metasomatic alterations most probably were formed by the influence of the granites of later phases.

Two mineral parageneses related to different phases of formation can be distinguished in the area of the Strelci deposit. The skarn mineral paragenesis present as pyrite, magnetite, magnetite and chalcopyrite with epidote, garnet and quartz as accompanying minerals is older. The second mineral paragenesis includes molybdenite as unique mineral with frequent occurrences of pyrite. Quartz, feldspar, calcite and rutile occur as accompanying gangue minerals.

Molybdenite chemical composition is constant as seen from the high Mo contents. At the same time it is a pure molybdenite with low amounts of Cu, Se and Fe.

The conclusions call for thorough examinations of existing data. Some have not been included in this analysis (geochemical investigations of granitoids, gravimetric and geometric investigations, etc.). Additional examinations related to the determination of the absolute age of granitoids, study and discovery of basic tectonic structures in the central part of Western Macedonia are also necessary.

#### REFERENCES

- CVILEVA T. N. Handbook for determination of ore minerals in reflected light. Moscow, Nedra, 1988 (in Russian).
- [2] STOJANOVIĆ M. Report on the prospect of molybdenite ore showings at the village of Strelci in 1960. Fund of Geol. Inst Skopje, 1961 (in Macedonian).
- [3] VUKAŠINOVIĆ S. Report on the aeromagnetic studies in Macedonia in 1960. Fund of Geol. Inst Skopje, 1961 (in Macedonian).
- [4] IVANOVSKI T. Annual report on the geological mapping in 1966. Fund Inst Prosp. Nucl. Raw Materials, Belgrade, 1968 (in Serbian).
- [5] ANTONOVIĆ A., T. JANČIĆ. Report on the geol. and geophys. Studies in the area of Berikovo-Tuin i Strelci in 1970.
- [6] JAKOVLEVIĆ M., I. VASIĆ. Annual report on regional geological studies in western Macedonia. Fund Inst Prosp. Nucl. Raw Materials, Belgrade, 1972 (in Serbian).

[7] JANČIĆ T., R. POPOVIĆ, A. ANTONOVIĆ. Report on studies in western Macedonia in the area of Makedonski Brod-Samokov, lokalities Strelci, Berikovo, etc. Fund Inst. Prosp. Nucl. Raw Materials, Belgrade, 1967 (in Serbian).

[8] POPOVIĆ R., T. JANCIĆ. Report on studies in western Macedonia, localities Streld, etc. Fund Inst. Prosp. Nucl. Raw Materials, Belgrade, 1968 (in Serbian).

[9] POPOVIĆ R., A. ANTONOVIĆ. Molybdenite ore deposits Strelci and Vrutok in western Macedonia. Proceedings Inst. Geol. Ore Prospection of Nuclear and other Raw Materials, 1973, No 8, 113–128, Belgrade (in Serbian).

Department of Mineral Deposits
Faculty of Mining, Geology and Polytechnic
"Goce Delčev" University – Štip
89, Goce Delčev
2000 Štip, Republic of Macedonia
e-mail: orce.spasovski@ ugd.edu.mk
e-mail: vojo.mircovski@ugd.edu.mk