Actinolite-Phengite-Chlorite Metasomatites From The Toranica Pb-Zn Ore Deposit In Macedonia

Aktinolit-Phengit-Klorit metasomatiti v Pb - Zn rudišču Toranica v Makedoniji

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Received: October 25, 2006 **Accepted:** December 10, 2006

Abstract: In this investigation we focused on the contact metamorphic-metasomatic products in the Toranica Pb-Zn ore deposit. In the regionally metamorphed parts of the deposit we detected sericite-chlorite sub-facies, in the frame of the greenschist facies with its very common parageneses: chlorite+K-feldspar, chlorite+epidote+actinolite and chlorite+quartz. The presence of phengite indicated that the metamorphic-metasomatic processes took place under a pressure of about 5 kilobars and at a depth of 18 - 19 km. The absence of wollastonite, diopside, hedenbergite and hornblende suggested a low-temperature, < 420 ºC, character for these contact metasomatic processes.

Povzetek: Članek obravnava nekatere značilnosti kontaktno metamorfno-metasomatskih procesov v Pb - Zn rudišču Toranica. Mineralna parageneza in prisotnost phengita v kontaktno metamorfni coni rudišča kaže, da so kontaktno metamorfni procesi potekali pri pritisku približno 5 kilobarov in v globini približno 18-19 km. Temperatura njihovega nastanka, kakor tudi temperatura kristalizacije rudnih mineralov najverjetneje ni presegla 420 ºC. To potrjuje tudi odsotnost wolastonita, diopsida, hedenbergita in rogovače, ki so značilni za skarne nastale pri višji temperaturi.

Key words: contact metamorphism, metasomatites, skarns, Pb-Zn ore deposit Toranica, Macedonia

Ključne besede: kontaktna metamorfoza, metasomatiti, skarni, Pb-Zn rudišče Toranica, Makedonija

INTRODUCTION

The Toranica Pb-Zn ore district is situated in northeastern Macedonia. It belongs to the Sasa-Toranica ore zone and shows the metallogenic features that are characteristic of this zone. The Toranica ore field occupies an area of approximately 30 km^2 with a vertical extent of mineralization between 1300 and 1800 meters. The ore deposit was discovered in 1974 and the exploration period ended in 1981. After the preparation for the

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exploita tion, which lasted until 1988, the deposit began with trial production (BOGOJEVSKI & GATEOVSKI, 1990). The ore reserves were estimated to be 12.6 million tones, with 4.47 wt % of Pb, 2.93 wt % of Zn and 20 μg g^{-1} Ag (DOBROVOLSKAYA & STANKOVSKI, 1997). The mine was in operation untill the beginning of 2000, butthen in 2005 the mining activities began again. Although many researchers, including the first author of this paper, have extensively investigated the Torrance Pb-Zn ore deposit, only a few data on the alteration zones associated with the mineralization are available so far. Therefore, the purpose of this study was to assess the contact metamorfic metasomatic product related to the formation of the Toranica deposit and to provide useful information for a further study of the origin and evolution of the fluids and rocks involved in the contact metamorphism.

Geological setting

The Toranica lead-zinc deposit is located in the Sasa-Toranica mining district in the Osogovo Mountains, eastern Macedonia (Figure 1). The geology of the Toranica ore deposit comprises various rocks of metamorphic origin and igneous rocks of the Tertiary age. The most abundant lithologies in the area are believed to be closely associated with mineralization. The ore bodies of the Toranica deposit consist of peneconcordant tabular ore bodies that wedge out owing to the transition to non-mineralized metasomatites and lens-sheeted ore bodies. The most important economic mineralization is closely related to quartz-graphite schists. The ore consists mainly of galena, sphalerite, chalcopyrite and pyrite. In addition, a detailed study using transmitted and reflected light as well as X-ray diffractometry and both energy dispersive and wavelength dispersive systems revealed the more complex mineralogy of the deposit: galena, sphalerite, chalcopyrite, pyrite, pyrrhotite, magnetite, martite, bornite, enargite, tetrahedrite, marcasite, barite, native gold, cubanite and native bismuth. Geochemical analyses also showed very high concentrations of Cu, Bi, Sb, Ag, Au and Cd (BOGOJEVSKI, 1990; BOGOJEVSKI & GATEOVSKI, 1990; SERAFIMOVSKI & ALEKSANDROV, 1995; SERAFIMOVSKI, et al., 1997; SERAFIMOVSKI, et al., 1998; SERAFIMOVSKI, et al., 1992; STANKOVSKI, 1997).

The productive quartzgraphite schist series, which occupies the central part, hosted the main Pb-Zn mineralization, mostly related to the typical metasomatic skarns formed along the contact zone between the limestone marbles (cipolines) and the felsic intrusions. The overall occurrence of the skarns is concordant with that of the host rock. This lithological unit containing carbonate rocks was susceptible to metasomatic processes, the development of skarns and mineralization, which is genetically closely related to quartzlatite intrusions of the Tertiary age (24.5 Ma). The location of the Pb-Zn orebodies is controlled by bedding-parallel faults so that their shape and occurrences vary with the geometry of the faults, and is generally parallel to the bedding of the host rocks (Figure 2). Figure 2 shows the elongation and the depth of the productive series with three ore bodies and their contacts with gneiss and quartzlatite. The ore bodies can be followed below a level of 1400 m (see drill hole SD-86), which must be taken into account during the further exploitation.

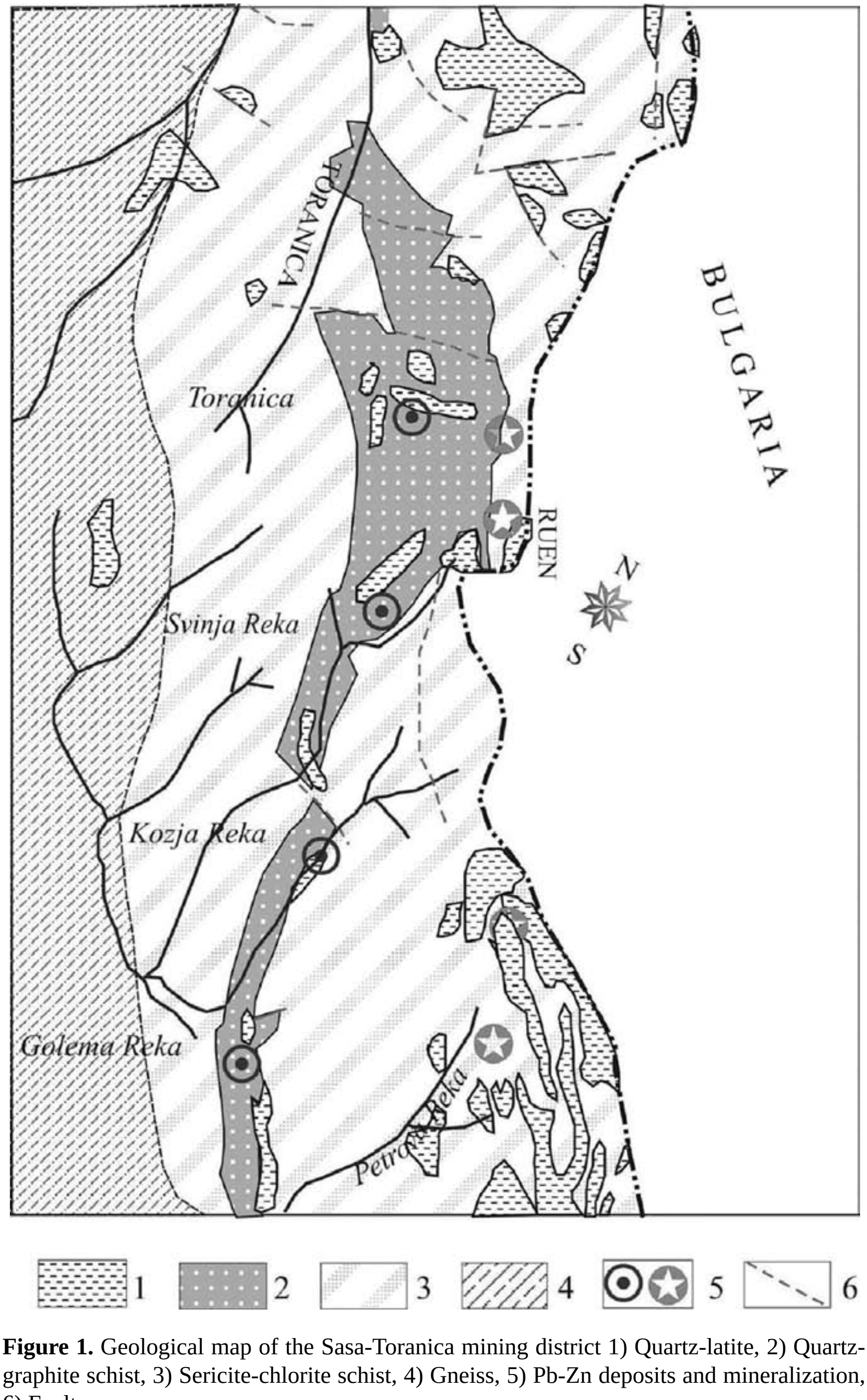

Figure 1. Geological map of the Sasa-Toranica mining district 1) Quartz-latite, 2) Quartz-graphite schist, 3) Sericite-chlorite schist, 4) Gneiss, 5) Pb-Zn deposits and mineralization, 6) Fault

Slika 1. Geološka zgradba rudonosnega območja Sasa-Toranica. 1) kremenovi latiti, 2) kremenovo-grafitni skrilavci, 3) sericitno-kloritni skrilavci, 4) gnajs, 5) svinčevo-cinkovo

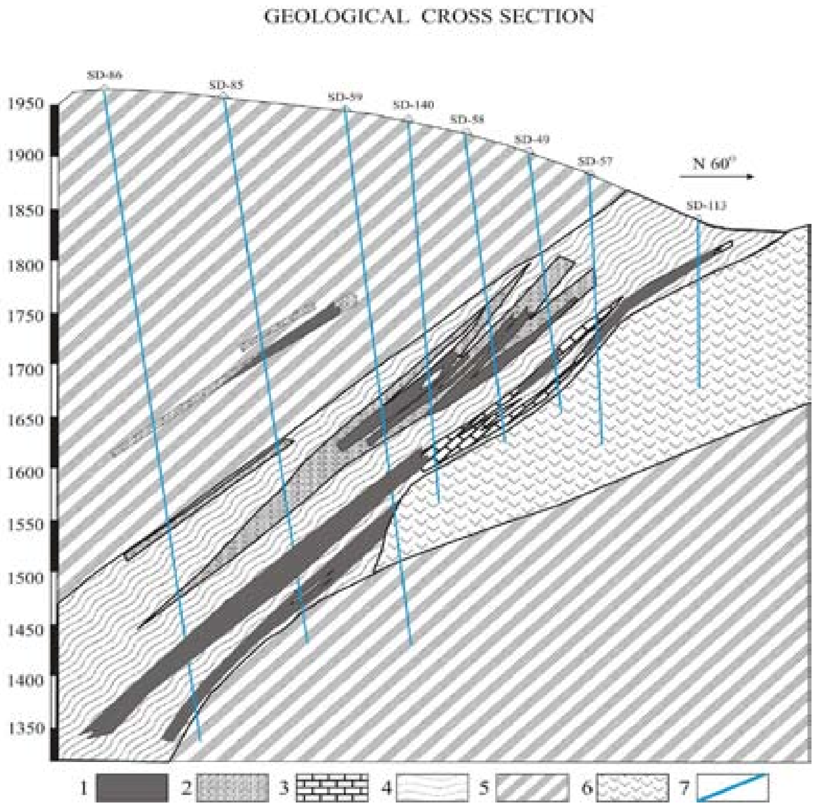

Figure 2. Geological section through the central part of the Toranica ore deposit 1) Ore body, 2) Pb-Zn mineralization, 3) Cipolino marble, 4. Quartzgraphite schist, 5) Gneiss, 6) Quartzlatite, 7 Drill hole

Slika 2. geološki profil skozi osrednji del rudišča Toranica 1) rudno telo, 2) Pb-Zn mineralizacija, 3) cipolinski marmorji, 4) kremenovo-grafitni skrilavci, 5) gnajsi, 6) kremenovi latiti, 7) vrtine

The determined contact-metamorphic-metasomatic products are also related with the schists and skarnoids series.

MATERIALS AND METHODS

In order to evaluate the contact-metasomathic phases related to Pb-Zn mineralization within the Toranica Pb-Zn deposit, 51 samples for petrographic and polished sections were collected during 2004 and 2005 at different levels in the Toranica mine. Most of the samples were taken at the 1600-m level, close to the contact of the quartz-latite dykes with quartz-graphite-schists, where the economically most important mineralization was located. Thirty-three samples were taken from the ore bodies, while 18 specimens sampled the rocks of the contact zone. All the samples were prepared for further analyses in the laboratory of the Faculty of Mining and Geology, Štip, Republic of Macedonia. After a detailed petrographic and ore microscopy study 12 samples of the host rocks and 6 polished samples were selected for further electron microprobe analyses. The electron-microprobe analyses were performed in the Laboratory of Petrology and Geochemistry, EUROTEST-CONTROL PLC, Sofia, Bulgaria. Quantitative X-ray spectral micro-analyses and second-electron photographs with a COMPO regime and the distribution of the elements within the minerals were performed with a Super probe 733 (JEOL, Japan). The following standards were used: for Bi, synthetic Bi_3S_3; for Cu, Fe and S, synthetic $CuFeS_2$; for Se, synthetic PbSe; and for Pb, synthetic PbS (I = 0.8 A, U = 25kV). A TUR-M-60 device connected to a RKD-57 camera was used to make the X-ray structural analyses of the individual minerals.

Results and discussions

The contact metamorphic processes in the Toranica ore deposit, as well as the alteration related to the ore mineralization, has been very rarely reported in the literature. There were practically no data concerning the processes of contact metamorphism and the relations between the newly formed metasomatites as a direct consequence of the contact-metamorphic-metasomatic processes and reactions that took place along the contacts between the different lithological units. For example, between the sub-volcanic intrusions and various schists, gneisses, as well as gneiss-schist, gneiss-volcanite, gneiss-carbonate and schist-carbonate where crystallized various rare minerals and mineral phases. The study of such processes and reactions is important for a better understanding of the multistage evolution of the metamorphic complexes and ore genesis in the broader area of the Osogovo Mountains.

The results of our preliminary study showed that the mineral assemblages of quartz-graphite schist and gneiss correlated well with those of the chlorite-sericite sub-facies of the greenschist facies of the regional metamorphism and indicated a temperature range between 320 and 350 ºC. This is also suggested by the mineral assemblages of chlorite + K-feldspar and chlorite + quartz. The presence of phengite with an elevated content of Mg, Fe and Si (Table 1) together with K-feldspars in altered gneiss indicated according to a Massonne and Schreye barometer (1987) that the pressure of the regional metamorphism was about 5 kbar, while the depth was not greater than 18-19 km. It is interesting to note that minerals with an increased content of Mn were found in the metamorphosed sedimentary rocks, which indicated that these rocks most probably served as a source of manganese during the contact metasomatic ore-forming processes. The contact metasomatic processes related to the quartzlatite dyke intrusions were basically low temperature in character. This is indicated by the absence of any of the most typical scarn minerals.

Analyses of the samples from the contact zone between the quartzlatite dykes and gneisses and/or schists revealed the presence of epidote, chlorite, calcite, muscovite-phengite and quartz. The chemical composition of some of these minerals obtained using microprobe analyses is presented in Tables 1-3.

Typical mineral assemblages in metamorphosed rocks of the Toranica ore deposit are illustrated in ACF diagrams (Figure 3 – A,B,C,D). This mineral assemblage is of primary character and shows no replacement

Table 1. Microprobe analyses of Mn-bearing actinolite and phengite from the regional and contact metamorphic rocks of the Toranica ore deposit (in %)
Tabela 1. Sestava Mn-aktinolita in phengita v (%) določena z elektronskim mikroanalizatorjem

Mineral	Actinolite			Phnengite					
Sample	173/2			173/3		173/5	173/6		173/90
SiO_2	54.56	53.73	54.28	49.11	47.71	48.06	48.87	47.99	48.97
TiO_2	0.10	0.06	0.09	0.32	0.45	0.32	0.06	-	0.38
Al_2O_3	0.85	0.65	0.93	29.44	28.05	31.50	30.47	30.16	32.14
FeO	15.28	15.46	15.58	5.22	6.22	4.47	4.61	5.67	2.56
MnO	3.10	3.44	3.29	0.19	0.08	-	0.12	0.17	0.11
MgO	12.32	12.03	12.32	1.03	1.91	1.05	0.85	0.58	1.65
CaO	11.25	12.24	11.74	0.01	-	0.05	0.11	-	-
Na_2O	0.16	0.17	-	0.25	0.04	0.49	-	-	0.42
K_2O	0.06	0.05	-	10.01	10.64	9.78	10.57	10.65	9.75
Total	97.68	97.83	98.23	95.58	95.10	95.72	95.66	95.22	95.98
Si	8.00	7.93	7.95	3.30	3.26	3.22	3.28	3.27	3.23
Al_{IV}	-	0.07	0.05	0.70	0.74	0.78	0.72	0.73	0.76
Al_{VI}	0.14	0.04	0.11	1.64	1.52	1.70	1.69	1.68	1.73
Ti	0.01	0.01	0.01	0.16	0.02	0.02	-	-	0.01
Fe	1.87	1.91	1.91	0.29	0.36	0.25	0.26	0.32	0.14
Mn	0.39	0.43	0.41	0.01	-	-	0.01	0.01	-
Mg	2.69	2.65	2.69	0.10	0.19	0.10	0.08	0.06	0.16
Ca	1.77	1.94	1.84	-	-	-	0.01	-	-
Na	0.04	0.05	-	0.03	0.01	0.06	-	-	0.05
K	0.01	0.01	-	0.86	0.93	0.84	0.91	0.92	0.82
X_{Fe}	0.41	0.42	0.41	-	-	-	-	-	-
X_{Na}	-	-	-	0.03	0.01	0.07	-	-	0.06

Table 2. Microprobe analyses of Mn-bearing calcite, albite and K-feldspar from the regional and contact metamorphic rocks of the Toranica ore deposit (in %)
Tabela 2. Sestava Mn-kalcita albita in K glinenca (v %) iz regionalno in kontaktno metamorfnih kamnin iz rudišča Toranica določena z elektronskim mikroanalizatorjem

Mineral	Calcite						Ab	Kfs
Sample	173/1	173/2	173/3	173/4	173/6		173/3	173/3
SiO_2	-	-	-	-	-	-	69.05	63.81
TiO_2	-	-	-	-	-	-	-	-
Al_2O_3	-	-	-	-	-	-	19.29	18.85
FeO	0.47	0.96	0.33	0.62	0.57	0.25	0.09	-
MnO	3.32	6.02	1.93	2.04	3.48	3.39	-	-
MgO	0.16	0.21	0.01	0.28	-	0.09	0.03	-
CaO	53.38	49.00	54.98	53.80	52.98	52.85	0.13	-
Na_2O	-	-	-	-	-	-		
K_2O	-	-	-	-	-	-		
Total	57.33	56.19	57.25	56.74	57.03	56.58	99.97	99.97
X_{Na}	-	-	-	-	-	-	0.99	0.04

Table 3. Microprobe analyses of Mn-bearing chlorites and epidotes from the regional and contact metamorphic rocks of the Toranica ore deposit (in %)

Tabela 3. Sestava Mn-klorita in epidota (v %) iz regionalno in kontaktno metamorfnih kamnin iz rudišča Toranica določena z elektronskim mikroanalizatorjem

Mineral	Chl							Ep						
Sample	173/1	173/2	173/3	173/4	173/5	173/9C		173/1	173/3	173/4	173/6		173/9A	173/9C
SiO_2	28.36	31.39	27.02	29.48	24.28	25.67	26.52	38.33	38.02	38.52	38.69	38.51	38.24	38.49
TiO_2	-	0.02	-	0.16	0.03	0.16	-	-	0.01	0.03	-	0.06	-	0.02
Al_2O_3	16.88	14.12	20.03	20.87	21.75	21.32	22.01	24.22	24.47	24.78	25.66	24.99	23.56	26.41
Fe_2O_3	-	-	-	-	-	-	-	12.01	12.44	11.14	10.02	11.36	12.90	9.11
FeO	23.49	23.63	25.21	15.55	36.41	24.05	21.08	-	-	-	-	-	-	-
MnO	4.16	1.98	2.01	1.65	0.74	4.00	4.68	0.44	0.44	0.87	0.51	1.35	1.52	0.94
MgO	14.95	16.69	14.25	20.93	5.28	14.12	13.98	0.06	0.11	0.03	-	0.17	-	-
CaO	0.20	0.40	0.28	0.36	-	0.12	0.08	23.11	22.74	22.31	22.76	21.78	21.65	23.19
Na_2O	0.27	0.17	0.09	0.13	-	0.17	0.12	-	-	-	0.11	-	-	0.07
K_2O	0.03	0.09	0.02	0.02	0.09	0.04	-	0.01	-	0.03	0.10	0.24	-	0.03
Total	88.34	88.49	88.91	89.12	88.58	89.65	88.47	98.18	98.23	97.71	97.85	98.46	97.87	98.26
X_{Fe}	0.47	0.44	0.50	0.29	0.79	0.49	0.46	-	-	-	-	-	-	-

by a high-temperature mineral paragenesis. However, minerals typical for the high-temperature skarn facies, such as wolastonite, diopside-hedenbergite and hornblende, were not found during this study. Instead of the wolastonite, calcite and quartz were formed, while instead of the hornblende there was crystallized actinolite, which contains elevated concentrations of Mn with 3.10 to 3.44 % of MnO. Like the actinolite, the calcite also exhibited an increased amount of manganese with the concentration level of MnO in the range of 1.96 to 6.02 % (Table 1 and 2). The elevated content of Mn in these minerals could serve as a source of Mn during the contact-mineralizing processes. In addition, chlorite from the contact metamorphic zone is also a Mn-bearing mineral with MnO in the range 0.74 to 4.16 % (Table 3). The MgO content in the analyzed chlorites ranges from 5.28 to 20.93 %, while the concentration of CaO varies between 0.08 and 0.40 %. Once again, the presence of manganese in concentrations such these could act as a source for this element in the frame of the contact-mineralizing processes.

Ilvaite, a Mn-pyroxene (bustamite) and johansenite, which were also determined during this study of samples from the Toranica mine, are stable at lower temperatures, mostly between 350 and 400 °C, respectively. Based on this we supposed that in the Toranica ore deposit, these minerals most probably crystallized at a relatively low temperature, which did not exceed 400-420 °C. The mineral assemblages found in the samples from mineralized skarns and in the contact zone between the quartzlatite and schists are very similar to those found in regionally metamorphic rocks of greenschists facies. The only difference was that the chlorite of the greenschists facies contains a smaller amount of Fe, while calcite is enriched with Mn, and the only amphibole present is actinolite. These results suggested that the temperatures of formation of the mineral assemblages were not above those characteristic for the regional metamorphism of the greenschists facies.

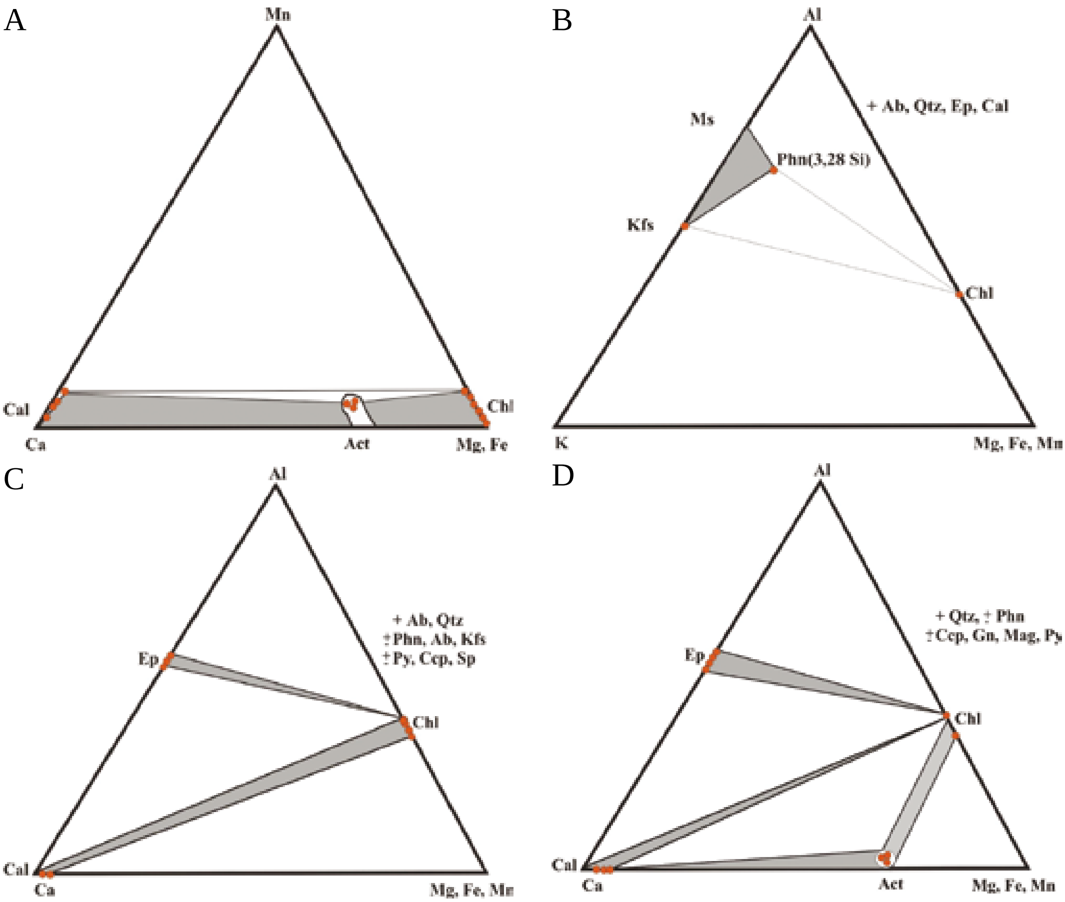

Figure 3. Typical mineral assemblages in contact metamorphic rocks from the Toranica Pb-Zn ore deposit: A cipolino, B metagranites C metamorphosed graphite schist, phylite and metagranite, D contact skarn. The mineral compositions were all measured by electron microprobe

Slika 3. Značilne mineralne parageneze v kontaktno metamorfnih kamninah iz Pb-Zn rudišča Toranica: A cipolino, B metamorfozirani graniti, C metamorfozirani grafitni skrilavci, filiti in metamorfozirani graniti, D kontaktni skarn. Sestava posameznih mineralov je določena z elektonskim mikroanalizatorjem

CONCLUSIONS

Mineral assemblages of actinolite-phengite and sericite-chlorite-epidote facies are a direct result of the contact metamorphic-metasomatic processes that took place in the Toranica ore deposit. They were related to the lithological complex of quartz-graphitic schists containing the Pb-Zn mineralization of economic importance. The mineral paragenesis determined during this study suggested that the temperature of their formation did not exceed the range 320 to 420 ºC. The presence of phengite indicated that metamorphic-metasomatic processes originated under a pressure of about 5 kilobars and at a depth of 18-19 km.

Acknowledgements

This research was financially supported by the Ministry of Higher Education, Science and Technology, Republic of Slovenia (Bilateral Project between Republic of Macedonia and Slovenia for the years 2004-2005), and Geoexp, d. o. o., Tržič, Slovenia. Thanks to Dr. Paul McGuiness for the linguistic corrections.

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