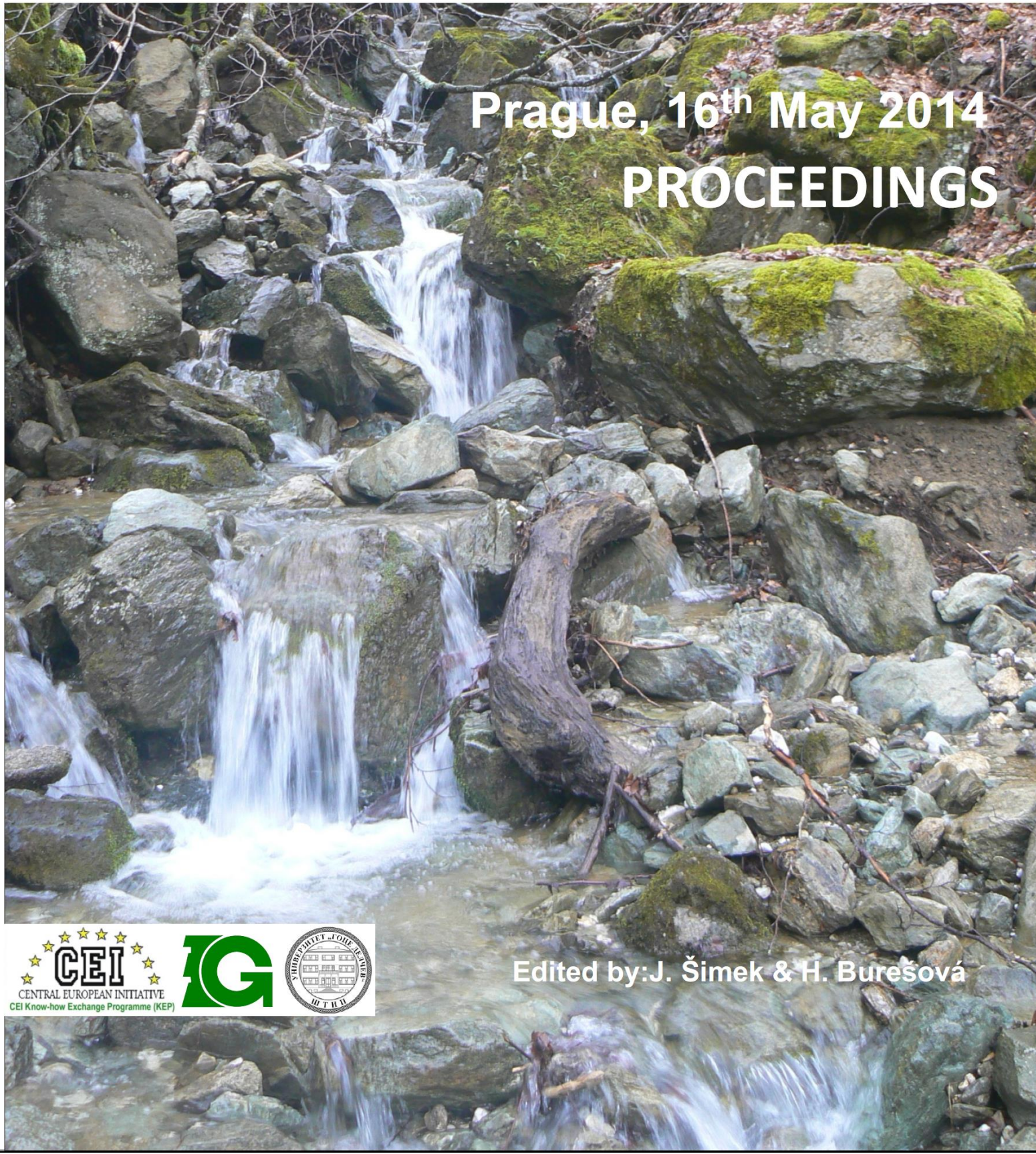
GIS-GEOINDUSTRY, s.r.o., Czech Republic CEI Know-how Exchange Programme

2nd INTERNATIONAL WORKSHOP

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



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MAJOR ORE DEPOSITS IN THE KOZUF METALLOGENIC AREA, R. MACEDONIA

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Abstract: The productive ore mineralization within the Kozuf metallogenic area, mainly, has been related to the Alpine metallogenic epoch while spatial and temporal has been spread during the Cretaceous stage and Pliocene period. During the Cretaceous metallogeny were formed several iron and nickel deposits related to the redeposited lateritic crusts developed over the Jurassic ultrabasic rocks (dunite, harzburgite, lherzolite). The most important lateritic crust mineralizations were determined in the Rzanovo ore deposit (40 Mt so 1.1% Ni), as well as occurrences at Studena Voda, Gradiste, Rakle and Nikodin. During the late Alpine metallogenic epoch in the Kozuf area were formed polymetallic Cu-Au-Sb-As-Tl-Pb-Zn mineralizations in Alshar and Dudica deposits, related to the Pliocene magmatism (6.0-1.8 Ma) and ring-radial structures related to that particular volcanism. Carlin-type gold (> 1 g/t Au), was determined in parts of the Alshar deposit.

Key words: Alpine metallogeny, lateritic deposit, polymetallic mineralization, Carlin-type

INTRODUCTION

Discontinued long-term geological explorations of the Kozuf metallogenic area allowed detection of interesting Fe-Ni contents in the Rzanovo-Studena Voda zone, as well as important polymetallic mineralizations with interesting gold concentrations in the complex Alshar deposit.

The Rzanovo deposit was discovered in 1952. Prospecting and exploration started in 1956 and continued until 1972. The Rzanovo Mine has worked with small breaks for more than 30 years. Its design output is 534 kt ore per year. About 11.2 Mt ore with an average grade of 0.92–0.94% Ni has mined since 1980 until now. The design depth of the open pit is 750 .a.s.l. Ore is currently mined at 775–760 m.a.s.l. Thus, about 2 Mt of ore have been left for open cast mining. This amount is sufficient for 3–4 years of operations at the mine and the metallurgical combine.

Productive arsenic and antimony mineralizations with up to 500 000 t of ore with 2.5% Sb and 2% As have been determined at the Alshar deposit, while explorations of the Carlin type gold mineralization shown flexible values of up to 20 t gold metal.

At the Dudica area explorations have been performed shortly after the end of the Second World War and during the 1960 and 1961 when were submitted the first official reports (Ivanov, 1961). Unlike Alshar here are not validated ore reserves, but have been determined existence of copper ore mineralization in form of quartz-pyrite-enargite veins with lead and zinc and stockwork-impregnated copper mineralization with up to 0.5% Cu in particular ore bodies.

Within this paper we give a review of metallogenetic features of the Kozuf metallogenetic area with special attention to the Rzanovo and Alshar deposits.

THE ALPINE METALLOGENY IN THE KOZUF AREA

The metallogeny within the Kozuf area in general belongs to the Alpine metallogenic cycle where during the Cretaceous have been created productive lateritic crusts with iron and nickel deposits, developed over the Jurassic ophiolite complexes.

At that particular stage were formed numerous iron and nickel deposits in so-called eastern ophiolite belt (Figure 1), of which at the territory of the Republic of Macedonia of special importance are lateritic iron-nickle deposits Groot near the city of Veles, Gradishte, Rakle and Nikodin near the city of Kavadarci as well as the most important deposits Rzanovo-Studena Voda within the Kozuf area. In late Alpine metallogenic stage, more precisely, during the Pliocene in Kozuf metallogenic area has been formed productive polymetallic mineralization of copper, gold, silver, antimony, arsenic, lead, zinc etc., mainly concentrated in Alshar and Dudica deposits. In this paper we will give a short overview of the two metallogenic stages within the Kozuf area.

DEPOSITS RELATED TO THE CRETACEOUS METALLOGENIC STAGE

The Macedonian ophiolitic complex is an essential part of the eastern Mediterranean, a region with one of the world's largest concentration of ophiolites. Most Jurassic ophiolites in this region belong to the Oman suprasubduction type (Robertson, 2006; Dilek and Thay, 2009). In terms of plate tectonics, the leading role in the regional architecture is played by the Tethys paleoocean and sutures left at the place of the reworked oceanic crust. Remnants of the oceanic crust related to the Vardar Suture and a number of pre-Alpine (Precambrian and Paleozoic) fragments alternating with Alpine sedimentary formations are predominant in the Alpine structure of Macedonia and Bulgaria (Zagorchev et al., 2008).

Remnants of the Tethian oceanic crust in the Balkan region are composed of ophiolitic sheets consisting of lherzolite, harzburgite, dunite, and basaltic pillow lavas, which are the most abundant in the southern Vardar Zone, where they locally alternate with thrust sheets of Triassic and Jurassic sedimentary rocks deposited on the continental slope. The Jurassic peridotites and weathering mantles developed after them are of special importance for the formation of Ni-silicate and Fe–Ni deposits. The ophiolites make up the western belt in the inner Albanides (Mirdita Zone) and the eastern belt along the Vardar Zone.

The Rzanovo (Rzanovo-Studena Voda) deposit one of the largest lateritic Fe–Ni deposits in the Vardar Zone-is situated near the Macedonian–Greece state border in the western subzone of ophiolitic belt of the Vardar Zone, which consists of several lithostratons different in mineralogy and petrology of rocks and specific geological history.

The Cretaceous rocks combine Barremian–Albian conglomerate and Turonian limestone. The upper Eocene sequences consist of basal conglomerate overlain by flysch (siltstone, clay, sandstone, and limestone layers). The Pliocene sequences are widespread in the southern part of the area and consist of conglomerate, clayey sandstone with interbeds of calcareous clay, volcanosedimentary and pyroclastic rocks.

THE RZANOVO DEPOSIT

Several large dislocations crosscut the massif of serpentinized ultramafic rocks in the ore field. The Rzanovo Zone is a system of parallel thrust sheets composed of altered serpentinite, schist, and marble. The younger faults make up a radiate structure. The ore lode at the deposit is traced for more than 4 km with a width of 1–40 m. The lode is heterogeneous in structure and consists of several varieties of ores and rocks. Peridotite, gabbrodolerite, and serpentinites are the major ore-bearing rocks that have been subjected to weathering.

Ultramafic rocks of the Rzanovo ore field correspond to Alpine type ultrametamorphic rocks (Maksimovic and Panto, 1981) and do not differ from similar rocks elsewhere in Balkan Peninsula.

Albian-Cenomanian limestone, Cretaceous redeposited lateritic Fe-Ni ore, presumably Cretaceous schists, serpentinite, gabbroic pegmatites and rodingite, as well as Tertiary volcanic rocks, participate in the geological structure of the deposit (Figure 1).

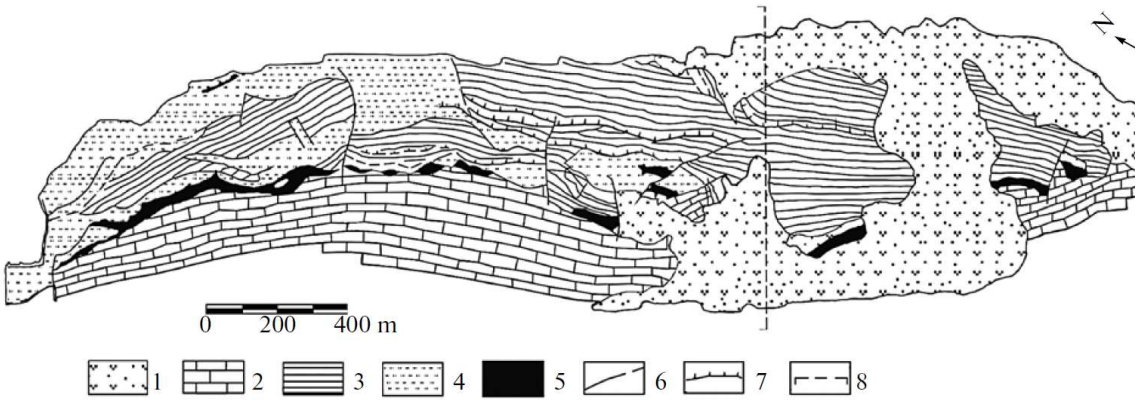

Fig. 1. Geological map of Rzanovo-Studena Voda Fe-Ni deposit. (1) Tertiary volcanic and pyroclastic rocks; (2) Albian-Cenomanian limestones; (3) presumably Cretaceous schists; (4) serpentinite, gabbroic pegmatite, and rodingite; (5) lateritic Fe–Ni ore; (6) fault; (7) thrust fault; (8) section line,

The morphology of orebody at the Rzanovo deposit directly depends on formation conditions of Fe–Ni ore layer as a result of scouring and redeposition of lateritic aposerpentinite weathering mantle during Jurassic and Early Cretaceous. The Fe–Ni deposit is localized at the contact between Jurassic serpentinite and schist in the footwall and Cretaceous limestone in the hanging wall.

The orebody dips nearly vertical and is overturned with Cretaceous sedimentary rocks in the footwall and the Jurassic serpentinite in the hanging wall of the orebody (Fig. 4). The inversion was as a result of tectonic movement at the end of Jurassic. As can be seen from geological section, the orebody is confined to the base of Cenomanian–Turonian limestones. At the surface it is traced for ~4 km with an average thickness of 30–50 m. The orebody is partly overlain by the thrust fault and by Neogene andesite in its southern part. It should be noted that in the depth interval of 955–470 m.a.s.l. (approximately 500 m by vertical), the orebody lies without indications of pinchout and is continuous despite intense dislocations in this region. The orebody plunges to east- northeast, bends with depth toward the southwest, and looks like a slightly curved sheet (Fig. 2). One can seen in geological sections that although the orebody retains vertical attitude, its thickness and morphology underwent significant changes with depth (Fig. 2). Section 17–17' shows that the orebody bends and divides into two thinner offsets (Fig. 2a).

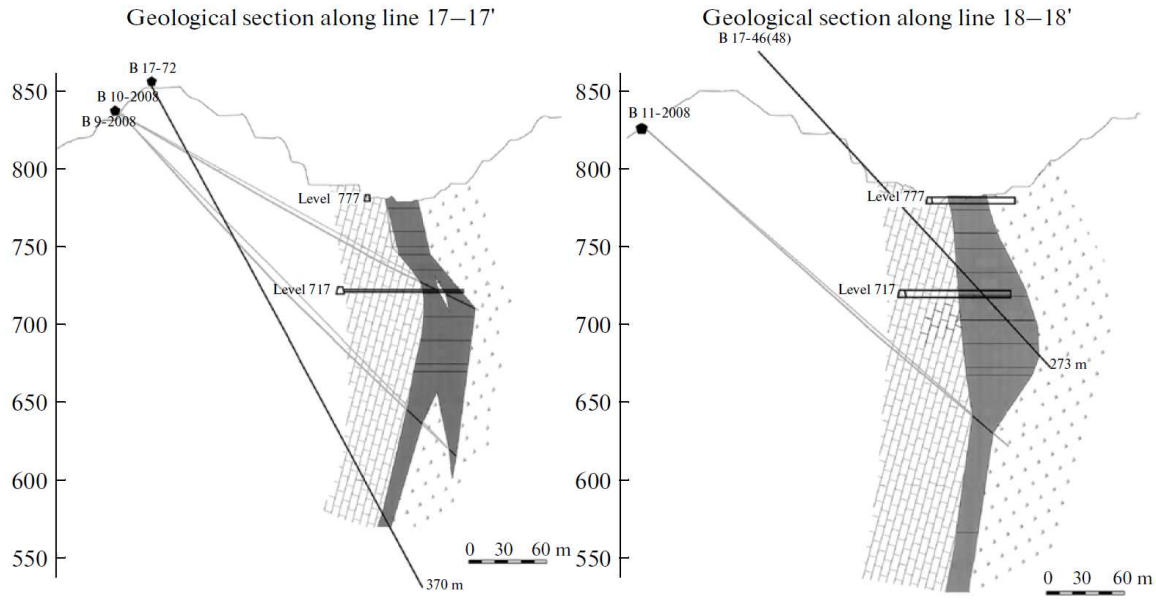

Fig. 2. Geological sections across Rzanovo deposit along exploration lines: (a) 17–17' and (b) 18–18', after data of geological survey of mine, 2011.
(1) Orebody; (2) limestone; (3) serpentinite; (4, 5) drill holes: (4) old and (5) new; (6) exploration adit.

In the next section 18–18', it is a thickened lens between levels 750 and 640 m.a.s.l. and abruptly decreases in thickness below 640 m.a.s.l. (Fig. 3b). These sections show that the orebody is not interrupted with depth. Further exploration must corroborate this conclusion. The aforementioned morphological features show that the orebody at the Rzanovo deposit consists of several segments with specific lithologic, mineralogical, and geochemical characteristics.

Like the preceding investigations, our study has shown that the orebody at the Rzanovo deposit is composed of the following types of ores and mineralized rocks: massive and fissile magnetite ores; oolitic, fissile, and massive hematite ores; riebeckite, stilpnomelane and dolomite–talc schists; and serpentinite.

The overview of the most important ore types is given below. The chemical composition of ore is given in Table 1.

The formation of Fe–Ni ore at the Rzanovo deposit is closely related to the erosion and redeposition of the lateritic weathering crust after Jurassic ultramafic rocks. The primary laterites are retained only as relics in serpentinites. No lateritic material with clastic structure, known at other Fe–Ni deposits in the Vardar Zone, is at the Rzanovo deposit. The laterites were formed at this deposit and other deposits nearby under stable conditions without supply of coarse clastic material (Ivanov, 1965), so that laterites were not diluted in the process of chemical and mechanical redeposition. Resistant chromites and most rock forming minerals were deposited in the process of mechanical migration, whereas sulfides were redeposited as products of chemical reactions.

Table 1. Chemical composition of various types of Fe–Ni ore in Rzanovo deposit, wt %

Oxide	Massive magnetite ore			Fissile magnetite ore			Oolitic hematite ore			Fissile hematite ore			Massive hematite ore			Riebeckite and stilpnomelane ores			Dolomite–talc schist			Talc schist		Serpen-tinite
	I/1	V/2	VIII/1	II/1	IV/1	VII/2	I/2	I/9	I/10	I/3	I/7	II/2	I/8	II/4	III/4	II/8	III/1	V/1	VI/1	VIII/3	VIII/4	VI/6	III/8	V/6
Al_2O_3	1.78	4.92	1.86	5.41	3.89	2.43	3.18	2.83	2.92	2.68	4.33	2.36	2.35	3.44	4.11	6.60	5.92	1.88	1.47	1.20	1.92	1.05	0.37	1.39
Fe_2O_3 (total)	32.91	62.58	39.38	59.86	41.01	34.64	59.30	65.67	58.37	40.51	43.69	43.97	49.20	49.34	50.11	16.72	43.89	40.05	35.55	19.72	42.01	11.17	7.50	12.35
MnO	0.24	0.04	0.45	0.16	0.32	0.44	0.20	0.38	0.35	0.48	0.75	0.37	0.39	0.47	0.41	0.73	0.18	0.23	0.43	0.81	0.59	0.26	0.11	0.16
MgO	18.40	6.42	13.91	8.27	11.37	15.98	9.15	6.91	8.21	17.66	12.27	13.94	10.27	9.10	11.41	7.62	9.35	8.36	14.73	18.88	14.46	28.64	27.90	31.67
Na_2O	0.50	0.82	0.85	0.55	0.84	0.69	0.37	0.60	0.93	0.50	0.82	0.58	1.35	1.35	0.57	5.07	0.66	0.80	1.23	0.84	0.74	0.59	0.70	0.83
K_2O	0.10	0.23	0.18	0.10	0.60	0.18	0.10	0.19	0.10	0.10	0.10	0.10	0.20	0.33	0.10	0.22	0.79	0.81	0.19	0.18	0.18	0.18	0.10	0.2
P_2O_5	0.17	0.49	0.46	0.29	0.53	0.48	0.17	0.26	0.32	0.17	0.25	0.53	0.32	0.31	0.44	0.36	0.49	0.38	0.43	0.34	0.40	0.40	0.50	0.4
SiO_2	40.02	16.60	32.90	16.05	32.38	35.19	19.80	15.75	19.84	30.30	26.69	26.64	27.52	25.99	23.71	46.33	27.06	25.37	32.23	48.79	29.96	48.77	55.67	41.31
SO_3	0.47	1.71	0.79	1.26	1.50	0.37	0.48	0.43	0.50	0.47	0.51	0.74	0.51	0.55	0.63	2.82	3.48	3.72	0.72	0.32	0.30	0.26	0.63	0.26
CaO	0.98	1.31	3.92	1.03	1.47	2.60	2.00	2.03	2.57	0.99	1.27	2.30	3.14	2.11	1.09	1.98	1.27	2.90	6.73	3.79	2.09	1.63	1.08	1.37
TiO_2	0.02	0.12	0.03	0.13	0.07	0.03	0.05	0.05	0.03	0.03	0.09	0.03	0.01	0.05	0.08	0.28	0.20	0.18	0.01	0.01	0.01	0.01	0.01	0.01
LOI	2.65	1.89	3.17	2.18	3.00	3.55	1.94	2.00	2.17	3.39	3.14	3.24	2.22	2.47	3.48	0.16	3.40	9.08	2.61	4.13	3.21	5.67	4.16	9.68
H_2O	0.24	0.97	0.28	0.53	1.22	0.26	0.70	1.01	0.86	0.40	0.83	0.38	0.51	0.70	0.76	0.28	1.27	1.31	0.18	0.14	0.24	0.30	0.16	0.73
NiO	0.90	1.17	0.69	1.28	1.0	1.10	0.91	0.94	1.21	1.27	1.24	1.08	0.93	1.18	1.49	2.13	0.79	1.10	0.80	0.87	1.06	0.75	0.34	0.37
Cr_2O_3	1.68	1.93	1.67	3.86	2.26	2.10	1.99	2.07	2.26	1.93	4.50	1.79	1.88	3.04	2.96	7.00	2.93	2.66	1.49	0.95	1.90	0.36	0.31	0.39
Total	101.06	101.2	100.54	100.96	101.46	100.04	100.34	101.12	100.64	100.88	100.48	98.05	100.8	100.43	101.35	98.3	101.68	96.17	98.8	100.97	99.07	100.04	99.54	101.12

PLIOCENE METALLOGENIC STAGE

This metallogenic stage belongs to the youngest ones within this particular metallogenic period at the territory of the Republic of Macedonia and wider. Within the Kozuf metallogenic area there are productive polymetallic mineralization formed during that youngest metallogenic stage. That are complex mineralization of arsenic, antimony, gold, copper, silver, lead, zinc etc., mostly concentrated in Alshar and Dudica deposits, while one part continues to the Aridea area in neighboring Greece. Mineralization control of this deposits is related to the regional and local structures, structures of volcanic apparatuses and Pliocene volcanism in the Kozuf area.

A schematic morphostructural map of the Kozuf district, was made using the anlaysis of satellite scanograms, aerophotos and geologic data obtained by field investigations (Figure 3).

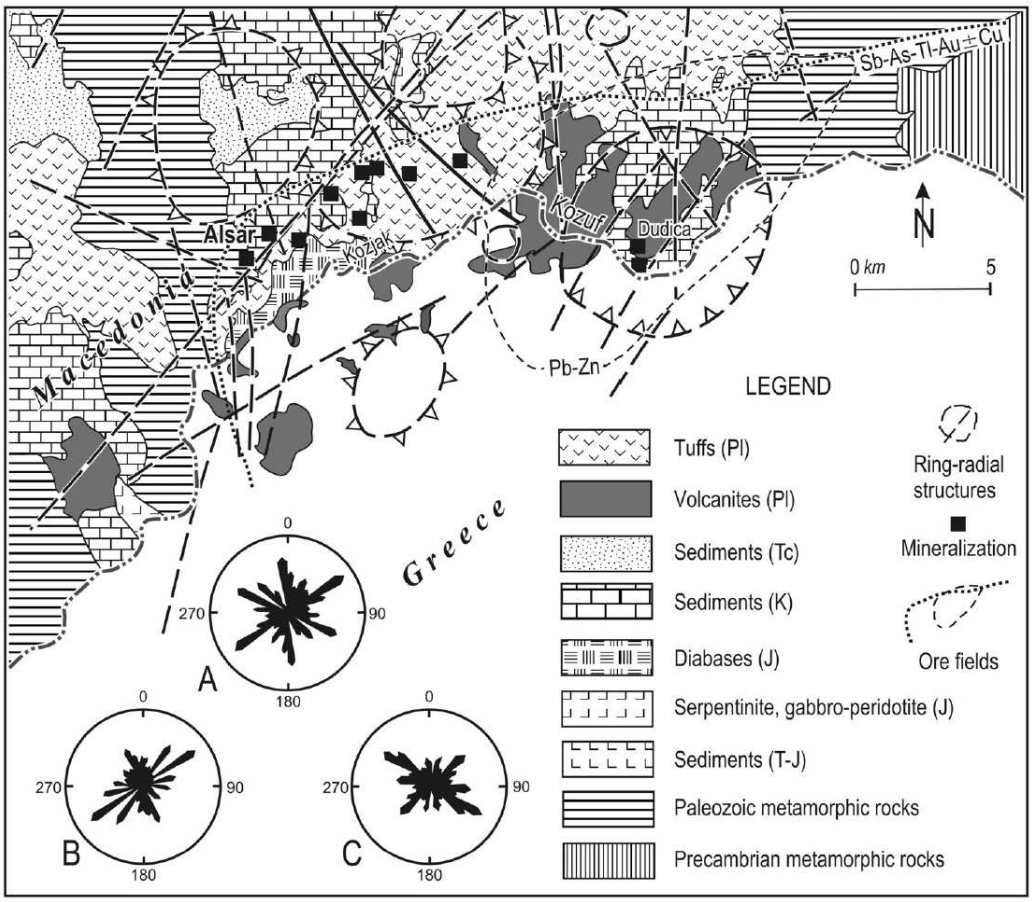

Fig. 3. Schematic morphostructural map of the Kozuf district (Boev, 1988, *modified*)

The neotectonic fault structures grouped into three systems.

A fault system of Vardar strike are reactivated fault structures, the oldest being those of NW-SE and the youngest of N - S orientation. Products of both incipient and major phases of volcanic activity are located along these faults. Intensive hydrothermal activity (in the area of Dudica and Alsar) of N-S strike took place affecting the products of incipient volcanic activity.

The second *system are faults of NE - SW to E - W strike,* relatively younger than the Vardar system manifesting recent seismic activity while the third system are the *ring structures* represented by several morphologically negative shapes (that can be seen in scanograms) and a positive structure in the area of Dudica (Boev and Jelenkovic, 2012).

THE ALSHAR DEPOSIT

The Alshar deposit is a part of the Serbian–Macedonian metallogenic province, or the Kožuf ore assemblages (Janković and Jelenković 1994; Janković *et al.* 1997; Volkov *et al*. 2006). The formation of the deposit is associated with the evolution of a complex intrusive volcanic structure of Pliocene age and the concomitant activity of hydrothermal ore-bearing systems.

The geology of the Alšar deposit has been studied in detail since 1960. The oldest lithologic members in the wider area of the deposit are dated Precambrian (albite gneiss, marble and mica schist) and the youngest geologic units are the Pliocene clastics, tufa, volcanic and pyroclastic rocks, and recent Quaternary deposits. Magmatism evolved in stages. Volcanism was central, developed over the intersection of regional-scale faults at the contact of Pelagonian Block and the Vardar Zone (Boev 1988; Karamata *et al.* 1994; Janković *et al.* 1997; Dumurdzanov *et al.* 2005; Dimanatopulos 2006; Volkov *et al.* 2006; Burchfiel *et al*. 2008).

The structural pattern of the Alšar deposit area is complex, composed of many ring structures and related fracture systems in different directions alongside regional faults of dominantly NW–SE to N–S (the Vardar direction) and E–W (Kožuf-Kukuš) trends. Establishing the primary depth of the formation of the Sb–As–Tl ore bodies in the Alšar deposit was preceded by a study of its geology, identification of the primary and additional controls of the spatial position, shape, textural ore varieties, mineral composition and association of essential and minor elements of the ore-body. The age of volcanism, time of hydrothermal solution control, facies of hydrothermal alteration, time and order of their formation and dating the ore mineralization were given particular consideration.

This was the basic information for establishing the primary formational depth of the ore bodies, which has been addressed since 1988. The mentioned explorations determined Palaeozoic age of the schist, the oldest geologic unit in the Alšar deposit, and Triassic age of the silicified dolomite and marble. Geological and trial excavation prospecting in parts of the deposit revealed some sub-volcanic latite intrusions and sporadic presence of quartz latite, trachyte, andesite and dacite (Figure 6). Most of the mentioned geologic units were covered by tuff and other pyroclastic materials in the closing phase of the geo logic history (Ivanov 1965b, 1986; Karamata *et al.* 1994; Percival and Radtke 1994; Janković and Jelenković 1994; Janković *et al.* 1997; Volkov *et al.* 2006).

The major elemental components of the Allchar deposit are Sb, As, Tl, Fe and Au, accompanied by minor Hg and Ba, and traces of Pb, Zn, Cu. Enrichment of Tl in the Allchar deposit is closely associated with increased concentrations of volatiles, such as As, Sb, Hg. The distribution of ore metals and their concentration rates display a lateral zoning. These zones are not sharply defined and typically a gradual transition exists between zones.

i. In the northern part of deposit As and Tl prevail, accompanied by minor Sb, locally traces of Hg and Au.
ii. The central part of deposit is dominated by Sb and Au, but also contains significant amounts of As, T1, minor Ba, Hg and traces of Pb.
iii. The southern part of the deposit is characterized by dominance of gold mineralization accompanied by variable amounts of antimony.

The most important ore minerals of the Allchar deposit are Fe-sulphides, As- and Tl minerals, cinnabarite, and Pb- and Sb-sulphosalts, accompanied by native gold or sometimes sulphur (Janković, 1960, 1993; Ivanov 1965; 1986; Janković and Jelenković 1994; Percival and Radtke 1994).

Ore mineralization at the Alshar deposit is developed as mineralized breccia at the contact of volcanic cover with dolomites, jasperoid beds in the carbonate rocks (Figure 4), and vein-disseminated zones in dolomites and Tertiary volcanic rocks. The Alshar deposit includes several ore bodies with specific geochemical association of elements and composition.

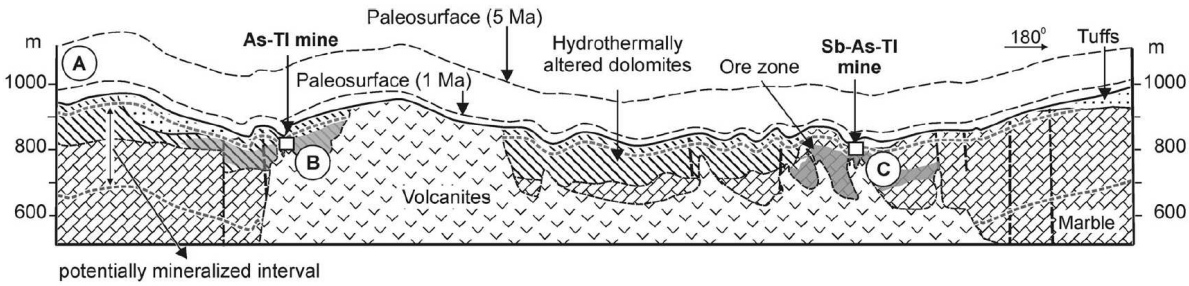

Fig. 4. Simplified geologic cross-section of the Alšar Sb–As–Tl deposit (Boev and Jelenkovic, 2012)
A: showing palaeosurfaces for different periods (5 Ma and 1 Ma), positions of the ore bodies and potentially mineralized rocks in the As–Tl mine (Crven dol) and the Sb–As–Tl mine (Central) locations. B: Characteristic geological cross-section at Crven dol (adit 823 m) and C: Characteristic geological cross-section at the Central part (adit 823 m) showing the positions of the identified ore bodies and the vertical intervals of ore mineralization verified in underground workings.

Namely, a few morphostructural types of orebodies are distinguished within the deposit: (1) mineralized breccia zones along contacts of subvolcanic intrusions with dolomite and tuffaceous dolomite and mineralized fault zones in carbonate rocks; (2) systems of mineralized veins and fissures in Tertiary tuffaceous dolomite and Triassic dolomite; (3) stratiform sulfide lodes hosted in tuffaceous dolomite; and (4) disseminated Sb mineralization (stibnite is prevalent) in association with gold-bearing pyrite and marcasite as stratiform bodies along the contact between the volcanosedimentary sequence and Triassic carbonate rocks and hosted in silicified volcanics and jasperoids as well. It should be noted that the geological exploration conducted at the deposit is insufficient for the ultimate estimation of reserves.

This is the only deposit in Macedonia, which has economic-grade contents of Tl (0.1–0.5%), Sb (up to 2.5%), As (1.5%), and gold (>1 g/t). It should be noted that gold is unevenly distributed in the ores. The highest Au contents (3–4 g/t; occasionally, up to 20 g/t or more) were found in jasperoid zones in the southern part of the deposit (Percival and Radtke, 1994). By analogy with the Carlin-type deposits in Nevada, Percival and Radtke (1994) distinguished four economicgrade types of gold ores at the Alshar deposit: (1) Sb–Au jasperoid ore (+ Au + As + Tl); (2) siliceous gold ore (+Au + Sb + Tl); (3) As–Au ore (+ Tl + Hg + Sb + Au); and (4) Tl ore. The ores form three mineral assemblages of different ages: pyrite–marcasite, antimonite, and orpiment–realgar–lorandite.

In general the Alshar polymetalic deposit is typical epithermal deposit where the formation of ore bodies is genetically associated with subvolcanic-hypabyssal intrusion/s/ of calc-alkaline composition. The timing of intrusive events, and the mineralization has not reliably been established.

CONCLUSION

The Alpine metallogeny used to be of high importance for the spatial and temporal distribution of deposits and occurrences within the Kozuf metallogenetic area. The Fe-Ni deposits related to the lateritic crust of weathering were developed during the lower Alpine metallogenic epoch, or more precisely during the Cretaceous.

The complex polymetallic Cu-Au-Sb-As, Tl, Pb-Zn in the Alshar, Dusdica and Aridea deposits were product of upper Alpine metallogenic epoch, created during the Pliocene stage related to the younger volcanic activity in the Kozuf-Aridea area.

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