

MINERALOGY AND GEOCHEMISTRY OF TRACE ELEMENTS FROM CRVEN DOL – ALŠAR DEPOSIT (REPUBLIC OF MACEDONIA)

Ivan Boev¹, Ajka Šorša², Goran Tasev¹, Dalibor Serafimovski¹, Blažo Boev¹

¹*Faculty of Natural and Technical Sciences, “Goce Delčev” University in Štip,
Blvd. “Krstev Misirkov” 10-A, P.O. Box 210, 2000 Štip, Republic of Macedonia*

²*Department of Geology. Croatian Geological Survey,
Sachsava 2, 10 000 Zagreb, Croatia
blazo.boev@ugd.edu.mk*

A b s t r a c t: The results of new mineralogical study by the X-ray diffractions and the results of the analysis of the trace elements and rare earth elements (REE) in the ore mineralization of Crven Dol by the ICP-MS are presented in this paper. Mineralogical study suggested very interesting mineral associations presented by lorandite, realgar, orpiment, vrbaitite, bernardite, jankovitchite, fangite, rosenite, farmacolite, marcasite, pyrite, sulfur, gypsum, dorallcharite, dolomite, quartz. The content of trace elements and REE in the surrounding rocks and in the ore mineralization suggested the idea of influence of the ultramafic rocks from the western flank of the Vardar zone in the hydrothermal activity in the Alšar deposit, especially in the ore body Crven Dol.

Key words: trace element; REE; lorandite; Crven Dol

INTRODUCTION

From a geotectonic point of view, the ore deposit Alšar is located on the edge of the Vardar zone and the metamorphic block Elen Supe, near the Macedonian-Greek border. The deposit is located in a tectonically labile zone which is bounded by the ophiolitic rocks from the Jurassic age in the west and the metamorphic rocks from the Triassic age in the east (Boev, 1988).

The deposit is elongated in the north-south direction and the following lithological units are part of its geological structure: silicified dolomites, marbles, pyroclastic rocks (tuffs, silicified tuffs and pyroclastics), subvolcanic magmatic rocks (andesites), fluvio-glacial sediments and alluvial sediments along the river of Majdan, running through the central part of the Alšar deposit. The ore mineralization is located in the contact point of the silicified dolomites and pyroclastic rocks and the subvolcanic andesites. Main mineralization

occurs in the central part of the deposit (Sb, As, Tl, Au, Ba) and in the northern part of the Crven Dol deposit (Tl, As, S, Hg).

Crven Dol is one of the famous rich Tl bearing locality in the world, especially due to the occurrence of the lorandite. This ore body lies in the northern part of Alšar. It was opened by two adits – no. 25 (Figure 1) at the level of 753 m on the western part and adit 21 at the level of 823 m on the eastern side (Figure 2) (Pavičević et al., 2006). The mineralization is explored underground at three levels – 753, 802 and 823 m connected by two vertical shafts. The most significant mineralization occurs close to the entrance of adit 21 m and the vertical shaft (Figure 2) (Balić-Žunić et al., 1993a, 1993b, 1994; Beran et al., 1990; Frantz et al., 1994; Janković et al., 1994, 1997; Pavičević et al., 2006; Percival et al., 1994; Volkov et al., 2006).

METHODOLOGY

The samples for mineralogical and geochemical investigations were collected from the Tl-As ore body in Crven Dol (adit 21) where 10 specimens were sampled.

The mineralogical content of the collected samples was determined using an X-Ray Siemens D 500 equipped with an automated computer and a Cu-monochromatic lamp working at 40 kV and

30 mA. Quantitative analysis of the present mineral phases was performed using the DIFRAC-11 software package and program support by EVAL and IDR.

Rare earth elements were analyzed at the Actlabs, Ontario, Canada,. Since it is well-known that rare earth elements and trace elements are among the most difficult to analyze properly it was essential that the sample be ground to 95% – 200 mesh to ensure complete fusion of resistate minerals. The analysis required a lithium metaborate-tetraborate fusion with subsequent analysis by ICP-OES and ICP-MS. Although the lithium metaborate-tetraborate fusion dissolution procedure has long been recognized as the best technique for ensuring geological samples go into solution. In the past this lithium metaborate-tetraborate solution was not highly compatible with ICP-MS sample introduction systems, but research and develop-

ment conducted by Actlabs into sample introduction into the ICP-MS has solved this shortfall where robotic fusion process also ensures very reproducible results impossible with manual fusion processes and provides highly accurate results in a cost-effective and rapid manner. The advantage of this procedure for major oxide analysis over XRF is that it is more matrix independent and any rock type (including sulphide-bearing samples) can be analyzed without special calibration or pre-treatment. Also, mass balance was required as an additional quality control technique and elemental totals of the oxides should be between 98 to 100%. Geochemical analysis was performed by ICP-MS technique on the instrument Agilent 7500 (Babington type atomizer). The power of plasma was 1500 W with pump speed of 0.1 rps, integration time 0.3 s, total time of aquisition 8 s, etc.

GEOLOGY AND POSITION OF THE CRVEN DOL – ALŠAR DEPOSIT

The Crven Dol locality is the northern part of the famous Alšar deposit, which is located in the southernmost part of the Vardar zone and belongs to the Serbo-Macedonian metallogenic province (Figure 1). The deposit is very specific due to its relation young volcanism and particular metallogenic setting, where As-Sb-Tl are dominant ore metals, but very interesting is gold, sporadically lead-zinc etc. From the geological point of view,

beside young volcanic rocks and tuff at the Alšar locality as dominant occur marble, dolomite, metamorphic rocks etc.

Deposition of sandstone and claystone, followed by bedded and massive carbonate rocks (limestone, dolomite, marble), took place in the Middle and Upper Triassic. These rocks are the basement of the Alšar deposit (Figure 1).

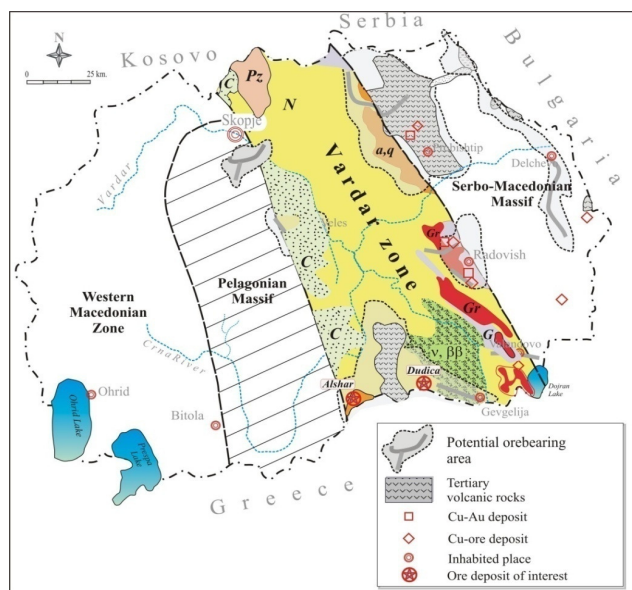


Fig. 1. Position of the Alšar deposit as the area of interest in the Vardar zone geotectonic and metallogenic unit
N – Neogene; *a, q* – volcanics; *C* – Cretaceous; *v, ββ* – gabbro-d diabase; *Gr* – granitoids; *Pz* – Paleozoic; *G* – gneiss

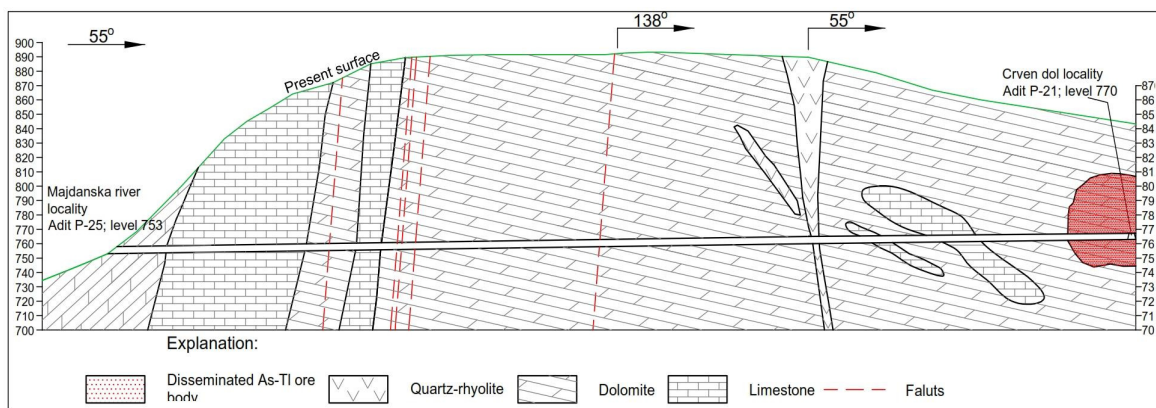


Fig. 2. Geological cross-section through the Crven Dol ore body with illustration of the adit P-25, level 753 m

The quartz-sericite-feldspar schists are developed along the eastern flank of the deposit, while the central part is built of dolomite, marble, and sporadically limestone. The dolomite series underlies marble. Based on fission traces the age of dolomite was determined as 250 m.y. (Lepitkova, 1995).

The Mesozoic rocks are unconformably overlain by Pliocene cover and glacial till. The earliest Tertiary rocks are very likely tuffaceous dolomite. It unconformably overlies the Mesozoic basement rock, particularly in the central, northern and southwest parts of the deposit. This unit is of volcano-sedimentary provenance and commonly mineralized.

The massive tuffaceous dolomite contains sporadically intercalated sequences of finegrained tuff, water lain ash or volcanic glass. This volcano-sedimentary unit is 100–130 m thick (Percival and Boev, 1990; Percival and Radtke, 1990, 1994; Percival et al., 1992).

The basal contact of the tuff and underlying Tertiary tuffaceous dolomite and pre-Tertiary rocks is often marked by an unconformity zone, 2 to 12 m thick. It consists of a mixture of unsorted and ungraded detrital material. This basal unconformity of the tuff unit indicates a discontinuity in the Tertiary stratigraphic section and the beginning of volcanic activity during which dolomite deposition took place (Percival and Radtke, 1990). The basal contact zone is of particular interest as a preferred environment of hydrothermal alteration and mineralization, particularly in the central and southern parts of the deposit (Figure 2).

The unit of Pliocene felsic tuffs covers a large portion of the Alšar deposit. This volcanic se-

quence includes ash, crystal tuffs, tuff breccia and lacustrine tuffaceous sediments. According to Percival and Radtke (1990), the lowest level of felsic tuffs consists of soft and friable ash tuffs, grading upwards to a crystal lithic tuff and then into a crystal tuff. These tuffs contain sanidine, biotite and quartz phenocrysts in an aphanatic ground mass. The composition of tuff braccia is similar to the crystal tuff. The tuffs deposited in the sublacustrine basins in the southern part of Alšar show bedding and contain tuffaceous sedimentary clay material (a volcano-sedimentary series). The Alšar volcanic complex was investigated in detail by Frantz (1994), Frantz et al. (1994) and Lepitkova (1995). Two principal volcano-intrusive phases have been identified in Alšar based on investigations carried out so far: Miocene phase of calc-alkaline rocks occurring as dykes had been determined as of Miocene age (14.3–8.2 Ma; Troesch and Frantz, 1992, $^{40}\text{Ar}/^{39}\text{Ar}$ method) on plagioclases from Crven Dol volcanic phase. The volcano-intrusive rocks of this volcanic phase were completely altered by hydrothermal solutes during the Pliocene; the most significant volcanic rocks in Alšar developed as part of the Kožuf volcano-intrusive activities.

Subvolcanic hypoabyssal intrusions formed, based on K-Ar study, during the period from 5.0 to 4.5 Ma (Lepitkova, 1995; Frantz et al., 1994). Results obtained from determination of age by K/Ar method of andesite affected by hydrothermal processes indicate to absolute age of 3.9 to 5.1 Ma (Lippolt and Fuhrmann, 1986). Crven Dol is composed of carbonate rocks (dolomite and minor limestone/marble) intruded by a subvolcanic magmatic body (quartz-rhyolite) highly hydrothermally altered, so that its primary composition is extremely difficult to reliably identify (Table 1).

Table 1

Instrumental neutron activation analyses of host rocks inside the Crven Dol ore body and comparison with a marble and dolomite outside from the Crven Dol valley (Frantz et al., 1994)

%	a	b	c	d	e	f	g	h
Element	Marble	Quartz-rhyolite	Bulk	Bulk	Dolomite	Dolomite	Dolomite	Marble
Mg %	d.l	d.l	d.l	d.l	8.700	d.l	13.00	d.l
Ca %	37.10	10.10	13.70	d.l	21.45	17.60	24.37	39.70
Fe (ppm)	0.2260	2.890	9.130	21.10	0.1170	5.900	0.0253	0.0583
Na	47.80	6230.0	98.70	75.30	103.0	62.20	83.50	41.30
Cl	d.l	d.l	d.l	d.l	< 80.00	< 900.0	51.00	d.l
K	229	18700	880.0	720.0	166.0	340.0	43.80	139.0
Sc	1.070	7.260	2.930	1.510	1.200	2.690	0.3700	0.2430
Cr	6.450	8.800	51.00	49.10	4.500	10.00	3.600	3.200
Mn	450	1220.0	11500	4350.0	392.0	5620.0	66.50	201.0
Co	1.440	5.810	1435.0	1470.0	0.4800	18.30	0.6700	0.2800
Ni	< 7.000	< 40.00	4340.0	4150.0	d.l	59.00	< 5.000	< 2.000
Cu	< 6.000	< 170.0	< 100.0	< 400.0	< 60.00	< 200.0	< 15.00	< 4.000
Zn	20.00	96.00	54.00	200.0	9.300	115.0	6.300	1.800
Ga	0.3200	18.60	< 2.000	< 30.00	d.l	d.l	d.l	0.1200
As	210	53.80	51600	82300	3040.0	36000	197.0	45.60
Se	13.20	< 0.2000	d.l	2.500	< 0.4000	< 0.3000	< 0.2000	< 0.0300
Br	< 0.2000	< 0.5000	< 2.000	d.l	0.3900	d.l	0.3200	0.1230
Rb	< 2.500	127.0	< 15.00	< 70.00	< 2.000	< 3.000	< 0.5000	1.100
Sr	68.00	285.0	< 120.0	< 150.0	70.00	90.00	41.00	116.0
Zr	d.l	200.0	d.l	< 150.0	d.l	d.l	d.l	< 3.000
Mo	0.8000	2.000	40.00	120.0	d.l	7.000	< 0.1500	0.2400
Ag	d.l	d.l	d.l	d.l	0.6500	d.l	d.l	< 0.0500
Cd	d.l	d.l	d.l	d.l	2.000	d.l	d.l	0.1600
In	d.l	d.l	d.l	< 0.2000	d.l	d.l	d.l	d.l
Sb	1.370	< 0.2000	16.70	32.80	0.1000	36.00	0.0640	0.9690
Cs	1.350	39.00	11.12	25.20	0.2000	7.060	0.0860	0.2900
Ba	11.00	1110.0	< 70.00	< 500.0	d.l	< 60.00	< 10.00	6.900
La	2.260	67.30	3.340	3.700	0.2500	3.250	0.2400	0.860
Ce	4.120	128.0	5.000	4.400	0.6500	5.100	0.2900	1.820
Pr	d.l	13.00	d.l	d.l	d.l	d.l	d.l	0.1300
Nd	1.400	51.80	d.l	d.l	0.3200	4.500	< 0.3000	0.5600
Sm	0.4750	8.310	0.9700	0.6400	0.0890	0.800	0.0660	0.1730
Eu	0.1020	2.090	0.1600	0.1300	0.0300	0.1800	0.0130	0.0302
Gd	d.l	d.l	d.l	d.l	d.l	d.l	d.l	0.1300
Tb	0.0860	0.9300	0.2300	< 0.0900	0.0220	0.1900	0.0130	0.0180
Dy	0.5280	4.990	< 0.9400	< 1.500	< 0.1500	< 2000	0.0740	0.1200
Ho	0.1500	1.100	d.l	d.l	d.l	d.l	d.l	0.0280
Yb	0.3100	2.440	0.6500	< 0.7000	0.0800	0.7100	0.0460	0.0760
Lu	0.0440	0.3680	0.0730	< 0.1800	0.0080	0.1400	0.0052	0.0110
Hf	0.0760	6.100	< 0.4000	< 0.3000	< 0.0500	0.0750	0.0130	0.0390
Ta	< 0.0200	0.9100	< 0.2200	< 0.2000	< 0.0300	< 0.0500	< 0.0250	0.0230
W	1.490	< 2.000	< 1.000	d.l	d.l	9.300	0.0630	0.9000
Ir	< 0.0025	< 0.0050	< 0.0085	d.l	< 0.0020	d.l	d.l	< 0.0003
Au	0.0017	0.0020	< 0.0080	d.l	1.098	0.0210	0.0897	0.0006
Hg	d.l	d.l	< 1.5000	6.600	0.1400	2.900	< 0.0700	0.2600
Tl	d.l	d.l	< 10.00	d.l	d.l	4500.0	< 400.0	d.l
Th	0.2430	61.50	< 2.50	< 0.4000	0.0660	0.1900	0.0370	0.2700
U	0.6000	9.200	4.400	< 2.000	0.1300	3.970	0.0540	0.4500

d.l – detection limit

The subvolcanic rock contains phenocrysts of sanidine, quartz and biotite; the groundmass consists mostly of K-feldspar and quartz. It has been so far named as quartz-rhyolite (Janković and Jelenković, 1994), andesite and rhyolitic tuff (Frantz, 1994). Table 1 shows instrumental neutron activation analyses of host rocks inside the Crven Dol ore body. These data are important when analyzing primary sources of metals mobilized later and concentrated in the Crven Dol ore body. Thallium content in carbonate rocks and in tuffs as well

(intrusive body?) is very low, whereas arsenic content is high (with the possibility to have originated from hydrothermal solutions). The LIL elements such as B, K, Rb, Cs, Ba and Sr are strongly enriched with regard to primitive mantle, particularly Cs (Frantz, 1994). The REE spider diagram of the altered subvolcanic intruded body and surrounding marble and dolomite shows enrichment in LREE up to a factor 100 normalized to the CI-chondritic values (Figure 3), (Frantz, 1994).

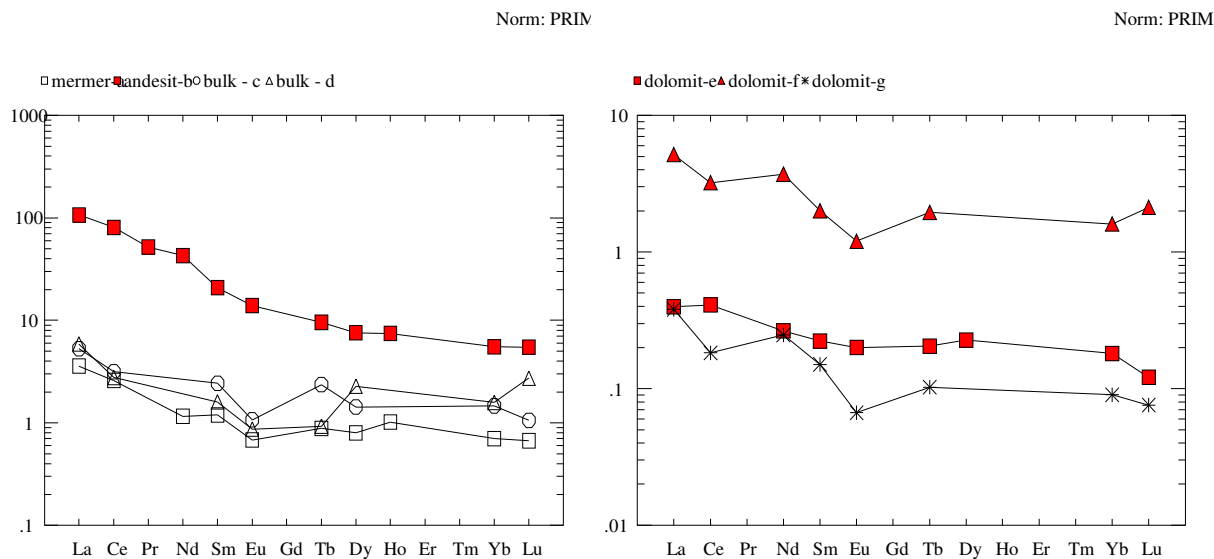


Fig. 3. Spider diagrams of samples inside and outside the mine from Crven Dol. Samples are normalized to C 1 – chondritic value (Janković et al., 1997)

MINERALIZATION

The Alšar deposit is a NNW-SSE oriented antiform. It comprises several orebodies within a zone 2 km long and around 300–500 m wide. The localization of mineralization is spatially associated with an environments characterized by increased porosity and permeability, typically related to fractures and fractured zones in the vicinity of subvolcanic intrusive bodies. Such steeply dipping ore-bearing structures resulted from sliptype shearing movements represented by brecciated rocks often in a fine-grained gougy matrix. The increased porosity and composition of the tuffs are favorable environment for hydrothermal fluid migration and introduction of ore elements. Another favorable environment is a porous and permeable basal zone developed as a strata-bound body along the Triassic erosion surface (Percival and Boev, 1990; Percival and Radtke, 1994).

Mineralization is associated with hydrothermally altered wallrocks including the Triassic carbonates (dolomites and marbles), the Tertiary magmatic rocks and volcano-sedimentary sequence (tuffaceous dolomite; Figure 4).

Silicification and argillitization are the most predominant alteration products, and quartz is very abundant in hydrothermally altered volcanoclastites (Percival and Radtke, 1994; Pavićević et al., 2006). The alteration is generally believed to be associated with Plio-Pleistocene andesite volcanism and latite intrusion, which extends from Mt. Kožuf in R. Macedonia to Mt. Voras in Greece (Janković, 1993; Pe-Piper and Piper, 2002; Yanev et al., 2008). The major elemental components of the Alšar 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 Alšar 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. Namely in the northern part of deposit As and Tl prevail accompanied by minor Sb, locally traces of Hg and Au (Figure 4).

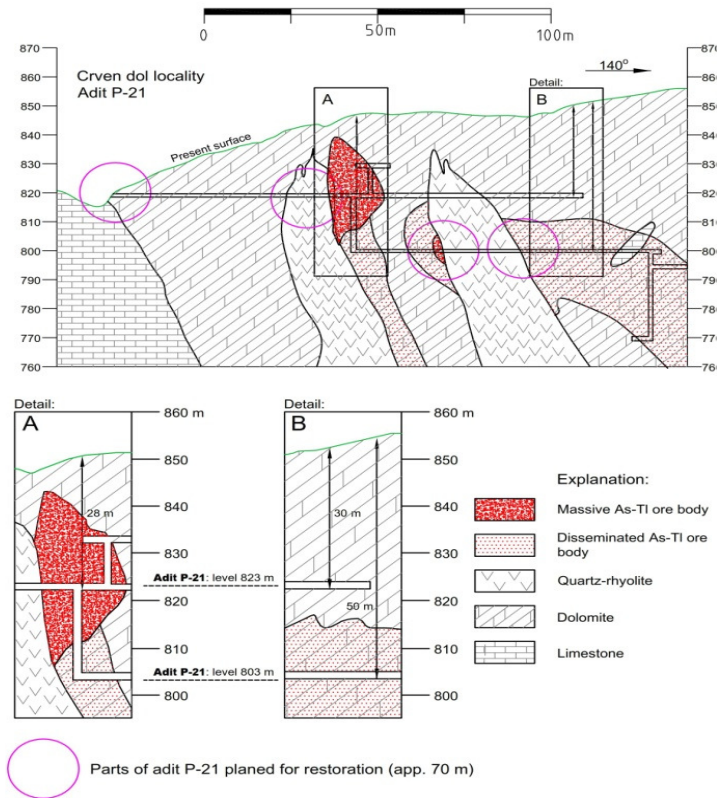


Fig. 4. Geological cross section and columns through the Crven Dol ore body, Alšar deposit, with illustration of massive As-Tl ore body at the levels of 823 m and 803 m

The central part of deposit is dominated by Sb and Au, but also contains significant amounts of As, Tl, minor Ba, Hg and traces of Pb, while 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 Alšar deposit are Fe-sulphides, As- and Tl-minerals (Figure 5), 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; Boev et al., 2001).



Fig. 5. Illustration of massive As-Sb-Tl ore from the Crven Dol ore body, Alšar deposit

RESULTS AND DISCUSSION

Three styles of low mineralization have been so far revealed, each with a distinct geochemical signature and mineral assemblage:

Massive realgar ore grading into stockwork formed in dolomite near or along its contact with subvolcanic intrusions. Sporadically high grade ore occurs in brecciated zone (Figure 6).

This ore is open at the level of 823 m and explored by short cross-cuts and shallow shaft. This ore body contains about 6,000 tones with 8 % As, 0.09 % Sb, 0.35 % Tl, 45 ppm Hg and 0.2 ppm Au. It is located approximately 30 m below the present surface.

XRD analysis was performed on 10 samples from the ore body Crven Dol. Due to their similarities, XRD plots of only four of them (samples

1, 3, 4 and 8) are given below (Figures 7, 8, 9 and 10).



Fig. 6. Realgar mineralizations in the ore body Crven Dol (foto: Boev, 2016)

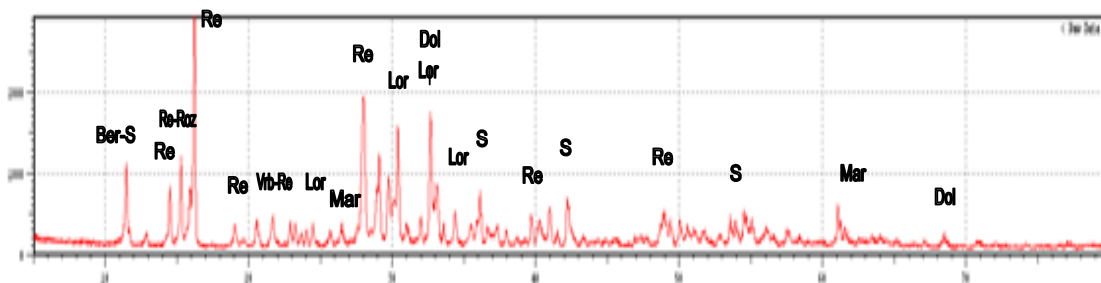


Fig. 7. XRD plot of typical minerals in sample 1 from the Crven Dol ore body, Alšar deposit

In the sample 1 (Figure 7) was determined presence of a very complex mineral assemblage that consists of: realgar (Re) rozenite (Roz), sulphur (S), vrbaite (Vrb), lorandite (Lor), marcasite

(Mar), dolomite (Dol) and bernardite (Ber), which in the best manner confirmed findings of Pasava et al. (1989), Boev et al. (2001), Makreski et al. (2014) and Boev et al. (2016).

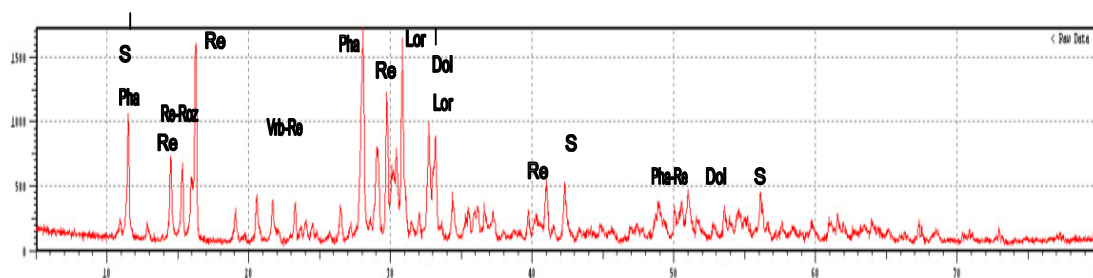


Fig. 8. XRD plot of typical minerals in sample 3 from the Crven Dol ore body, Alšar deposit

In the sample 3 (Figure 8) were determined various mineral representatives such as: realgar (Re), rozenite (Roz), sulphur (S), vrbaite (Vrb), lorandite (Lor), pharmacolite (Pha) and dolomite

(Dol), which confirmed already mentioned findings of Boev et al. (2001), Makreski et al. (2014) and Boev et al. (2016), as well as those of Rieck (1993) in regards to pharmacolite.

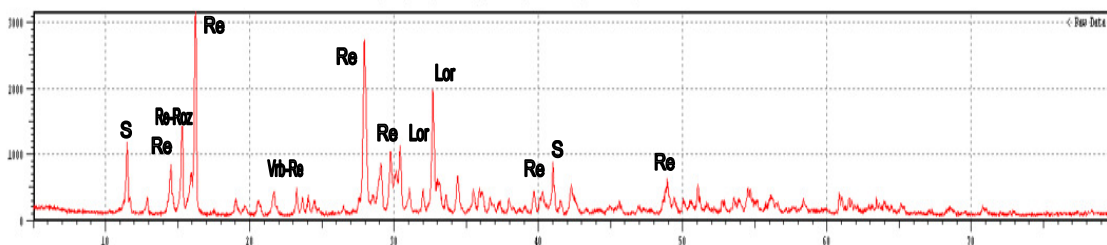


Fig. 9. XRD plot of typical minerals in sample 4 from the Crven Dol ore body, Alšar deposit

The sample 4 (Figure 9) XRD analysis did not show any new mineral species than previous two (samples 1 and 3) and dominant were realgar

(Re), lorandite (Lor), vrbaitite (Vrb), rozenite (Roz) and sulphur (S), while the other minerals only occurred in trace amounts.

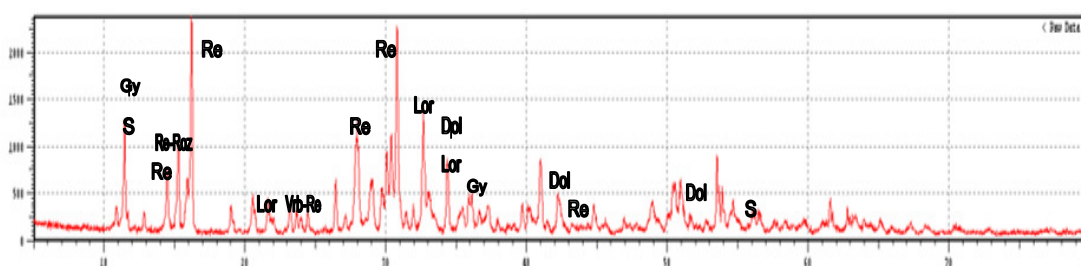


Fig. 10. XRD plot of typical minerals in sample 8 from the Crven Dol ore body, Alšar deposit

Similar to some of the previous samples, the sample 8 XRD analysis (Figure 10) showed dominance of realgar (Re) and lorandite (Lor) followed by vrbaitite (Vrb), rozenite (Roz), sulphur (S), dolomite (Dol) and gypsum (Gy).

Realgar is dominant mineral accompanied by marcasite, minor orpiment and thallium minerals (Volkov et al., 2016). Realgar encloses lorandites and marcasites. It appears as crystals, often of large size, and as massive pods and lenses. It is usually intergrown with orpiment and it frequently hosts lorandite. In some places realgar is found to cement "gel-marcasite".

Orpiment occurs in massive ore as small aggregates intergrown with realgar, but locally it forms plate crystals.

Marcasite and **pyrite** are widespread minerals. Collomorph textures are characteristic for both, particularly marcasite. Marcasite occurs in crystal forms, but frequently marcasite grains are rounded. Some marcasite grains consist of a core, a thin rim and globules of an As rich composition (Frantz et al., 1994). A detailed investigation of the mineral assemblages of the ore by Frantz et al. (1994) revealed a mineral phase with the composition of

arsenolithe (As_2O_3). It occurs along fissures inside of realgar crystal. This mineral phase is probably a secondary product from oxidation of elemental arsenic or from alteration of realgar. Process of oxidation may take place during the precipitation of realgar, in the first stage of mineralization.

Thallium minerals. The massive realgar ore body of Crven Dol contains numerous Tl-minerals, some of them have been recently discovered. The list of Tl-minerals from Crven Dol is still incomplete.

Lorandite is the most common thallium mineral. Lorandite occurs in close association with realgar and less frequently with orpiment, locally with marcasite. It sporadically forms large aggregates and/or individual crystals.

Vrbaitite occurs, mostly as small crystals with realgar and orpiment (Jezek, 1912). The aggregates of realgar, orpiment and vrbaitite crystals of variable sizes are found in hydrothermally altered dolomite and tuffaceous dolomite. Its deposition follows precipitation of As-sulphides.

Table 2 shows major and trace elements of realgar mineralization with lorandite within the ore body of Crven Dol.

Table 2

Major and trace elements in realgar-lorandite mineralization in Crven Dol (by ICP-MS; mg/kg)

	1	2	3	4	5	6	7	8	9	10
Fe	119777	120446	115261	82893	37789	56383	72372	108728	88894	174530
As	68833	58975	168833	66679	49848	38162	46731	212415	183314	88659
Ca	19461	18304	44781	15873	24824.87	23425	11303.34	66164	90391	15988
Mg	974	818	14424.20	246	253	261	447	27682	38458	2007
Tl	19749	14281	29672	29124	10923	29879	39314	14350	10787	38291
Al	2900	3952	2914	1804	1369	1189	4222	3902	4052	1741
K	1204	1210	1214	1544	867	521	1507	1325	1914	759
Na	88	104	200.82	569	117	287	288	126	25	117
Ti	5051	5941	6959.91	1742	4109	3263	5248	9775	11942	1392
P	2151	1447	830.82	978	1297	1151	1314	471	1267	1903
Mn	786	905	1930	167	200	340	388	2483	4241	10108
Zn	183.63	143.39	105.21	3.32	63.84	11.95	28.77	86.94	98.43	205.97
Sb	22.48	15.81	79.98	66.74	18.56	65.23	67.47	24.06	17.40	52.32
Ni	26.46	23.01	36.55	3.10	1.74	2.59	4.37	35.78	24.75	16.77
V	26.81	42.32	28.45	22.98	18.50	19.09	33.93	32.59	37.01	33.48
Co	26.27	24.10	35.05	2.09	0.73	3.82	4.94	34.62	22.80	17.38
Pb	5.91	3.34	0.53	2.40	0.30	2.32	0.70	2.51	4.88	2.93
Cr	9.69	13.54	9.87	5.63	4.41	4.15	11.34	11.99	12.97	4.57
Cu	7.98	2.01	4.83	1.28	2.84	1.90	0.79	4.88	4.04	0.71
Mo	16.65	18.25	15.48	7.63	5.06	5.95	8.45	12.37	17.72	11.43
Cd	3.31	3.25	0.55	<0.1	<0.1	<0.1	<0.1	0.37	0.45	0.72
Ba	35.49	10.50	7.22	4.69	4.00	3.39	10.99	12.52	10.46	4.05
Rb	9.29	12.48	6.76	5.18	3.49	3.01	12.83	8.91	9.88	3.38
Sr	4.17	2.92	5.84	5.28	5.34	5.47	2.86	14.22	17.60	2.74
Li	3.38	5.02	2.89	1.90	1.35	1.22	3.64	3.99	3.77	1.78
Be	0.31	1.00	0.69	0.12	0.17	0.47	0.52	0.63	0.89	8.28
Ga	0.99	0.46	0.29	0.23	0.16	0.13	0.49	0.46	0.39	0.18
Ge	2.81	2.70	2.56	1.86	0.99	1.43	1.61	2.56	1.54	3.88
Cs	5.53	7.20	4.18	2.45	1.60	1.52	5.88	5.86	6.27	1.62
Se	0.23	0.16	0.62	0.10	0.15	0.18	0.28	0.37	0.50	0.16
Pd	0.26	0.35	0.49	0.07	0.06	0.11	0.08	0.24	0.31	0.32
Ag	0.36	<0.1	<0.1	0.25	<0.1	0.19	<0.1	<0.1	<0.1	<0.1
Sn	0.80	0.71	0.47	0.54	0.48	0.74	0.94	0.62	1.43	0.51
Bi	<0.5	2.42	<0.5	2.85	<0.5	<0.5	<0.5	11.24	<0.1	<0.5
Th	0.69	0.74	0.68	0.39	0.34	0.38	0.83	0.75	0.89	0.47
U	3.64	2.94	2.36	0.92	0.92	1.04	1.66	1.99	2.42	2.87

It is possible to distinguish several geochemical associations on the base of the geochemical analysis, such as:

- Geochemical associations which are related to the volcanic activity in the Kožuf area: (Al, K, Ti, P, Na, Ba);
- Geochemical associations which are related to the hydrothermal activity in the Alšar area: (As, Tl); (Be, Ga, Se); (Bi, Th, U); (Cd, Sr, Li, Ge, Cs); (Mn–Zn);
- Geochemical associations associated with the basement litology (Fe, Ca, Mg).
- Geochemical associations which are related to the ultramafic rocks in the western flank of the Vardar ophiolitic belt (Pb, Cr, Cu, Mo, Rb); (Pd, Ag, Sn); (Sb, Ni, V, Co).

Based on the data shown in Table 2 was performed statistical analysis correlation of particular elements, and specific correlation parameters are given in Table 3.

The highest positive correlation was noted for certain mineral pairs such as: Fe-Ge (0.979), Fe-U (0.779), As-Sr (0.803), As-Ni (0.796), As-Se (0.790), Tl-Sb (0.857), Ti-Sr (0.836), Ti-Cr (0.786), Ti-Th (0.783), Ni-Co (0.996), Ni-Pd (0.852), V-Li (0.844), V-Cr (0.797), Co-Mo (0.819), Co-U (0.717), Rb-Cs (0.957), Rb-Li (0.932), Rb-Th (0.887), Li-Cs (0.980), Li-Th (0.883), Cs-Th (0.926), Pb-U (0.726) and U-Mo (0.885). Some of the most representative correlations are shown at Figure 11.



Fig. 11. The most representative elemental correlation pairs. Crven Dol ore body, Alšar deposit

Table 4 shows contents of the REE in the ore of Crven Dol, while Table 5 and Figure 12 present the normalized value of the REE. This diagrams show enrichment in the LREE and the very clearly negative Eu anomaly which is related to the very strong influence of the interactions between the hydrothermal solutions and the ultramafic rocks in the deeper part of the deposits.

Table 4

Rare earth elements in the realgar–lorandite mineralization in Crven Dol (by FUS-MS; in ppm)

Elements	Detection limits	Sample No				
		1	2	3	4	5
La	0.1	2.8	2.9	2.8	3	3
Ce	0.1	5.1	5.3	5.2	5.4	5.5
Pr	0.05	0.63	0.68	0.65	0.69	0.68
Nd	0.1	2.9	3.2	2.9	3.1	3
Sm	0.1	0.7	0.8	0.7	0.7	0.7
Eu	0.05	0.17	0.19	0.18	0.18	0.18
Gd	0.1	1	1.1	1	1	1
Tb	0.1	0.2	0.2	0.2	0.2	0.2
Dy	0.1	1.2	1.3	1.2	1.2	1.2
Ho	0.1	0.3	0.3	0.3	0.3	0.3
Er	0.1	0.9	0.9	0.9	0.9	0.9
Tm	0.05	0.14	0.14	0.13	0.14	0.14
Yb	0.1	0.9	0.9	0.9	0.9	0.9
Lu	0.01	0.14	0.15	0.15	0.15	0.15
Hf	0.2	0.3	0.3	0.5	0.8	0.2
Ta	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
W	1	24	44	41	47	5
Tl	0.1	> 1000	> 1000	> 1000	> 1000	> 1000
Pb	5	17	5	6	6	< 5
Bi	0.4	0.7	< 0.4	< 0.4	0.6	< 0.4
Th	0.1	0.6	0.6	0.6	0.6	0.6
U	0.1	5.3	5.6	5.3	5.4	5.2

Table 5

The REE results from the Crven Dol locality were normalized using the average C1 chondrite abundances of Boynton (1984)

Sample	La _N	Ce _N	Pr _N	Nd _N	Sm _N	Eu _N	Gd _N	Tb _N	Dy _N	Ho _N	Er _N	Tm _N	Yb _N	Lu _N
1	9.03	6.31	5.16	4.83	3.59	2.31	3.86	4.22	3.73	4.18	4.29	4.32	4.31	4.35
2	9.35	6.56	0.57	5.33	4.1	2.59	4.25	4.22	4.04	4.18	4.29	4.32	4.31	4.66
3	9.03	6.44	5.33	4.83	3.59	2.45	3.86	4.22	3.73	4.18	4.29	4.01	4.31	4.66
4	9.68	6.68	5.6	5.17	3.59	2.45	3.86	4.22	3.73	4.18	4.29	4.32	4.31	4.66
5	9.68	6.81	5.57	5	3.59	2.45	3.86	4.22	3.73	4.18	4.29	4.32	4.31	4.66

Trace elements, especially rare earth elements (REE), are widely used to model the petrogenesis and evolution of igneous sedimentary and metamorphic rocks (e.g. Haskin, 1984; Fleet, 1984), especially as REE are generally regarded as insensitive to hydrothermal alteration. However, literature supporting REE mobility during hydrothermal processes has been rapidly expanding in the last two decades (Nesbitt, 1979; Alderton et al., 1980; Humphris, 1984; Marsh, 1991; Williams-Jones and Wood, 1992; Gouveia et al., 1993; Mongelli, 1993; Prudencio et al., 1993; Van der Weijden and Van der Weijden, 1995). Recently, the potential of REE to provide information about ore forming processes through REE mobility or immobility during ore formation processes has widely been recognized, and detailed REE investigations have been performed on many metallic deposits (Taylor and Fryer, 1980, 1982; Campbell et al., 1984; Gieré, 1986; Whitford et al., 1988; Lottermoser, 1992; Parr, 1992; Wood and Williams-Jones, 1994; Bierlein, 1995; Bierlein et al., 1999). The mobility of trace elements in altered host-rocks, and their distribution in host rocks and ores may provide constraints regarding the physico-chemical characteristics of the ore-bearing fluids, and may contribute to understanding the ore-forming processes (Lottermoser, 1992).

Rare earth elements in realgar and lorandite were normalized to the chondrite standard value of REE as quoted from the data of Boynton (1984). The abundance characteristic parameters and distribution pattern of REE in analyzed 5 samples from the Crven Dol locality are distinctive (Table 5, Figure 12).

The distribution trends are shown as log-normalized REE abundances versus the atomic numbers of the REEs (Figure 12).

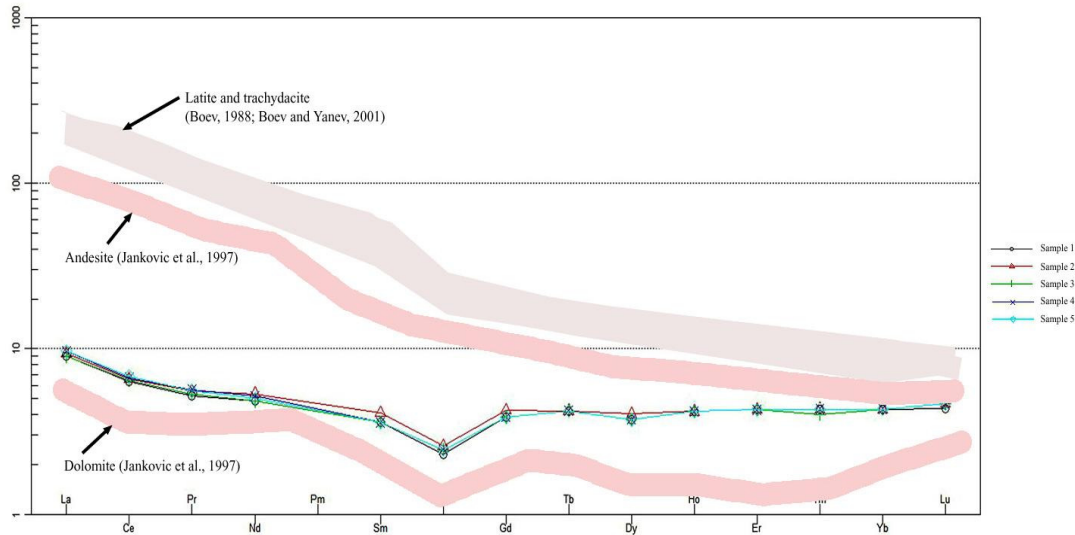


Fig. 12. REE normalized plots of several different geological units (Boev, 1988; Boev and Yanev., 2001; Janković et al., 1997) and realgar and lorandite mineralization from the Crven Dol ore body, Alšar deposit

The REE profiles of samples from the surrounding lithologic units (latite, trachydacite, andesite and dolomite) of the Kožuf volcanic area are subparallel with only minor differences (Boev, 1988; Janković et al., 1997; Boev and Yanev., 2001). (Figure 12). However, the REE profiles of the minerals of interest (realgar and lorandite) are with slightly different shape. Realgar and lorandite always have a lower concentration in all elements compared to the host rock, which can be attributed to a dilution. Although the REE patterns of the ores (realgar and lorandite) and the host rocks are quite similar, minor but consistent differences are still discernable. The $(La/Yb)_N$ ratios of the ores ($2.0951 \div 2.2459$), are apparently lower than those of the host rocks ($3.1250 \div 25.5820$) indicating a fractionation of REE during the hydrothermal alteration (Bau, 1991).

The two patterns are near parallel, with however a progressive depletion from Gd to Lu compared to the host rock. The light rare earth elements (LREE) – heavy rare earth elements (HREE) ratio is still higher in realgar and lorandite than in its host rock. In the example $La_N/Yb_N = 35-45.95$ for latite and trachydacite, $3.125-27.581$ for dolomite and $2.095-2.2459$ for realgar and lorandite, meaning that HREE are more fractionated in the latite, trachydacite and dolomite. This is consistent with the hypothesis that HREE are more incompatible than LREE, and so stay preferentially in the host rock. Representative samples from dolomitic zones in the Crven Dol locality have low REE abundances and more pronounced negative Eu

anomalies than the other rock units very similar to findings in some other localities (Bozkaya and Gokce, 2004). Simply, the profiles with negative Eu anomalies and the LREE sections of these profiles are negatively sloped, while the HREE sections are relatively flat as is common in sediments (McLennan 1989).

The Σ_{REE} in realgar and lorandite are relatively higher. Namely, $\Sigma_{REE} = \sim 62.77-66.74$ ppm, $\Sigma_{LREE}/\Sigma_{HREE} = \sim 0.8316-0.9881$, and $La_N/Yb_N = \sim 2.0951-2.2459$. The distribution patterns belong to the “L_{REE} enriched” type. Specifically, the fractionation is obvious for the L_{REE} ($La_N/Sm_N = \sim 2.2805-2.6964$), but not obvious for the H_{REE} ($Gd_N/Yb_N = \sim 0.8956-0.9861$). Further calculations showed, both Eu and Ce, negative anomalies as can be seen from Table 6.

Table 6

Calculated Eu and Ce anomalies in the Crven Dol locality

Sample	Eu anomaly	Ce anomaly
1	0.6205	0.8270
2	0.6205	0.8190
3	0.6582	0.8440
4	0.6582	0.8170
5	0.6582	0.8387

Eu was calculated as:

$$\text{Eu}^* = \frac{\text{Eu}_N}{\sqrt{\text{Sm}_N}},$$

while Ce anomaly was calculated as:

$$\text{Ce}^* = \frac{3 \cdot \text{Ce}_N}{2 \cdot \text{La}_N + \text{Nd}_N}.$$

Both Eu and Ce show a weak negative anomaly. Eu showed $\text{Eu}^* = \sim 0.6205 - 0.6582$ (average of 0.6393), while Ce showed values of $\text{Ce}^* = \sim 0.8170 - 0.8440$ (average of 0.8267). In regards

to that we may point out that the weak negative Ce anomalies and negative Eu anomalies (Table 6) show that the ore-forming environment was rather reducing (Bau, 1991). The negative Eu anomaly probably reflects that Eu may be leached out of footwall rocks in the hottest part of the hydrothermal system (Gale et al., 1997). A chondrite normalized plot reflects this Eu depletion (Figure 12; Boev, 1988; Janković et al., 1997; Boev and Yanev, 2001). This provides a potential vectoring device for the exploration geologist.

CONCLUSION

The hydrothermal system of Crven Dol includes As-Tl-Fe-S minerals, sparse Sb and barite, traces of Au and Hg, as well as minor silica. The same minerals are determined in the antimony mine in the central part of the deposit.

The main minerals determined by the X-ray diffractions are: lorandite, vrbaita, bernardite, realgar, orpimente, marcasite, pyrite, rozenite, sulfur, gypsum, dorallcharite, dolomite, quartz, farmakolite, fangite, jankovicite.

The process of mineralization took place in shallow depth. in a strong oxidation environment, under high arsenic and thallium fugacity the period of the dominance of arsenic was followed by high

concentrations of thallium decreasing gradually to the end of precipitation of primary mineralization.

Since trace elements of investigated rocks in and near Crven Dol show that As and Tl contents of carbonate rocks are low, it appears that volcanics are the most probable ultimate source of ore metals, mobilized by hydrothermal fluids, which was confirmed by trace elements concentrations and REEs in the ore mineralization from Crven Dol. Trace elements concentrations and REEs in the ore mineralization from Crven Dol indicated that the influences of the ultramafic rocks are significant in the genesis of this mineralizations.

REFERENCES

- Alderton, D. H. M., Pearce, J. A. and Potts, P. J. (1980): Rare earth elements mobility during granite alteration: evidence from southwest England. *Earth and Planetary Science Letters*, **49**, 149–165.
- Balić-Žunić, T. and Makovicky, E. (1993a): Contributions to the crystal chemistry of thallium sulphosalts, I. The O-D nature of imhofite. *N. Jb. Miner. Abh.*, **165**, 3, 317–330.
- Balić-Žunić, T., Möelo, Y., Lončar, Ž. and Michelsen, H. (1994): Dorallcharite. $\text{Tl}_{0.8}\text{K}_{0.2}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, a new member of the jarosite–alunite family, *Eur. J. Mineral.*, **6**, 255–263.
- Balić-Žunić, T., Stafilov, T. and Tibljaš, D. (1993b): Distribution of thallium and the ore genesis at the Crven Dol locality in Alšar. *Geologica Macedonica*, **7**, 1, 45–52.
- Bau, M. (1991): Rare–earth element mobility during hydrothermal and metamorphic fluid–rock interaction and the significance of the oxidation state of europium. *Chemical Geology*, **93**, 219–230.
- Beran, A., Gotzinger, M. and Rieck, B. (1990): Fluid Inclusion in Realgar from Allchar. *Proceedings of the Symposium on Thallium Neutrino Detection*. Dubrovnik.
- Bierlein, F. P. (1995): Rare–earth element geochemistry of clastic and chemical metasedimentary rocks associated with hydrothermal sulphide mineralisation in the Olary Block, South Australia. *Chem. Geol.*, **122**, 77–98.
- Bierlein, F. P., Waldron, H. M. and Arne, D. C. (1999): Behaviour of rare earth and high strength elements during hydrothermal alteration of meta–turbidities associated with mesothermal gold mineralization in central Victoria, Australia, *Journal of Geochemical Exploration*, **67**: 109–125.
- Boev, B. (1988): *Petrological, geochemical and volcanic features of volcanic rocks of the Kožuf Mountain*. PhD Thesis. Faculty of Mining and Geology. Štip. 195 pp (in Macedonian).
- Boev, B., Bermanec, V., Serafimovski, T., Lepitkova, S. and Mikulčić, S. (2001): Allchar Mineral Assemblage. *Geologica Macedonica*, **15–16**, p. 1–23 (2001–2002) Suppl.
- Boev, B., Yanev, Y. (2001): Tertiary magmatism within the Republic of Macedonia: A review, *Acta Vulcanologica*, **13** (1–2), 57–72.
- Boev, B., Šorša, A. and Boev, I. (2016): Geochemical and mineralogical characteristics of the central part of the Alšar deposit (Republic of Macedonia) with particular reference to investigations by X–ray diffraction. *Geologica Macedonica* **30**, pp. 115–127.

- Boynton, W. V. (1984): Geochemistry of the rare earth elements: meteorite studies. In: Henderson, P. (ed.), *Rare Earth Element Geochemistry*, Elsevier, 63–114.
- Bozkaya, G. and Gokce, A. (2004): Trace- and Rare-Earth Element Geochemistry of the Karalar (Gazipasa–Antalya) Barite–Galena Deposits. Southern Turkey. *Turkish Journal of Earth Sciences (Turkish J. Earth Sci.)*, Vol. **13**, pp. 63–76.
- Campbell, I. H., Leshner, C. M., Coad, P., Franklin, J. M., Gorton, M. P. and Thurston, P. C. (1984): Rare earth element mobility in alteration pipes below massive Cu-Zn-sulfide deposits, *Chem. Geol.*, **45**, 181–202.
- Fleet, A. J. (1984): Aqueous and sedimentary geochemistry of the rare earth elements (Chapter 10). In: Henderson, P. (Ed.), *Rare Earth Element Geochemistry (Developments in Geochemistry, 2)*, Elsevier, Amsterdam, 343–374.
- Frantz, E. (1994): *Mineralogische, geochemische und isotopen-geochemische Untersuchungen der As–Tl Sulfide in der Lagerstätte von Allchar*. Doctoral Dissertation, Mainz, 1994.
- Frantz, E., Palme, H., Todt, W., El Goresy, A., Pavičević, M. K. (1994): Geochemistry of Tl–As minerals and host rocks at Alšar (FYR Macedonia). Solar neutrino detection with Tl–205 the “LOREX” Project: geology, mineralogy and geochemistry of the Alšar deposit locality Crven Dol. *N. Jb. Miner. Abh.*, **167**, 359–399.
- Gale, G. H., Dabek, L. B. and Fedikow, M. A. F. (1997): The application of rare earth element analyses in the exploration for volcanogenic massive sulphide type deposits. *Explor. Mining. Geol.*, Vol. **6**, number 3., pp. 233–252.
- Giere, R. (1986): Zirconolite, allanite and hoegbomite in a marble skarn from the Bergell contact aureole: implications for mobility of Ti, Zr and REE, *Contrib. Mineral. Petrol.*, **93**, 459–470.
- Gouveia, M. A., Prudencio, M. I., Figueiredo, M. O., Pereira, L. C. J., Waerrnborgh, J. C., Morgado, I., Pena, T. and Lopes, A. (1993): Behavior of REE and other trace and major elements during weathering of granitic rocks, Evora, Portugal. *Chem. Geol.*, **107**, 293–296.
- Haskin, L. A. (1984): Petrogenetic modeling — use of rare earth elements (Chapter 4). In: Henderson, P. (Eds.), *Rare Earth Element Geochemistry. (Developments in Geochemistry, 2)* Elsevier, Amsterdam, 115–152.
- Humphris, S. E. (1984): The mobility of the rare earth elements in crust. In: P. Henderson (Ed.), *Rare Earth Elements Geochemistry (Developments in Geochemistry, 2)*. Elsevier, Amsterdam, pp. 317–342 (Chapter 9).
- Ivanov, T. (1965): Zonal distribution of elements and minerals in the deposit Alšar,– *Symp., Problems of Postmagmatic Ore Deposition*, II. 186–191, Prague (in Russian).
- Ivanov, T. (1986): Allchar – the richest ore deposit of Tl in the world, GSI-report, 86–9. Darmstadt, pp. 6.
- Janković, S. (1960) Allgemeine Charakteristika der Antimonit Erzlagerstätten Jugoslawiens, *N. Jb. Mineral. Abh.*, **94**, 506–538.
- Janković, S. (1993): Metallogenic features of the Alšar, epithermal Sb–As–Tl deposit, The Serbo-Macedonian Metallogenic Provincem, *N. Jb. Miner. Abh.*, **166**, 1, 25–41, Stuttgart.
- Janković, S. and Jelenković, R. (1994): Thallium mineralization in the Alšar Sb–As–Tl–Au deposit. *N. Jb. Mineral. Abh.*, **167**, 283–297
- Janković, S., Boev, B. and Serafimovski, T. (1997): *Magmatism and tertiary mineralization of the Kozuf metallogenic district, the Republic of Macedonia with particular reference to the Alšar deposit*, Univ. “St. Kiril and Metodij” – Skopje., Faculty of Mining and Geology, Geological Department, Special Issue No. 5, 262 p.
- Jezek, B. (1912): Vrbait. ein neues Thallium Mineral von Allchar in Macedonien, *Z. Kristallogr.* **51**, 3, 365–378.
- Lepitkova, S. (1995): *Petrologic Features of the Volcanic Rocks in the Vicinity of the Alšar Deposit, with Particular Reference to Lead Isotopes*, Master Degree Thesis. Faculty of Mining and Geology, Štip, 139 (in Macedonian).
- Lippolt, H. J. and Fuhrmann, U. (1986): K–Ar age determination on volcanics of Alšar mine/Yugoslavia, In: *Proceed. Workshop on the feasibility of Solar Neutrino Detection with ²⁰⁶Pb by geochemical and mass spectrometrical measurements*, Nolte E. (Ed.) Report GSI-86–9, Technische Univer, München.
- Lottermoser, B. G. (1992): Rare earth elements and hydrothermal ore formation processes, *Ore Geology Review*, **7** (1), 25–41.
- Makreski, P., Jovanovski, G. and Boev, B. (2014): Micro-Raman spectra of extremely rare and endemic Tl-sulfosalts from Allchar deposit, *J. Raman Spectrosc.*, **45**, pp. 610–617.
- Marsh, J. S. (1991): REE fractionation and Ce anomalies in weathered Karoo dolerite, *Chem. Geol.*, **90**, 189–194.
- McLennan, S. M. (1989): Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary process. Review of mineralogy, **21**, 169–200.
- Mongelli, G. (1993): REE and other trace elements in a granitic weathering profile from "Serre", Southern Italy, *Chem. Geol.*, **103**, 17–25.
- Nesbitt, H. W. (1979): Mobility and fractionation of rare earth elements during weathering of a granodiorite, *Nature* (London), **279**, 206–210.
- Parr, J. M. (1992): Rare-earth element distribution in exhalites associated with Broken Hill type mineralisation at the Pinnacles deposit, New South Wales, Australia, *Chem. Geol.*, **100**, 73–91.
- Pasava, J., Pertlik, F., Stumpfl, E. F. and Zemann, J. (1989): Bernardite, a new thallium arsenic sulphosalt from Alšar. Macedonia, with a determination of the crystal structure. *Mineralogical Magazine*, **53**, pp. 531–538.
- Pavičević, M. K., Cvetković, V., Amthauer, G., Bieniok, A., Boev, B., Brandstätter, F., Göttinger, M., Jelenković, R., Prelević, Prohaska, T. (2006): Quartz from Alšar as monitor for cosmogenic ²⁶Al: Geochemical and petrogenetic constraints, *Mineral. Petrol.*, **88**, 527–550.
- Pe-Piper, G. and Piper, D. J. W. (2002): *The igneous rocks of Greece*, The anatomy of an orogen, Gebrüder Borntraeger, Berlin–Stuttgart, 573 p.
- Percival, T. J., Boev, B. (1990): As-Tl-Sb-Hg-Au-Ba mineralization, Alšar district, Yugoslavia: A unique type of Yugoslavian ore deposit, In: *Symp. on Thallium Neutrino Detection*, Dubrovnik. 36–37 (abstr.).

- Percival, T. J., Radtke, A. S. (1990): Carlin Type Gold Mineralization in the Alšar District, Macedonia, Yugoslavia, *Proceeding of the Eight Quadrennial IAGOD Symposium, Ottawa, Canada*. Program with Abstracts. P. A., 108.
- Percival, T. J., Radtke, A. S., Jankovic, S., Dickinson, F. (1992): Gold Mineralization of the Carlin-type in the Alšar district, SR Macedonia, Yugoslavia, – Y. T. Maurice (Ed.), *Proc. the IAGOD Symp., Ottawa, Canada Proceed.*. E. Schweizerbarische Verlag. 637–646. Stuttgart.
- Percival, T. J., Radtke, A. S. (1994): Sedimentary–rock-hosted disseminated gold mineralization in the Alšar District, Macedonia, *Canad. Mineralogist.*, 32, 649–665.
- Prudencio, M. I., Braga, M. S. A. and Gouveia, M. A. (1993): REE mobilization, fractionation and precipitation during weathering of basalts, *Chem. Geol.*, 107, 251–254.
- Rieck, B. (1993): Famous mineral localities: Allchar, Macedonia. *Mineralogical Record*, 24 (6), pp. 437–449.
- Taylor, R. P. and Fryer, B. J. (1980): Multi-stage hydrothermal alteration in porphyry copper systems in northern Turkey: the temporal interplay of potassic, prophylic and phyllic fluids, *Canadian Journal of Earth Sciences.*, 17, 901–926.
- Taylor, R. P. and Fryer, B. J. (1982): Rare earth element geochemistry as an aid to interpreting hydrothermal ore deposits. In: A. M. Evans (Editor): *Metallization Associated with Acid Magmatism*. Wiley, New York, N. Y., pp. 357–365.
- Troesch, M. and Frantz, E. (1992): $^{40}\text{Ar}/^{39}\text{Ar}$ Alter der Tl–As Mine von Crven Dol, Allchar (Macedonia), *Eur. J. Mineral.*, 4, 276.
- Van der Weijden, C. H. and Van der Weijden, R. D. (1995): Mobility of major, minor and some redox-sensitive trace elements and rare earth elements during weathering of four granitoids in central Portugal, *Chem. Geol.*, 125 (3/4), 149–168.
- Volkov, A. V., Serafimovski, T., Kochneva, N. T., Thomson, I. N. and Tasev, G., (2006): The Alshar epithermal Au–As–Sb–Tl deposit, southern Macedonia, *Geology of Ore Deposits* 48, 175–192.
- Whitford, D. J., Bird, M. I., Craven, S. J., and Chivas, A. R. (1988): Strontium isotopic study of alunites from Australia. *Australian Conference on Geochronology* (abs), Bureau of Mineral Resources, Geology and Geophysics, Canberra, and Research School of Earth Sciences, The Australian National University, Canberra.
- Williams-Jones, A. E., Wood, Scott A. (1992): A preliminary petrogenetic grid for REE fluorocarbonates and associated minerals, *Geochimica et Cosmochimica Acta*, 56, 725–738.
- Wood, S. A. and Williams-Jones, A. E., (1994): The aqueous geochemistry of the rare-earth elements and yttrium 4. Monazite solubility and REE mobility in exhalative massive sulfide – depositing environments, *Chemical Geology*, 115, 47–60.
- Yanev, Y., Boev, B., Doglioni, C., Innocenti, F., Manetti, P., Pecskey, Z., Tonarini, S. and D’Orazio, M. (2008): Late Miocene to Pleistocene potassic volcanism in the Republic of Macedonia, *Miner. Petrol.*, 94, 4, pp. 5–60.

Резиме

МИНЕРАЛОГИЈА И ГЕОХЕМИЈА НА ЕЛЕМЕНТИТЕ ВО ТРАГИ ВО ЦРВЕН ДОЛ – НАОЃАЛИШТЕ АЛШАР (РЕПУБЛИКА МАКЕДОНИЈА)

Иван Боев¹, Ајка Шорша², Горан Тасев¹, Далибор Серафимовски¹, Блажо Боев¹¹Факултет за природни и технички науки. Универзитет “Гоце Делчев” во Штипи, Бул. Крсте Мисирков 10-А, П.О.Фах. 210., 2000 Штипи., Република Македонија²Институт за геологија, Хрватски геолошки завод, Сахсова 2, 10 000 Загреб, Хрватска, blazo.boev@ugd.edu.mk**Клучни зборови:** елементи во траги; елементи на ретки земји; лорандит; Црвен Дол

Во трудот се претставени нови резултати од минералошките испитувања извршени на примероци од рудната минерализација од Црвен Дол со примена на рендгенска дифракција, како и резултати од испитувањата на присутноста на елементи во траги и ретки земји извршени со примена на методите на ICP-MS. Од минералошките испитувања може да се заклучи дека во испитуваниот локалитет е присутна многу ретка минерална асоцијација претставена од лорандит, реалгар, аурипигмент, врбаит, бер-

нардит, јанковиќит, фангит, росенит, фармаколит, марказит, пирит, сулфур, гипс, доралшарит, доломит, кварц. Дистрибуцијата на елементите во траги и ретките земји во околните карпи, како и во самата рудна минерализација ја сугерира идејата за големо влијание на ултрабазичните карпи од подлогата на западниот офилолитски појас на Вардарската зона во еволуцијата на составот на хидротермалните раствори во локалитетот Црвен Дол.