

МАКЕДОНСКО ГЕОЛОШКО ДРУШТВО

ВТОР КОНГРЕС

на

Геолозите на Република Македонија

**ЗБОРНИК НА ТРУДОВИ**



*Уредници:*

Јовановски, М. & Боев, Б

*Крушево, 2012*

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## ПРЕДГОВОР

Геолошката наука на територијата на Република Македонија има долга традиција, а е поврзана пред се со рударската активност. Познати се локалитети каде се најдени монети од бакарната и бронзената доба. Сочувани се траги на експлоатација на злато од речниот нанос на Коњска Река-Гевгелиско и на други места, од времето на Александар Македонски. Во источна Македонија рударењето било интензивно за римско време.

Први геолошки податоци на научна основа за територијата на Македонија се јавуваат во првата половина на XIX век, а првите печатени геолошки трудови за нашите простори се среќаваат кај А.Буче (1828-1870) и Виксенел (1842). Од крајот на XIX век па се до денес во зависност од интензитетот на истражувањата напишани се голем број на трудови од сите области на геологијата.

Активностите на стручните лица од областа на геологијата се изведуваат преку Македонското Геолошко Друштво кое е формирано во 1952 година.

Во 2008 година се одржа Првиот Конгрес на Геолозите на Република Македонија од кој излезе зборник со преку 50 научни трудови од кои добар дел беа подготвени од меѓународни тимови.

Во периодот помеѓу 2008 и 2012 година во нашата земја се изведоа голем број на активности во сите полиња на геологијата. Особено важни да се споменат се интензивните истражувања на металични и неметалични минерални сировини, регионалните, геохемиските и инженерско-геолошките, итн.

Вториот Конгрес на Геолозите на Република Македонија претставува сублимат на научните сознанија базирани на споменатите геолошки истражувања и испитувања кои се одвиваа на територијата на нашата земја во периодот од 2008-2012 година. Исто така, на конгресот е презентирани и дел од работата на колеги геолози од соседните земји, така да и овој пат со задоволство може да констатираме дека конгресот има меѓународен карактер.

## PREFACE

Geological science on the territory of Republic of Macedonia has long tradition, and is mainly connected to the mining activities. There are numerous localities where coins from copper and bronze age are found. Traces from exploitation of gold in the river Konjska-Gevgelija and other places are known, in the time of Alexander the Great. In eastern Macedonia the mining was very intensive during the Roman period.

First scientific geological data for the territory of Macedonia are found in the first half of XIX century, and the first printed papers for our region are found at A.Bue (1828-1870) and Viksenel (1842). From the end of XIX century until today, depending on the intensity of the investigations numerous publications are presented in all fields of geology.

The activities of geological scientists are performed in the frame of the Macedonian Geological Society which is formed in 1952.

In 2008 the First Congress of Geologists of Macedonia was held. Proceedings with over 50 papers were published. Numerous papers were prepared by international teams.

In the period between 2008 and 2012 investigations in all fields of geology were performed. Especially important to mention are the investigations of metallic and non-metallic mineral resources, regional, geochemical, engineering-geological, etc.

The Second Congress of Geologists of Republic Macedonia presents sublimates of scientific knowledge based on the mentioned geological investigations which were conducted in the period 2008-2012. Also, the congress presents part of the work of colleagues from neighboring countries, so with great pleasure we can once again confirm its international character.

**Претседател  
на организационен одбор**

**President  
of organizing committee**

Проф. д-р Милорад Јовановски

# GEOLOGY AND MINERALOGY OF ALLCHAR Sb-As-Tl-Au DEPOSIT

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## Abstract

Allchar (Alšar) locality belongs to the group of complex, polychrono-polygenetic volcano-hydrothermal Sb-As-Tl-Au deposits. It is formed in the heterogeneous geological environment and in the complex physico-chemical processes of extraction of ore constituents from the primary sources in the form of hydrothermal solutions and their later deposition. Mobilization, transport and deposition of the ore mineralization as well as the supergene transformations of the primary minerals have been influenced and partly accompanied by intense pre- and post-ore structural-tectonic terrain transformations. As a consequence of the mentioned complex processes of formation at Allchar deposit, a large number of morphostructural types of ore bodies as well as different texture-structural ore varieties and complex mineral and element associations are created (produced). The mentioned complexity and diversity of mineral associations, especially the Tl-mineral association, makes Allchar the world-wide unique mineral deposit.

**Key words:** Allchar, polychrono-polygenetic volcano-hydrothermal Sb-As-Tl-Au deposits, diversity of mineral associations

## GEOGRAPHICAL POSITION AND HISTORY OF THE LOCALITY

Allchar deposit is settled on the very South part of the Republic of Macedonia (about 40 km far from Kavadarci) being located on the east part of Mtn. Kozjak (Mariovo region). To the east the area spreads to the very west branches of Mtn. Kožuf (Zelen Breg, 2165 m). The central part of the area spreads between the rivers Majdanska Reka and Bistrica, the tributaries of rivers Bistrica and Crna Reka, respectively.

**Allchar** (derived from the names **Allatini** - banker, owner of the concession and **Charteau** - mining engineer who worked in the mine) or, as it is well known among the people, Majdan (Turkish word for the mine) has a long history which originates from the ancient Macedonia period, and through the Roman and the Ottoman Empire period pass away to nowadays. The Allchar (Majdan) mine history is rather interesting but at the same time very scarcely documented. Here some historical facts which confirm the long tradition of this mine will be quoted. The most curious one among them is that minerals from the Allchar locality are found at the most famous archeological site in the

Republic of Macedonia – the ancient city of Stobi, first mentioned in documents from the 2<sup>nd</sup> century B. C.

In the written documents, the Allchar (Majdan) mine is for the first time mentioned in the Turkish notebooks (originally known as Turkish defters) from 1481 (MILETIC et al., 1927). In this document concerning to the Rožden district (Rožden village is in the close vicinity of Allchar mine), the annual income of the Turkish sultan related to Allchar mine activity is mentioned (SURIN, 1927). Similar data are also given after the population listing in 1519 where the annual production of the Allchar mine is mentioned (KAMCEVSKI, 2001). After population listing in 1528/1929 it is registered that the annual production of Majdan is: 30 kantars (kantar is an old Turkish unit amounting 56,452 kg) pure arsenic; 60 kantars non-pure arsenic. Similar quantities are mentioned for the years 1554/1545 and 1568/1569: 28 kantars pure arsenic; 70 kantars non-pure arsenic. It is evidently that Sultan has registered significant tax income from the production of the arsenic from Allchar mine

reaching about 35 % of the total taxes from the Mariovo district. Next data related to the Allchar mine production come from the documents from 1877 when the mining village Majdan has been established. At that period Allchar mine has been given under concession of the English-French company established in Thessaloniki, the production being controlled by mine engineer Charteau. The number of employed miners coming from the surrounding villages of Mariovo district has reached about 500, most of them being from the Rožden village. In the meantime (1980-1912) the small center for mine grinding and separation of useful minerals has been established at Allchar mine. Using the horses and mules the grinded and separated ore has been transported to village S'botsko and Thessaloniki and later by train to the smeltery in Freiburg, Germany. The ore transported by the mentioned train has been used for the separation and discovering of the first samples of Tl containing minerals from Allchar mine by the end of XIX and beginning of the XX century (VRBA, 1894; KRENNER, 1895; GOLDSCHMIDT, 1899; JANNACH, 1904; LOCZKA, 1904; JEZEK, 1912 & 1913). The exploitation of the Allchar mine during the Balkan Wars (1912-1913) and the First World War (1914-1918) has been stopped, the geological activities being renewed after the Second World War (1939-1945) but not the exploitation. During the geological investigations in 1953-1957 and 1962-1965 periods around 300.000 tons of antimony, arsenic and thallium ores have been discovered (containing 1.5, 2.2 and 0.11-0.22% of Sb, As and Tl, respectively) (IVANOV, 1963). In the early 80-thies of the XX century minerals from Allchar locality, especially lorandite, become rather attractive regarding the idea to use them as neutrino detectors coming from the sun (PAVICEVIC, 1988).

#### **GEOLOGICAL CONSTITUTION OF THE WIDER REGION OF ALLCHAR DEPOSITE**

Allchar locality is in fact settled in the volcanic complex of Mtn. Kožuf having a common frontier with Mtn, Kozjak. This volcanic complex is east-west oriented being about 30 km long. On the east the complex spreads to the Demir Kapija-Gevgelija ophiolitic complex, whereas to the west it reaches the overthrust structure which separates the

Pelagonian metamorphic complex and Vardar zone (BOEV, 1988). The development and evolution of this volcanism is closely related to the development and evolution of the Vardar zone. Thereby the labile geotectonic unit is formed in the period from the Mio-Pliocene to the Quarter (ARSOVSKI, 1962). In the Neotectonic period (from the end of Oligocene to the Pliocene) the territory of the Republic of Macedonia is characterized by the processes of radial tectonics and formations of longitudinal and transferzal grabens structures (KOCHNEVA et al., 2006; VOLKOV et al., 2006). Formation of some of these grabens related to the activation of the neogen magmatism in the territory of the Republic of Macedonia (BOEV, 1988) as well as with the neogen volcanism in the Mtn. Kožuf region. This volcanism is of central type and is localized on the cross section between the transfersal structure Kožuf-Kilikis (E-W) and the structures of Vardar zone (NW-SE to N-S) (IVANOV, 1963). This central type of volcanism is pointed out by the numerous ring structures characteristic for the Mtn. Kozuf region (BOEV, 1988; KOCHNEVA et al., 2006). From the geological point of view, the surroundings of the Allchar locality consists of several geological formations arranged in five stratigraphic complexes (Fig. 1):

- complex of Precambrian metamorphic rocks,
- complex of Mezozoic (Triassic-Jurassic) rocks,
- complex of upper Kreda sediment rocks,
- complex of Pliocene sediments, pyroclastites and volcanic rocks,
- complex of quaterner sediments.

**Complex of Precambrian metamorphic rocks** is presented by albite gneisses and marbles in the metamorphic block of Mala Rupa region (in the Eastern part of Mtn. Kožuf), and by gneisses and mica schists in the tectonic block Elen Šupe (in the Western part of Mtn. Kožuf) (ARSOVSKI, 1962).

**Complex of Mezozoic (Triassic-Jurassic) rocks** consists of rocks with sediment and metamorphic genesis as well as rocks of magmatic genesis. The complex of rocks with sediment and metamorphic genesis is presented by facies of colourful clay schists with intercalations of limestones, and with the facija of limestones and dolomite limestones of Triassic-Jurassic age. The rock series of Jurassic age is presented by facies of plate and

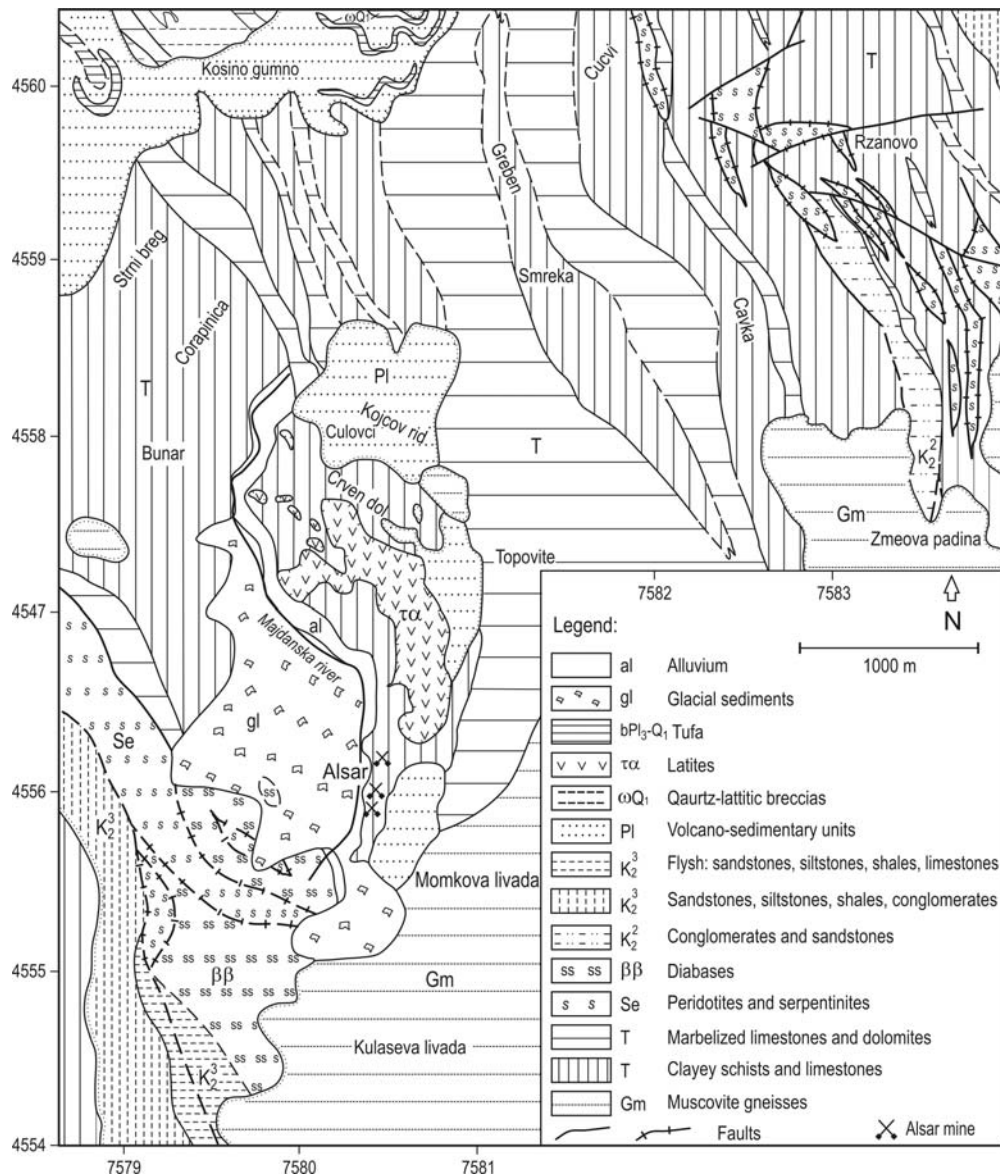
massive limestones and facies of sandstones and clay schists, quartzlites and cherts. The rock series of Triassic age is presented by marbleized limestones and dolomites, clay schists and sandstones with intercalation of diabases and green schists. In this complex of mezozoic rocks the magmatic rocks are also included being presented by ofiolitic rocks (serpentinized dunites, serpentized harzburgites, gabbros, basalts, diabases and gabbropegmatites).

**The complex of Upper-Cretaceous sedimentary rocks** consists of series of sandstones and conglomerates of Alb and Baramian age and series of limestones of Turonian age.

**The complex of Pliocene sediments, pyroclastites and volcanic rocks** consists of lake sediments laying over the sediments of upper Eocene. Pliocene sediments are presented by roughly grained conglomerates and claystone sediments, clay carbonate sediments and marls. In this series

sometimes horizons of diatomaceous earth appear. The complex of Pliocene sediments terminates with the appearance of tufas and travertines overlaid by a series of pyroclastite rocks. This series of pyroclastite rocks is presented by various types of lakustriski tuffs, volcanic agglomerates and volcanic glasses. The volcanic rocks of Pliocene age are widely spread on the Mtn. Kozuf (Republic of Macedonia (BOEV, 1988), and Mtn Voras (Greece) (KOLIOS et al., 1980). This complex of volcanic rocks spreads on about 2000 km<sup>2</sup> and, in general, consists of alkali basalts, andesites, latites, trachites and rhyolites. Their age ranges from 1.8 to 6.5 million years (Boev, 1988).

**The complex of quaterner sediments** consists of various terrace sediments, fluvio-glacial sediments and alluvial sediments.



**Figure 1.** Geological map of the Alsar area



## Local Geological Setting

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 Alsar deposit (Fig. 2).

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 marbel. Based on fission traces the age of dolomite was determined as 250 m.y. (LEPITKOVA, 1995). The data of trace elements geochemistry shows pronounced negative anomalies (normalized values) of Rb, Ba and Hf, but positive anomalies of U. This data indicates a marine origin of dolomite. In addition, increased contents of metals such as Zn, Hg, Tl, Mn, and Au can be noticed in dolomites affected by hydrothermal solutes.

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 fine-grained tuff, water lain ash or volcanic glass. This volcano-sedimentary unit is 100-130 m thick (PERCIVAL & BOEV, 1990).

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 & BOEV, 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.

The unit of Pliocene felsic tuffs covers a large portion of the Alshar deposit. This volcanic sequence includes ash, crystal tuffs, tuff breccia and lacustrine tuffaceous sediments.

According to PERCIVAL & BOEV (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 Alshar show bedding and contain tuffaceous sedimentary clay material (a volcano-sedimentary series).

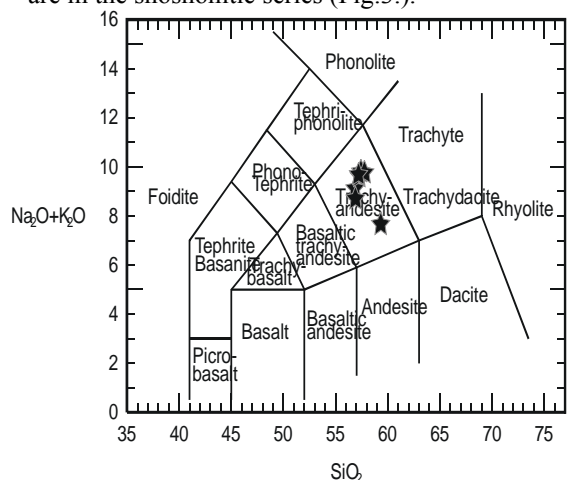
## PETROLOGY AND AGE DETERMINATIONS OF ALSAR VOLCANIC COMPLEX

The Alsar volcanic complex was investigated in detail by BOEV (1988), FRANTZ et al. (1994), and LEPITKOVA (1995). Volcano-intrusive rocks of Alsar include trachy-andesite (Table 1) and (Fig. 2).

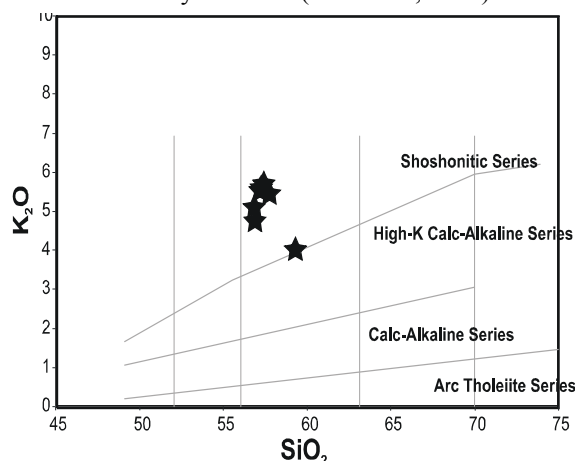
**Table 1.** Chemical and geochemical compositions of the volcanic rocks from Alsar

SiO <sub>2</sub>	56.86	56.9	57.28	57.43	57.77	57.2	59.32
TiO <sub>2</sub>	0.9	0.88	0.72	0.77	0.75	0.68	0.7
Al <sub>2</sub> O <sub>3</sub>	17.7	17.9	17.29	17.41	17.68	18	17.9
Fe <sub>2</sub> O <sub>3</sub>	5.3	5.32	5.6	5.62	5.3	5.62	5.26
FeO	0.37	0.57	0.21	0.19	0.41	0.93	0.93
MnO	0.1	0.1	0.06	0.08	0.06	0.06	0.1
MgO	1.88	1.98	1.89	1.6	2	1.8	1.66
CaO	5.12	4.95	4.42	4.23	5.35	4.68	5.07
Na <sub>2</sub> O	4.01	3.95	4.01	4.1	4.31	4.15	3.65
K <sub>2</sub> O	5.1	4.75	5.6	5.7	5.45	5.53	4.01
P <sub>2</sub> O <sub>5</sub>	0.48	0.44	0.57	0.51	0.5	0.51	0.52
H <sub>2</sub> O <sup>+</sup>	2.6	2.9	2.3	2.3	1.1	1.95	1.56
In ppm							
Ba	1750	1650	1560	1650	1680	1700	1650
Rb	201	211	246	252	238	223	233
Sr	1100	1018	1136	1182	1341	964	946
Y	24	34	41	49	49	36	32
Zr	222	347	393	401	384	342	291
Nb	25	28	30	30	28	18	17
Th	33	31	30	31	29	30	28
Pb	85	80	78	86	92	88	90
Ga	22	19	20	21	23	21	20
Zn	57	60	61	54	55	60	58
Cu	48	45	47	44	43	46	48
Ni	20	18	17	14	14	14	16
V	120	117	124	114	129	125	127
Cr	15	14	17	12	15	17	13
Hf	5.98	5.38	4.98	5.3	5.11	4.87	5.21
Cs	31.2	35.6	36.5	33.5	34.5	33.4	34.5
Sc	10	9	9	11	10	11	10
Ta	0.84	0.81	0.78	0.85	0.84	0.8	0.78
Co	10	10	11	10	11	10	12
Li	12	11	10	12	13	11	12
U	9.7	10.1	9.56	10.2	9.8	10.2	9.8
W	3.2	4	4.12	3.5	4.11	4	3.5
Mo	3	2.5	2.7	2.8	3	2.8	3
La	78.5	77.8	79.2	77.5	80.1	80.2	81.1
Ce	157	160	145	158	160	155	160
Pr	7.8	7.6	7.3	7.4	7.2	7.4	7.3
Nd	63	50	58	59	60	60	59
Sm	8.54	7.3	8.21	7.7	8.11	8.2	7.4
Eu	1.71	1.7	1.72	1.7	1.7	1.7	1.7
Tb	0.69	0.68	0.69	0.68	0.69	0.68	0.69
Dy	3.8	3.56	3.45	3.7	3.54	3.65	3.54
Ho	1.4	1.3	1.4	1.3	1.3	1.4	1.3
Tm	0.32	0.3	0.38	0.35	0.38	0.38	0.38
Yb	1.84	1.85	1.84	1.85	1.84	1.85	1.85
Lu	0.3	0.28	0.28	0.3	0.28	0.3	0.28

On the base of the diagrams of PECCERILLO & TAYLOR (1976) the volcanic rocks of the Alshar area are in the shoshonitic series (Fig.3.).



**Figure 2.** Diagrams of:  $SiO_2/Na_2O+K_2O$  of volcanic rocks in the vicinity of Ashar (La Maitre, 1989)



**Figure 3.** Diagrams of a:  $SiO_2/K_2O$  of volcanic rocks in the vicinity of Ashar

Trachy-andesite of Alshar area. are porphyry volcanic rocks (calc-alkaline) composed of idiomorphous phenocrysts of andesine, sanidine, amphibole, biotite and clinopyroxene (Table 2). The groundmass is microcrystalline composed of microliths and plagioclases. sanidine, biotite and pyroxene. Apatite, ilmenite, rutile, pyrite and magnetite occur as accessory minerals. Chemical and geochemical analyses show that latites are intermediary rocks in which the  $SiO_2$  content ranges from 56.86 to 59.32 %, and that of  $Al_2O_3$  from 17.29 to 17.90 %. It should be mentioned that they have relatively uniform amounts of major oxides such as CaO,  $Na_2O$ , and  $K_2O$  that classifies these rocks as monzonites. The MgO content ranges from 1.60 to 2.00 % which is a characteristic of calc-alkaline rocks (Table 1).

The volcanics of Alshar contain variable amounts of trace elements and REE. Table 1 shows the values of trace elements and REE from seventh samples of trachytes (LEPITKOVA, 1995). Fig.4 (a,b) shows

the distribution of REE in the volcanic rocks of Alshar. It can be inferred that there is certain enrichment in light REE in regard to heavy elements. The relative enrichment in La is characteristic for the volcanic rocks of Alshar. whereas the Ce content (145-160 ppm), as well as Ce/Y (around 6) point to certain impoverishment in heavy elements. The Nd content is also high.

From the analysis it can be inferred that the enrichment in light REE elements indicates that magma originated from the continental crust and that it distinguishes it from toleitic basalts. The slightly pronounced minimum of Eu and the pronounced minimum of Dy indicate to the fractionation processes of primary magma and its contamination by rocks from the upper and lower crust (LEPITKOVA, 1995).

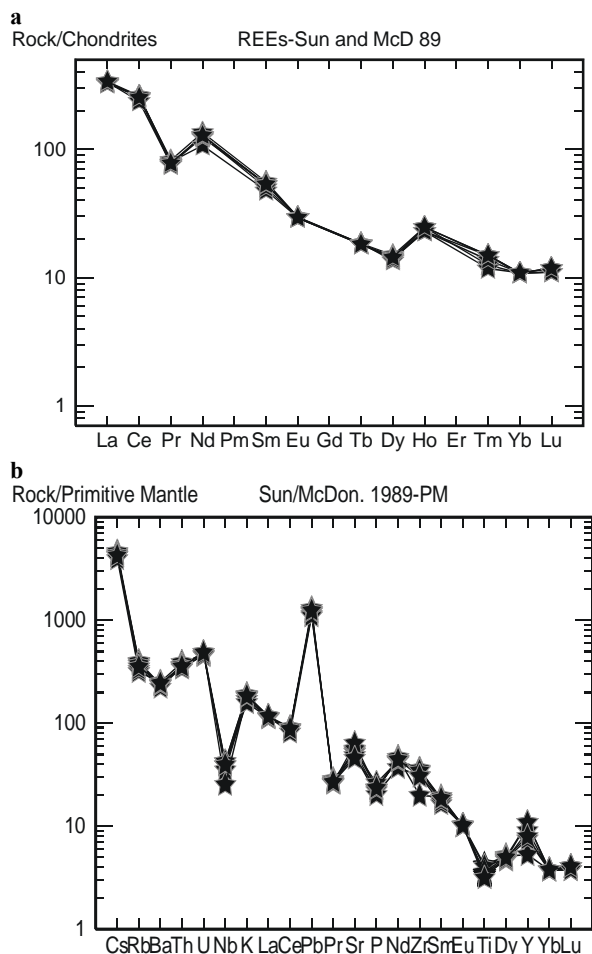
**Table 2.** Chemical composition for clinopyroxene, amphibole, biotite, plagioclase and sanidine determined by EMA analysis (in %) and recalculations showing individual and total moles cation.

Oxides	Clinop <sup>a</sup>	Amp <sup>a</sup>	Bio <sup>a</sup>	Plag <sup>a</sup>	San <sup>a</sup>
SiO <sub>2</sub>	53.483	42.65	38.2	58.712	64.418
TiO <sub>2</sub>	0.490	1.72	3.96		
Al <sub>2</sub> O <sub>3</sub>	2.823	13.97	14.04	25.977	19.913
FeO	7.673	9.96 <sup>b</sup>	18.1	0.382	0.585
MgO	13.987	14.66	13.84		
MnO	0.367	0.11	0.27		
CaO	20.597	11.97		7.691	1.113
K <sub>2</sub> O	0.013	1.09	9.31	1.184	8.047
Na <sub>2</sub> O	0.757	2.23	0.64	5.903	5.732
<b>Total</b>	<b>100.190</b>	<b>98.36</b>	<b>98.36</b>	<b>99.848</b>	<b>99.808</b>
Element	6(O) <sup>c</sup>	23(O) <sup>c</sup>	22(O) <sup>c</sup>	32(O) <sup>c</sup>	32(O) <sup>c</sup>
Si	1.967	6.187	5.613	10.530	11.684
Ti	0.014	0.188	0.438		
Al	0.123	2.389	2.432	5.493	4.258
Fe	0.236	1.208	2.224	0.057	0.089
Mg	0.767	3.170	3.031		
Mn	0.011	0.014	0.034		
Ca	0.812	1.860		1.480	0.216
K	0.001	0.202	1.745	0.270	1.863
Na	0.054	0.627	0.182	2.055	2.015
<b>Total</b>	<b>3.985</b>	<b>15.845</b>	<b>15.699</b>	<b>19.885</b>	<b>20.125</b>

<sup>a</sup>The obtained results represent average value from three independent measurements.

<sup>b</sup>The content of T(Fe) is determined.

<sup>c</sup>The number of oxygen cations taken for the moles cation calculations.



**Figure 4.** Distribution pattern of rare elements b) and REE a) of the trachy-andesite from Alshar (LEPITKOVA, 1995)

Two principal volcano-intrusive phases have been identified in Alshar based on investigations carried out so far:

(a) Miocene phase of calc-alkaline rocks occurring as dikes. TROESCH & FRANTZ (1992) have determined a Miocene age (14.3 - 8.2 m.y.) for the volcanic phase. The age was determined based on Ar/Ar data obtained for plagioclase from Crven Dol. The volcano-intrusive rocks of this volcanic phase were completely altered by hydrothermal solutes during the Pliocene.

(b) The most significant volcanic rocks in Alshar developed as part of the Kozuf volcano-intrusive activities. Subvolcanic hypoabyssal intrusions formed, based on data from K-Ar investigations, during the period from 4.5 to 5.0 m.y. (LEPITKOVA, 1995; FRANTZ et al., 1994).

Results obtained from determination of age by K/Ar method of trachy-andesites affected by hydrothermal processes indicate to absolute age of 3.9 to 5.1 m.y. (LIPPOLT & FUHRMAN, 1986). It can be inferred that the volcanic activity in Alshar took place in the period between 3.9 to 5.1 m.y.. Based on  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for trachy-andesites (0.70856) it can be inferred

that parent magma derived from lower continental crust/upper mantle domain (BOEV, 1990/91).

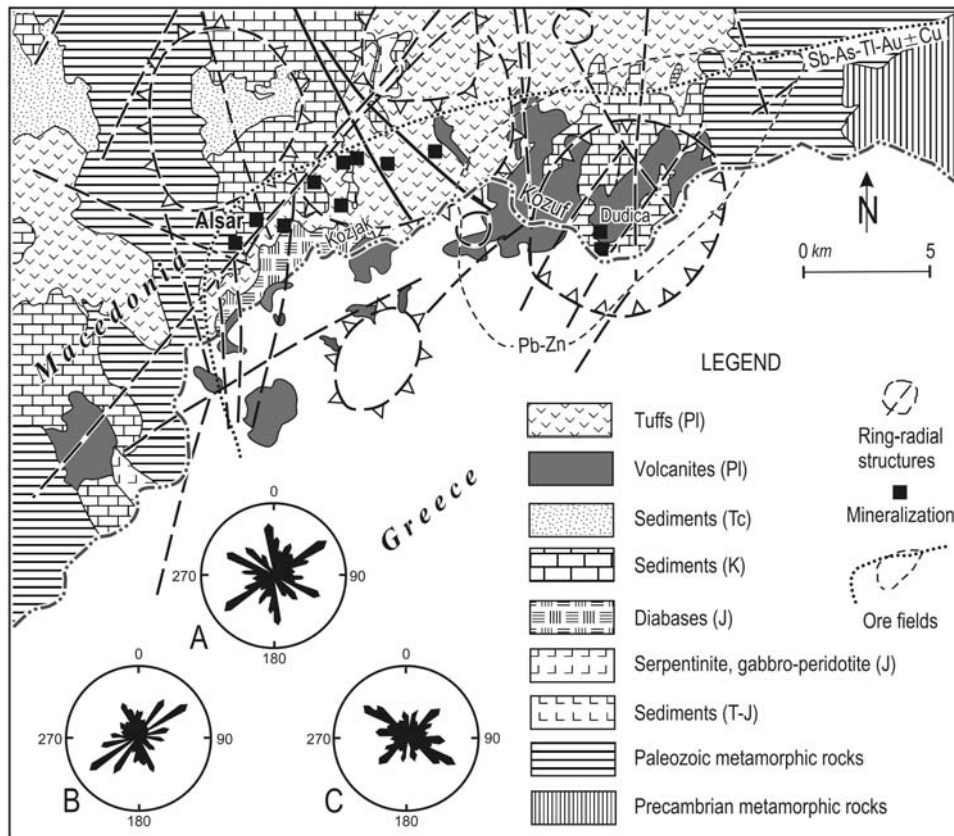
### STRUCTURAL FEATURES

The main structural discontinuances in the region of the Allchar deposit are in close correlation with overthrust structures in the Mtns. Kožuf and Kozjak (Fig. 5). Three main systems of tectonic structures are present in this region (BOEV, 1988):

- System of overthrust structures of Vardar direction (NW-SE to N-S). Thereby, the system of the NW-SE directed overthrust structures is older, whereas the N-S oriented structures (along which the products of the initial and the main volcanic phase of Mtns. Kožuf and Kozjak are located) are younger. Along this overthrust system (N-W) the intense hydrothermal activity of Allchar region is also manifested.

- System of NE-SN to E-W directed overthrust structures. Compared to the system of structures with Vardar direction, this system is younger. Along this system of structures the seismo-tectonic activity of this region is manifested. At the cross-sections of this rasedni structures with the Vardar oriented structures the appearance of the youngest volcanic activity on the Mtns. Kožuf and Kozjak is manifested. The ore mineralization of the Allchar locality is related to this youngest volcanic activity.

Ring structures presented by several morphologically dominant negative structures (collapse caldera in the region of the Allchar and Vasov Grad deposits) and one positive structure in the Dudica region. The faults and fault zones of the Alshar deposit are grouped into three principle sets based on strike orientation (PERCIVAL & BOEV, 1990): N - NE20E, N35-50E, and N40-50W. Only in the southern part a series of E - W faults dominates. Most of the structural features are marked by tectonic brecciation "juxtaposed stratigraphic relationships, topographic discontinuities and by a marked increase in hydrothermal alteration intensities along their traces" (PERCIVAL & BOEV, 1990). A major structural zone is developed along the northerly trending of the valley of the River Majdan. On the east side of this structure cliff-like outcrops of extensively silicified rocks (i.e. tuffaceous dolomite a.a.), sporadically mineralized, are developed (Fig.1). In the underground antimony mine workings several NE-trending faults are identified, reaching the surface of the terrain. These fractured zones control localization of antimony mineralization. Many of the structures exhibit a strip-type shearing movement, whereby the fault trace is actually a zone of sheared and broken rocks in a fine-grained gougy matrix. They contain large clay component (PERCIVAL&BOEV,1990).



**Figure 5.** Schematic morphostructural map of the Kozuf district (BOEV, 1988)

**Environments of mineralization.** The localization of mineralization is partially associated with 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 slip-type shearing movements represented by brecciated rocks often in a fine-grained gougy matrix. The increased porosity and composition of tuffs are a favourable environment for hydrothermal fluid migration and for introduction of sulphides and gold. A second favourable environment is a porous and permeable basal zone developed as a stratabound along the Triassic erosion surface. It is 5 - 10 m thick and several metres long (PERCIVAL & BOEV, 1990). Carbonate rocks such as dolomite and marble are also favourable environment for deposition of mineralization in the Alshar deposit. In conclusion, complex Sb-As-Tl-Au mineralization is hosted by the Triassic carbonates (dolomites and marble), the Tertiary volcanics and volcano-sedimentary sequence (tuffaceous dolomite).

**Structural control.** The position of ore bodies is strongly controlled by high-angle faults, along which hydrothermal fluids moved upwards and subsequent mineralization took place. It is not certain whether one or more faults served as pathways for the movement of hydrothermal ore-bearing fluids into

favourable lithologic environment where precipitation took place.

**Magmatic control.** Although a spatial relationship between the subvolcanic intrusions and mineralization has been evident in the central part of the Alshar deposit, still the timing between the intrusive events and the Sb-As-Tl-Au mineralization has not been reliably established. It is only certain that some phases of mineralization, particularly pyrite, occur along the contact of the hydrothermally altered intrusive latite, and it postdates the intrusions. This is revealed by underground antimony workings. But it is very likely that mineralization is genetically related to multi phase subvolcanic-hypabissal intrusive activities.

**Wall-rock alteration.** Hydrothermal alteration of host rocks and the distribution facies of alteration are described in detail by PERCIVAL & BOEV (1990). The most significant alteration facies are silicification and argillitization. The silicification mostly prevails in the central part of the deposit, while argillization along slight silicification occurs mainly in the northern part, i.e. the Crven Dol ore body.

Various forms of *silica* were deposited at different times during the lifetime of the hydrothermal system.

- Complete replacement of dolomite and tuffaceous dolomite by microcrystalline silica. Decalcification is characterized by removal of calcite and dolomite by acidic solutions in a pyrite stable field. Apart from widespread replacement of carbonate rocks, crystalline silica filled the open space. This precipitation of silica took place during cooling of the hydrothermal fluids. Silification is mostly of strong intensity often grading into jasperoids.
- Formation of quartz veins, veinlets and stockwork-veinlets (in previously silicified rocks, jasperoids and in silicified tuffs) where fractures were easily formed (the stage of ore mineralization).

**Argillization** is mainly developed above and lateral of tuffs and tuffaceous dolomite. The lateration intensity ranges from weak clay replacement to complete destruction of the parent rock textures in the pervasively altered host rock. The latered tuffs contain mixtures of kaolinite, illite, fine-grained quartz and jarosite, iron oxide and gypsum.

Small occurrences of **ankeritization** are found sporadically in dolomite (the Crven Dol ore body (BALIĆ ŽUNIĆ et al., 1993)).

Distribution of the hydrothermal alteration facies is characteristically zoned from a silicified core grading laterally into argillized rocks. Locally silicification is intermixed with argillically altered rocks.

Introduction of disseminated pyrite (marcasite into volcanic rocks and tuffaceous dolomite e.g. Crven Dol - level 800 m) may be considered as a specific facies of hydrothermal alteration.

**Supergene alteration.** This type of alteration is widespread in the Alsar deposit, involving the following processes and products:

(i) *Oxidation of iron* and to some extent antimony, arsenic sulphides, locally thallium sulphosalts resulted in the formation of gossans, composed of ochreous limonite-manganese oxides mixed with argillic clays. Some of the gossane zones are silicified. They are developed in the vicinity of mineralization.

Limonite and jarosite derive from primary iron sulphides, while stibnite was transformed into cervantite, stibiconite etc., As-sulphides into scorodite, arsenolite etc. intermixed with limonite, sporadically manganese oxides, argillic clays and microcrystalline quartz. Some of the recently identified thallium minerals such as dor-allcharite were formed in the process of supergene alteration of primary Tl-mineral (BALIĆ ŽUNIĆ et al., 1993).

(ii) *Argillic alteration* is mostly a follow-up process of oxidation of primary sulphides, when sulphuric acid, as a by-product affected the host rocks. The products of these processes are represented by clays containing abundant limonite and manganese oxides, locally concentrations of residual sulphides.

(iii) *Weak lateritic weathering* of igneous and sedimentary rocks (predominantly developed in tuffs and tuffaceous dolomite) indicates the hot and humid climate after mineralization.

## MINERALIZATION

The Alsar deposit consists of several ore bodies and numerous occurrences, each characterized by specific associations of metals and mineral assemblages.

**Morphostructural types of mineralization.** Several distinct types of mineralization occur in the Alsar deposit including

(i) Mineralized brecciated zones developed along the contact between the subvolcanic intrusions, with dolomite and/or tuffaceous dolomite or along shear zones in the carbonate rocks and/or silicified tuffs.

(ii) Massive lenses of realgar ore occurring in the carbonate rocks and grading into stockwork-type mineralization. Massive sulphide mineralization, mainly pyrite/marcasite occupies sporadically steeply-dipping fault/shear zones. Massive sulphide-bearing jasperoids occur sporadically only as small pods.

(iii) A Mineralized systems of veinlets and fractures occur in the tuffaceous dolomite and the Triassic dolomite.

(iv) Disseminated mineralization, mostly stibnite, pyrite/marcasite, gold occurs (a) as stratabound bodies along the contact between the basal portion of volcano-sedimentary tuffaceous dolomite and/or tuffs, and underlying Triassic carbonate rocks, (b) in silicified volcanics (with variable amounts of argillization), and (c) as abundant finely disseminated pyrite-marcasite and stibnite in the jasperoids, locally accompanied by arsenic sulphides and Tl-minerals.

Ore bodies occur most frequently as steep-dipping lenses, irregular in shape, sporadically as ore-shoots. The size and shape of these ore bodies depend on cut-off grades.

(v) system of thin, up to 10 cm wide, subparallel veins of orpiment are identified in the Crven Dol ore body at 800 m level.

**Association of metals.** The major elemental components of the Alsar deposit are Sb, As, Tl, Fe, S and Au, accompanied by minor Hg and Ba and traces of Pb, Zn, Cu, U and Th.

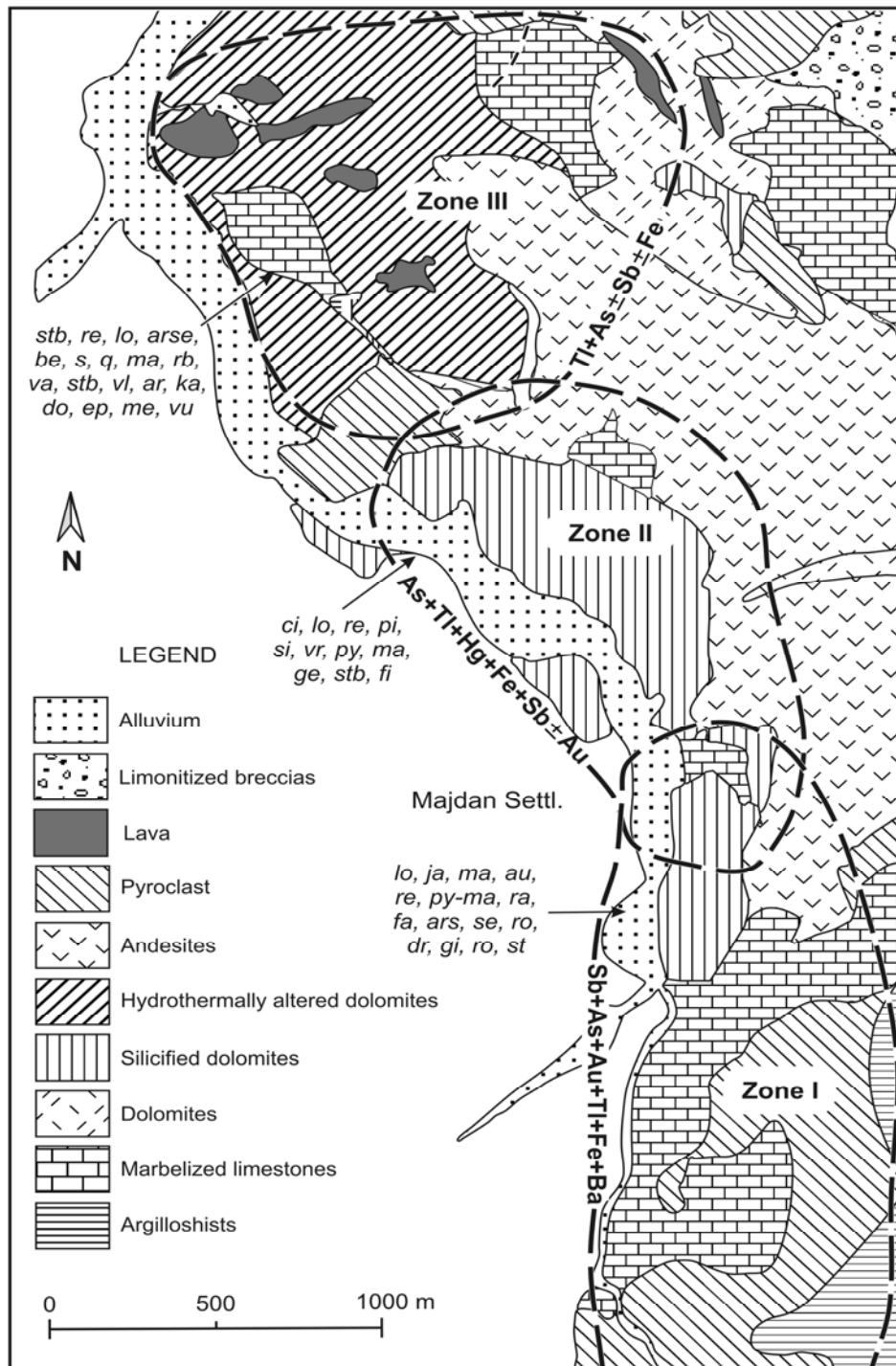
Enrichment in gold in the Alshar deposit is closely associated with enrichment in silica, while enrichment in Tl is related to increased concentrations of volatiles, such as As, Sb, Hg, S. The distribution of ore metals and their concentration rates display a lateral zoning (Fig.6). These zones are not sharply defined and typically a gradual transition exists between zones.

- In the northern part of the deposit (zone III) As and Tl prevail, accompanied by minor Sb, locally traces of Hg and Au. The average grade of mineralization in the Crven Dol ore body is 6% As, 0.3% Tl, 0.08% Sb and 0.2 ppm Au (JANKOVIC & JELENKOVIC, 1994).

- The central part of the deposit (zone II) is dominated by Sb and Au. but it also contains significant amount of As. Tl. minor Ba. Hg. and traces of Pb. The ore bodies contain 2 - 3% Sb. 2% As. up to 0.4% Tl. up to 3.5 ppm Au and 435 ppm Ba. Fig. 48 shows variation of thallium, antimony and arsenic contents within some ore bodies explored

by underground workings in the central part of the deposit.

- The southern part of the deposit (zone I) is characterized by dominance of gold mineralization accompanied by variable amounts of antimony and arsenic.



**Figure 6.** Zonal distributions of metals and minerals in the Alsar area

Stb-stibnite; re-realgare; lo-lorandite; arse-arsenolite; be-bernardite; s-native sulphure; q-quartz; ma-marcasite; rb-rebulite; va-vaisbergite; vl-valentinite; ar-aragonite; ka-calcite; do-dolomite; ep-epsomite; me-melanterite; vu-vulfenite; ci-cinabarite; picopolite; si-simonite; vr-vrbaite; py-pirite; ge-getite; fi-fibroferite; ja-jankovite; au-orpiment; py-ma-pirite-marcasite; ra-raguinite; fa-fangite; ars-arsenopirite; se-senarmontite; ro-romeite; dr-doralsarite; gi-gypsum; st-stibiconite;

## MINERAL ASSOCIATIONS

**Table 3.** Minerals present at the Allchar deposit

No	Mineral	Formula	Studied		
			IR	Raman	XRPD
	<i>Elements</i>				
1	Gold	Au			
2	Sulfur	S			
	<i>Sulfides and Sulfosalts</i>				
3	Pyrite	FeS <sub>2</sub>			
4	Marcasite	FeS <sub>2</sub>	+	+	+
5	Orpiment	As <sub>2</sub> S <sub>3</sub>	+	+	+
6	Realgar	As <sub>4</sub> S <sub>4</sub>	+	+	+
7	Pararealgar	AsS	+	+	+
8	Cinnabar	HgS			
9	Stibnite	Sb <sub>2</sub> S <sub>3</sub>	+	+	+
10	Arsenopyrite	FeAsS			
11	<b>Lorandite</b>	TlAsS <sub>2</sub>	+	+	+
12	<b>Raguinite</b>	TlFeS <sub>2</sub>	+	+	
13	<b>Weissbergite</b>	TlSbS <sub>2</sub>			
14	<b>Picotpaulite<sup>b</sup></b>	TlFe <sub>2</sub> S <sub>3</sub>			
15	<b>Fangite</b>	Tl <sub>3</sub> AsS <sub>4</sub>			
16	<b>Simonite<sup>b</sup></b>	TlHgAs <sub>3</sub> S <sub>6</sub>			
17	Bernardite <sup>a</sup>	Tl(AsSb) <sub>5</sub> S <sub>8</sub>			
18	<b>Parapierrotite</b>	Tl(Sb,As) <sub>5</sub> S <sub>8</sub>			
19	<b>Vrbaite</b>	Tl <sub>4</sub> Hg <sub>3</sub> As <sub>8</sub> Sb <sub>2</sub> S <sub>20</sub>	+	+	
20	<b>Rebulite<sup>b</sup></b>	Tl <sub>5</sub> Sb <sub>5</sub> As <sub>8</sub> S <sub>22</sub>			
21	<b>Jankovcite<sup>b</sup></b>	Tl <sub>5</sub> Sb <sub>9</sub> (AsSb) <sub>4</sub> S <sub>22</sub>			
	<i>Oxidex and hydroxides</i>				
22	Arsenolite	As <sub>2</sub> O <sub>3</sub>			
23	Valentinite	Sb <sub>2</sub> O <sub>3</sub>			
24	Cervantite	Sb <sub>2</sub> O <sub>4</sub>			
25	Goethite	FeO(OH)	+	+	+
26	Stibiconite	Sb <sub>3</sub> O <sub>6</sub> (OH)			
27	Roméite	(Ca,Fe,Mn,Na) <sub>2</sub> (Sb,Ti) <sub>2</sub> O <sub>6</sub> (O,OH,F)			
	<i>Carbonates</i>				
28	Calcite	CaCO <sub>3</sub>			
29	Aragonite	CaCO <sub>3</sub>			
30	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>			
	<i>Sulfates and Molybdates</i>				
31	Barite	BaSO <sub>4</sub>			
32	Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O			
33	Starkeyite	MgSO <sub>4</sub> ·4H <sub>2</sub> O			
34	Rozenite	FeSO <sub>4</sub> ·4H <sub>2</sub> O			
35	Epsomite	MgSO <sub>4</sub> ·7H <sub>2</sub> O	+	+	+
36	Melanterite	FeSO <sub>4</sub> ·7H <sub>2</sub> O			
37	Jarsoite	KFe <sup>3+</sup> <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>			
38	<b>Dorallcharite<sup>b</sup></b>	Tl <sub>0.8</sub> K <sub>0.2</sub> Fe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>			
39	Fibroferrite	FeSO <sub>4</sub> (OH)·5H <sub>2</sub> O			
40	Wulfenite	PbMoO <sub>4</sub>			
	<i>Arsenates</i>				
41	Pharmacolite	CaHAsO <sub>4</sub> ·2H <sub>2</sub> O			
42	Picropharmacolite	Ca <sub>4</sub> Mg(AsO <sub>3</sub> OH) <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·11H <sub>2</sub> O	+	+	
43	Hörnesite	Mg <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O			
	<i>Silicates</i>				
44	Quartz	α-SiO <sub>2</sub>			

<sup>a</sup>Allchar thallium minerals are marked in bold. <sup>b</sup>Endemic thallium minerals.

### **1. Gold**

The presence of gold in the Sb-As-Tl association at Alšar has been suggested (STAFILOV, 1985; IVANOV, 1986; STAFILOV & TODOROVSKI, 1987). Between 1986 and 1989, gold mineralisation was systematically explored. It was shown that the geological, geochemical, mineralogical and hydrothermal alteration features are similar to those that characterise the Carlin-type mineralisation of the western United States (PERCIVAL & RADTKE, 1990 & 1994; PERCIVAL et al., 1990).

### **2. Sulfur**

Sulfur at Allchar locality forms small bright yellow well-developed crystals reaching 1 mm in size. It also appears in the form of earthy yellow masses. On the exposure to sunlight it is unstable and tends to become milky earthy. Most frequently, it is associated with gypsum (JANKOVIC et al., 1997).

### **3. Pyrite**

Pyrite crystals, mainly found as corroded grains and in the core of marcasite nodules, are morphologically unattractive. This mineral has been established as the first crystallized sulfide from Allchar being of high importance in the process of formation of some rare iron-bearing thallium sulfosalts. As in the other Carlin-type deposits, pyrite is responsible for the precipitation of gold (JANKOVIC et al., 1997).

### **4. Marcasite**

Marcasite is found within the polymetallic ore mineralisations related to Tertiary volcanism. Excellent marcasite samples can be seen in the central parts of the Alšar deposit where large marcasite crystals have been found on horizon 754 m. Here, it is often associated with realgar and stibnite and contains rather high quantities of arsenic (JANKOVIC et al., 1997).

### **5. Orpiment**

Orpiment appears predominantly in its northern parts close to the village of Majdan. It was mined as early as the Turkish Empire. Arsenic production (orpiment) was first mentioned in 1481 when the production of arsenic ore was mentioned in the annual revenue of the sultan of Rožden. The best orpiment crystals in Alšar can be seen in the Crven Dol locality, particularly on the horizons of 800 and 780 m. There, orpiment crystals reach sizes of over 10 cm. Orpiment has been described as a stoichiometrically pure mineral (PALME et al., 1988), although it does contain traces of K, Cl, Cr, Mn, Fe and Cu. It

occurs mainly as compact masses sometimes weighing several hundred kilograms. Bright yellow, elongated idiomorphic crystals with adamantine lustre faces are very rare. Orpiment usually forms fan-shaped aggregates or hemispheres, mainly having a brownish yellow colour and dull lustre. The crystal size of a few millimetres is typical. The presence of lorandite near the realgar and orpiment zones has been observed.

### **6. Realgar**

Realgar, as one of the most widespread minerals in this locality, occurs as nice crystals, particularly in the northern part of the Crven Dol site. In the dolomite series, large realgar crystals occur along with lorandite and orpiment. The physical and chemical characteristics of realgar were first described at the beginning of the 20<sup>th</sup> century (FOULLON, 1904). It occurs as crystals of up to 2 cm in size, which are elongated red-coloured prisms that (exposed to light) decompose and transform to yellow pararealgar. Realgar is the host for the mineral lorandite.

### **7. Pararealgar**

Pararealgar occurs in the Alšar deposit, particularly in the northern part of the Crven Dol site when realgar, one of the most widespread minerals in the Alšar locality in Macedonia, is exposed to light (DOUGLASS et al., 1992). The mineral appears as very tiny yellow-coloured crystals or in the form of a powder.

### **8. Cinnabar**

Cinnabar is very rare mineral detectable only in polished sections appearing in the form of grains up to 150 micrometers in size (RIECK, 1993). Occasionally, inclusions in realgar belong to cinnabar as well. Among the samples deposited in the Croatian Natural History Museum in Zagreb are single crystals of cinnabar up to 2 mm in size.

### **9. Stibnite**

The best stibnite crystals can be found in the central parts of the Alšar mine, particularly horizon 754 m. There, stibnite crystals occur as ring-radial aggregates with well-developed elongated prismatic crystals with high lustres. They can reach a length up to 10 cm. The most attractive specimens of stibnite are often accompanied by small realgar crystals (BOEV et al., 1993).



### 10. Arsenopyrite

A unique occurrence of arsenopyrite has been mentioned in the northern part of the As-rich deposit (FOULLON, 1904). The occurrence was reported as small lustrous crystals embedded in massive orpiment.

### 11. Lorandite

Lorandite is a world-famous mineral described as the first thallium-bearing mineral. It occurs only in this locality, particularly in its northern part called Crven Dol (KRENNER, 1895). It occurs in silicified dolomites associated with realgar and orpiment. Since its first discovery in Alšar in 1884 smaller quantities have been found in only a few other localities worldwide. The monoclinic tabular aggregates of lorandite are typically dispersed throughout realgar and orpiment hosts. Well-developed crystals are much rarer and show many different forms. Lorandite can easily be distinguished from realgar by its darker red colour, its semimetallic lustre and its perfect cleavage on {001}, {201} and {110}. Some crystals are coated by a brownish yellow crust. Lorandite crystals of 1 cm are typical for this locality, although single crystals up to 5 cm in size have occasionally been found. Lorandite is named after the Hungarian physician Lorand Eötvös (1848–1919).

The investigations in connection with the LOREX program have revealed some interesting features. The Alšar lorandite is pure, containing only traces of K, Cr, Fe, Cu and Zn (PALME et al., 1988). The ore-grade in the richest zone contains about 18,000 m<sup>3</sup> of ore with an average Tl content of 0.35%. Microprobe analyses in recent investigations have shown the presence of Hg. Scientists became interested in the mineral at the beginning of 1980s when the American physicist M. S. Freedman proposed that it could be used to detect solar neutrinos (FREEDMAN et al., 1976).

### 12. Raguinite

Raguinite is found in the central zone of the Alšar thallium ore body (HOFMANN, 1891), associated with orpiment, realgar and lorandite. Raguinite crystals are elongated in the form of fibres. Such bundles of fibres have a brilliant bronze colour. Usually it is intimately intergrown with pyrite. In reflected light, it is a grey white to pinkish white. The mineral shows very strong polarisation colours with a dominant orange. Only small quantities of this mineral have been recovered to date. Holotypes have been deposited in the mineral collection of the École nationale supérieure des mines de Paris.

### 13. Weissbergite

Weissbergite from Alšar was first reported in 1993 (RIECK, 1993) and is the second known location for this mineral after it has been firstly described in the Carlin mine (DICKSON & RADKE, 1978). The mineral was identified on a single specimen of realgar, in the form of elongated prismatic crystals with a maximum size of 0.5 mm. It is steel grey and has a metallic lustre, with deeply striated faces. Its well-developed cleavage in four different directions helps distinguish it from the other thallium sulfosalts.

### 14. Picotpaulite

In the lorandite-bearing zone of the Alšar deposit, picotpaulite was found as inclusions mainly up to 0.5 mm. Its color is bronze but under reflected light it appears creamy white showing a very strong anisotropic character. Picotpaulite is rhombic (BALIĆ-ŽUNIĆ et al., 2008), but the crystals are usually pseudo-hexagonal because of its common twinning penetration (JOHANN et al., 1970). Holotypes have been deposited in the mineral collection of the École nationale supérieure des mines de Paris. Allchar is the type locality for this mineral.

### 15. Fangite

This mineral has so far only been identified using reflected light microscopy and microprobe analysis (EL GORESI & PAVICEVIC, 1988). It forms rims around lorandite. Its chemical composition for the first time has been confirmed in 1994 (FRANTZ et al., 1994), later a mineral with the same chemical composition being found in the Mercur gold deposit in Utah, USA (WILSON et al., 1993).

### 16. Simonite

The small orange-red crystals of simonite were found only as inclusions in rebulite. The crystal structure of this new sulfosalt mineral was solved in 1982 (ENGEL et al., 1982). The crystals have an irregular shape reaching in size from 0.1 to 0.2 mm. Its light orange-red colour can easily be confused with realgar. Allchar is the type locality for this mineral.

### 17. Bernardite

A detailed description of the physical, chemical and structural characteristics of bernardite were reported in 1989 (PASAVA et al., 1989). It forms thick tabular crystals – the largest reported being 4 mm in size. The mineral has black colour with occasional dark red internal reflections and

a red streak. The mineral occurs in associations with orpiment and realgar. Holotype specimens have been deposited in the NarodniMuseum in Prague and the NaturhistorischesMuseum in Vienna.

### 18. Parapierrotite

The single elongated crystals of parapierrotite (3 mm in size) most frequently appear as in cavities of massive realgar (JOHANN et al., 1975). They are black with a semimetallic lustre. The mineral is named on account of its relationship to pierrotite. Holotypes have been deposited in the mineral collection of the École nationale supérieure des mines de Paris.

### 19. Vrbaite

Vrbaite, described as a new mineral and named in honour of his teacher Karl Vrba (1845–1922) (JEZEK, 1913), for the first time was noticed in 1912 (JEZEK, 1912). It was found in a small cavity of realgar, the major constituents of the samples being thallium, arsenic, antimony and sulfur. Vrbaite occurs as dark grey minute tabular or flat bipyramidal crystals with a bluish sheen and a semimetallic lustre. In thin sections, vrbaite is dark red translucent. Its good cleavage on {010} is usually observable and can be used for identification. The preliminary composition determined as  $TlAs_2SbS_5$  or  $Tl(As, Sb)_3S_5$  was found to be incomplete (KREHLIK, 1912 & 1913). Later, the results of microprobe work (CAYE et al., 1967; NOWACKI, 1968) have shown that Hg is a major constituent of the composition, leading to the now commonly accepted chemical formula of  $Tl_4Hg_3As_8Sb_2S_{20}$  (OHMASA & NOWACKI, 1971).

### 20. Rebulite

This mineral is named in honour of well-known geologist Boris Rebula from Macedonia who has hardly worked on Alšar mineral characterisation. The crystals of rebulite are dark grey with a metallic lustre and a brownish red streak. Well-developed crystals up to 2 mm in size are associated with realgar and simonite. Rebulite chemical composition was established by means of EDX analysis, and X-ray powder patterns were calculated according to the crystal structure (BALIĆ-ŽUNIĆ & ŠČAVNIČAR, 1982). Later, the contribution towards the crystal chemistry of rebulite was given (MAKOVICKY & BALIĆ-ŽUNIĆ, 1998) Allchar is the type locality for this mineral.

### 21. Jankovičite

This mineral was named in recognition of Professor S. Janković for his work on the mineralogy and geology of Alšar. As a new sulfosalt mineral from the Alšar deposit, it was described in 1995 (LIBOWITZKY et al., 1995; CVETKOVIC et al., 1995). The crystal structure determination has confirmed that the As sites are partially substituted by Sb. Its structure shows close resemblance with the rebulite structure. Later, a contribution towards the crystal chemistry of rebulite was given (MAKOVICKY & BALIĆ-ŽUNIĆ, 1998). Allchar is the type locality for this mineral.

### 22. Arsenolite, $As_2O_3$

The chemical composition of this mineral at the Alšar locality was determined in 1994 (FRANTZ et al., 1994). It has been detected in the form of a small vein between the realgar grains. Which of the two minerals (arsenolite or claudetite) with this composition ( $As_2O_3$ ) is present remains unknown. The presence of both mineral forms is included. Owing to the small quantities that have been found this question is still open.

### 23. Valentinite, $Sb_2O_3$

The occurrence of this antimony oxide mineral was predicted in 1890 (FOULLON, 1890) and found in 1892 (FOULLON, 1892) after studying the material given by a mine engineer. No further description of Alšar valentinite has been given by any other author (RIECK, 1993).

### 24. Cervantite, $Sb_2O_4$

This mineral appears on stibnite crystals as a yellow glassy coating designated as “antimony ochre”. It was revealed that their major component in most cases is cervantite,  $Sb^{3+}Sb^{5+}O_4$ , with small subordinate amounts of roméite  $(Ca,Fe,Mn,Na)_2(Sb,Ti)_2O_6(O,OH,F)$  and stibiconite  $Sb_3O_6(OH)$  (STIEGLITZ, 1990).

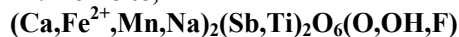
### 25. Goethite

Goethite appears like a dark brown to earthy masses and minute crystals in association with limonite and pyrite. In the past, this mineral from Allchar deposit has been considered as a new mineral being consequently described as “allcharite” (JEZEK, 1913; CECH & JOHANN, 1967). Pseudomorphs after pyrite crystals consist almost entirely of this mineral.

### 26. Stibiconite, $\text{Sb}_3\text{O}_6(\text{OH})$

An earthy yellow to brown coatings and powdery masses of stibiconite occur in association with the massive stibnite. Rarely, stibiconite forms pseudomorphs after stibnite (STIEGLITZ, 1990).

### 27. Roméite,



Roméite forms glassy coatings on stibnite, which consist predominantly of cervantite  $\text{Sb}^{3+}\text{Sb}^{5+}\text{O}_4$  and yellow powdery coatings (STIEGLITZ, 1990). This mineral appears as an alteration product of stibnite.

### 28. Calcite

Calcite is widely spread in the form of marble as a part of the host rock. Calcite has been also found in grains and veins of dolomite where it appears as fine-grained masses of minute scalenohedral crystals (RIECK, 1993).

### 29. Aragonite

Aragonite crystals occur in association with stibnite and realgar. In the Allchar's mineral paragenesis it usually appears in the form of white crusts consisting of fibrous tiny crystals (RIECK, 1993).

### 30. Dolomite

Massive dolomite forms have been established as the major host rock of the Allchar deposit. The crystals are usually brownish colored by iron-bearing weathering. Mostly they are small and do not exceed 1 mm in size. Dolomite is partly or wholly replaced by silica by later hydrothermal processes (RIECK, 1993).

### 31. Barite

In the Alšar mine, barite occurs as lodes in association with quartz and stibnite ((STIEGLITZ, 1990; BARIĆ, 1958). It appears as platy, colourless clear to milky coloured crystals up to a maximum size of 6 mm. Barite is commonly associated with calcite, dolomite, quartz and pyrite.

### 32. Gypsum

Nice gypsum crystals are found in the Alšar site, predominantly in its northern portion. Very nice 1 m thick gypsum crystals of variable sizes (white to transparent) develop because of the large amount of sulfides in dolomites after rainfall. Gypsum at the Alšar locality is spread over all types of ore and host rock. Single crystals are rather small with a typical flat habit. In large quantities, it appears as efflorescence on

wall rock and even on timbering. Stalactitic masses sometimes exceed 25 cm (RIECK, 1993).

### 33. Starkeyite, $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$

Starkeyite appears in the form of fibrous aggregates partly filling the space between realgar crystals (RIECK, 1993). The crystals have white colour with a silky sheen.

### 34. Rozenite, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$

Rozenite occurs either in the form of white crusts of prismatic crystals or stalactitic aggregates. It is spread throughout the deposit on altered host rock and ore in association with other sulphate and arsenate minerals (melanterite, gypsum, fibroferrite and hornesite) (ZEBEC et al., 1993). Rozenite is the product of the decomposition of melanterite, pyrite and marcasite.

### 35. Epsomite

Beautiful present day epsomite crystals in the form of the white fibrous aggregates can be seen in the Alšar deposit (BERMANEC, 1999). In the old mine pits, because of the large presence of magnesium carbonates (dolomites) and sulfides in mutual reaction with water, very nice epsomite stalagmites have developed with the appearance of cave jewellery. It is associated with gypsum and with various sulfides and iron sulfates.

### 36. Melanterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

The mineral has been described as green crusts and stalactitic aggregates without observing the crystals (BARIĆ, 1958; ZEBEC et al., 1993). The crystals are greenish-blue, transparent and from 2 to 3 mm in size. In atmospheric conditions, melanterite decomposes in rozenite by losing three molecules of water. The authenticity of the studied mineral was confirmed by chemical analyses and X-ray investigations (ZEBEC et al., 1993).

### 37. Jarosite, $\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$

Jarosite occurrence in the Allchar locality is related to iron and sulfide mineralization. It is related to the transformation processes of iron minerals. Goethite often occurs in association with jarosite. It is usually associated with other sulfate minerals (MAKRESKI et al., 2005).

### 38. Dorallcharite, $(\text{Ti}, \text{K})_2\text{Fe}^{3+}_6(\text{SO}_4)_4(\text{OH})_{12}$

Dorallcharite appears as yellow earthy masses of submicroscopic crystals being found in the oxidation zone of the ore body (BALIĆ-ŽUNIĆ et al., 1993 & 1994). As a member of the alunite-jarosite family, it is isomorphous with jarosite. It

is often associated with an amorphous Fe-Mn sulfate–arsenate free of Tl. The mineral specimen is deposited in the Geological Museum of Copenhagen. Allchar is the type locality for this mineral.

#### 39. Fibroferrite, $\text{FeSO}_4(\text{OH})\cdot 5\text{H}_2\text{O}$

This mineral in Alšar paragenesis has been described as hemispheres of yellow fibres (RIECK, 1993). It is associated with hornesite, rozenite and gypsum on altered host rock in the vicinity of realgar veins.

#### 40. Wulfenite, $\text{PbMoO}_4$

Wulfenite was the first lead-bearing mineral discovered in the Alšar deposit (ŠOUFEK et al., 1998). Several authors have investigated the Pb content in Alšar minerals. Wulfenite crystals have been observed on one sample built of microcrystalline quartz aggregates that fill the cavities in stibnite–realgar ore bodies. Orange-yellow crystals of wulfenite up to 8 mm in size together with well-developed crystals of realgar have crystallised over such microcrystals of quartz. Wulfenite is obviously a very late mineral in this part of the ore body. The lead present in wulfenite is because of a previous decay of U and Th and not as a result of the transformations of  $^{205}\text{Tl}$  to  $^{205}\text{Pb}$  caused by neutrino interaction with Tl.

#### 41. Pharmacolite, $\text{CaHAsO}_4\cdot 2\text{H}_2\text{O}$

The presence of pharmacolite in this deposit was first reported in 1993 (RIECK, 1993). The

mineral was described as radiating an acicular coating on realgar, orpiment and host rock. Single crystals are rarely observed.

#### 42. Picropharmacolite, $\text{Ca}_4\text{Mg}(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2\cdot 11\text{H}_2\text{O}$

Picropharmacolite occurs as dense coatings with a maximum thickness of 0.5 mm along fracture surfaces (RIECK, 1993). Crystal sizes up to 50  $\mu\text{m}$  are bladed and give the specimen a silky white or colourless sheen. Occasionally, it appears in association of realgar and vrbaita.

#### 43. Hornesite, $\text{Mg}_3(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$

The crystals of hornesite are prismatic and elongated (RIECK, 1993). They are usually aggregated to crusts and stalactites being associated with other efflorescent minerals. It is sometimes intimately intergrown with gypsum.

#### 44. Quartz

Clear to milky crystals of quartz are found in the central zone of Allchar deposit. They are associated with stibnite and realgar reaching up to 2.5 cm in size. An appearance of quartz in the form of chalcedony and jasper is also evidenced (RIECK, 1993).

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