

## GEOCHEMICAL AND MINERALOGICAL CHARACTERISTICS OF THE CENTRAL PART OF THE ALŠAR DEPOSIT (REPUBLIC OF MACEDONIA) WITH PARTICULAR REFERENCE TO INVESTIGATIONS BY X-RAY DIFFRACTION

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**Abstract:** The Alšar deposit consists of several ore bodies and numerous occurrences, each characterized by specific associations of metal and mineral assemblages. The antimony-arsenic-thallium-gold mineralization occurs within a zone almost 3 km long and 200 – 300 m wide. Sb and gold dominate the central part of the deposit, but it also contains significant amounts of arsenic, thallium, minor barium, mercury and traces of lead. The ore bodies contain 2 to 3% antimony, 2% arsenic, up to 0.4% thallium, up to 3.5 ppm gold and 435 ppm barium. In this paper geochemical and mineralogical characteristics of the central part of the Alšar deposit are presented along with the results of new investigations of some specimens from this area.

**Key words:** XRF-diffraction; rebulite; marcasite; quartz; gizmondine; vrbaita; Alšar

### HISTORY

The mine of Alšar is mentioned as Majdan (i.e. mine) in Turkish books from 1481. A document that relates to the area of Rožden (village of Rožden is adjacent to the Alšar mine) mentions the annual income of the Turkish Sultan to be 13,380 akçes (an akçe is a silver coin) of which the mine and the sale of arsenic ore accounted for 1500 akçes. In 1519 the population census was conducted along with a review of the Sultan's income from this region. In this census the Turkish books (defters) note that the population of the region was 175 families, 4 unmarried persons, 11 widows and an income of 21,517 akçes. In the census of 1528/29 it was recorded that in the region there were 156 families, 35 unmarried persons, 6 widows and annual income of 21,500 akçes. In this census it was also registered that the annual production of the mine was 90 Majdan (i.e. Alšar) scales of arsenic ore and that one scale was sold for 180 akçes, equating to a total of 16,200 akçes. In the census made in 1544/45, the population in the region counted 113 families and a total income from the work of the mine was 98 scales, with one scale selling for 189 akçes, equating to a total of 18 522 akçes.

It should be mentioned that the census conducted in 1568/69 mentioned the work of the Alšar mine with the production of 98 scales and a total income of around 20,000 akçes. This overview shows that a significant proportion of the Sultan's revenue in this part of Mariovo came from the production of arsenic in the Alšar mine. During the 15<sup>th</sup> and 16<sup>th</sup> centuries the region of Mariovo was relatively well developed as a result of the mine, which contributed to 35% of the total income of the Sultan from this region.

The following information relating to the Alšar mine (Majdan) are found in documents from 1877 when the mining settlement Majdan began to form (now the village of Majdan). During this period the mine was given as a concession to an Anglo-French company based in Thessaloniki whose owners were brothers Allatini and work in the mine was managed by a mining engineer Charteau, whom workers called "chelepijata". Initially, the mine employed about 500 miners from the nearby village of Mariovo and, more commonly, from the village of Rožden. With the development of the mine the settlements increased and slowly grew into villages. In documents from 1890 to 1912 it is

stated that in the village of Majdan there were 32 houses. Within the Alšar mine there was also a

small separation for crushing ore. Traces of this separation can still be seen in the mine (Fig. 1).



**Fig. 1.** Traces of separation in the central part of Alšar

Crushed and separated ore was transported in cart and mule caravans via the village of Sobotsko to Thessaloniki where it was transported by train to the smelting plants in Freiburg in Germany. It was from these train wagons containing ore from Alšar that the first samples were taken in which the presence of minerals containing thallium were determined in the late 19<sup>th</sup> and early 20<sup>th</sup> centuries (Vrba, 1894; Krener, 1895; Jannach, 1904; Ježek, 1912a,b, 1913a,b). During the Balkan Wars and the First World War the Alšar mine stopped working. Mining activities were restored only after the Second World War.

In the period after World War II Alšar was generally only geologically investigated without active exploitation. Studies were performed on several occasions during the period from 1953 to 1957 and from 1962 to 1965, during which significant amounts of antimony, arsenic and thallium ore were detected (500,000 tons of antimony-arsenic ore containing 1.5% antimony and 2.2%

arsenic). It is especially important to mention that these studies also determined the existence of thallium in concentrations of 0.11 to 0.22%, especially in the northern part of the site in the section called Crven Dol (Ivanov, 1965. 1986; Janković, 1960).

In the early 1990's geological exploration of epithermal gold was started by the American company Nassau Limited from California. The English company RTZ, who determined there to be 20 tons of gold in total, continued gold exploration after that (Janković and Jelenković, 1994; Percival and Radtke, 1994).

The interest in the Alšar mine increased in the second half of the 1980's with the establishment of a scientific project to detect solar neutrinos using thallium minerals from the mine. This interest still exists and the project, named LOREX, is still active (Nolte and Pavičević, 1988; Pavičević, 1994; Pavičević and Amthauer, 1994; Pavičević et al., 2004; 2006).

## INTRODUCTION

Alšar is a complex antimony-arsenic-thallium-barium-gold deposit and its mineralogical composition is a rarity in the world. It contains significant concentrations of thallium, estimated to be around 1,000 tons of metal. This site also has

significant concentrations of antimony and arsenic and the explorations performed during the 1980's and 1990's proved the existence of Carlin-type gold for the first time in the Balkans (Janković and Boev and Serafimovski, 1997).

Percival and Radtke (1994) suggested that gold could exist in association with the antimony-arsenic-thallium-barium deposits at Alšar. After this, in the period 1986 to 1990, mineralization of gold in Alšar was the subject of systematic research.

The results of both field and laboratory studies showed that the geological, geochemical, mineralogical and hydrothermal alteration features are strikingly similar to those that characterize the Carlin-type mineralization of the Western United States (Percival and Radtke, 1994).

Unlike the Carlin-type gold deposits in the Western USA, the Alšar mineralization is hosted in volcanics as well as sediments.

Special interest in thallium as possible solar neutrino detector gave a new impetus for systematic investigations of thallium mineralization in

the northern part of the Alšar deposit (i.e. the Crven Dol ore body). This conducted was under the international LOREX Project, which aimed to establish the reliability of the mineral lorandite from this deposit as a thallium solar neutrino detector. Some adits, such as no. 21, were reopened to enable sampling. This activity lasted from 1987 through 1993. Later it was restricted to laboratory investigations (Kirsten, 1990).

For the results of previous studies of the Alšar deposit, the reader is referred to Ivanov (1965, 1968), Janković (1960, 1994, 1997), Percival and Radtke (1994) and Boev (1988), Boev and Lepitkova (1991), Boev et al. (2001–2001), Balić-Zunić et al. (1993), Beran et al. (1990), El Goresy et al. (1998), Lippolt et al. (1986), Frantz et al. (1994), Jelenković et al. (1994) and Volkov et al. (2006).

## METHODOLOGY

The mineralogical contents of the collected samples in the central part of the Alšar deposit were determined using an X-Ray Siemens D 500 equipped with an automated computer and a copper-monochromatic lamp working at 40 kV and 30 mA. Quantitative analysis of the mineral phases

was performed using the DIFRAC-11 software package and program support by EVAL and IDR. Inductively coupled plasma with mass spectroscopy (ICP-MS) was used to perform geochemical investigations on some specimens.

## MAIN GEOLOGICAL CHARACTERISTICS OF THE ALŠAR DEPOSIT

The Alšar deposit is polychronous and polygenetic. It formed as a result of complex physico-chemical processes occurring in a heterogeneous geological environment, brought about by the interaction of multi-stage hydrothermal fluids with products of polyphase magmatic activity and surrounding sedimentary and metamorphic rocks. Mobilization, transportation and deposition of ore mineralization, as well as the supergene transformations of primary ore minerals, were determined by, and partly accompanied with, intensive pre-, sin- and post-ore structural-tectonic terrain shaping. In those processes, several orebodies of varying shapes, textural-structural varieties and with various mineral and elemental associations localized in various, tectonically predisposed geological environments were formed (Janković et al., 1997).

The Alšar deposit is NNW-SSE oriented. It comprises several ore bodies within a zone 3 km long and 200 to 300 m wide. The localization of mineralization is spatially associated with environments characterized by increased porosity and per-

meability, 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 the tuffs produced a favourable environment for hydrothermal fluid migration and introduction of ore elements. Another favourable environment was the porous and permeable basal zone developed as a strata-bound body along the Triassic erosion surface (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) (Fig. 2). Silicification and argillitization are the most predominant alteration products and quartz is very abundant in hydrothermally altered volcanoclastites (Percival and Radtke, 1994; Pavičević et al., 2006). The alteration is generally believed to be associated with

Plio-/Pleistocene andesite volcanism and latite intrusion, which extend from Mt. Kožuf in Republic of Macedonia to Mt. Voras in Greece (Karamata et

al., 1994; Kolios et al., 1980; Lepitkova, 1995; Troesch and Frantz, 1992; Kochneva et al., 2006; Yanev et al., 2008).

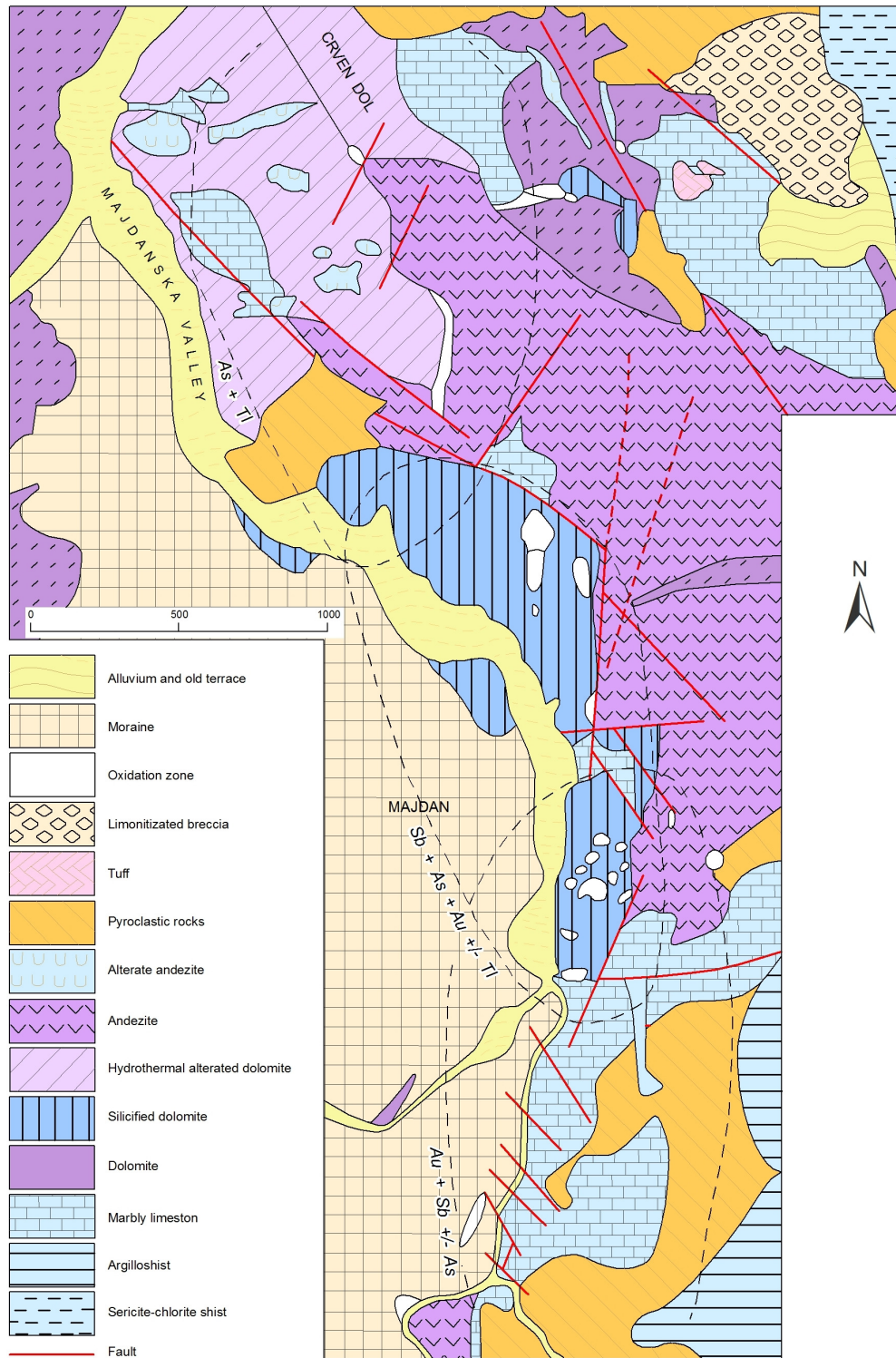


Fig. 2. Geological map of the Alšar deposit (Boev, 2016)

The major elemental components of the Alšar deposit are antimony, arsenic, thallium, iron and gold, accompanied by minor mercury and barium and traces of lead, zinc and copper. Enrichment of thallium in the Alšar deposit is closely associated with increased concentrations of volatiles, such as arsenic, antimony and mercury.

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 (Ivanov, 1965).

(i) In the northern part of the deposit arsenic and thallium prevail, accompanied by minor antimony and local traces of mercury and gold.

(ii) The central part of deposit is dominated by antimony and gold, but also contains significant amounts of arsenic, thallium, minor barium, mercury and traces of lead.

(iii) The southern part of the deposit is characterized by a dominance of gold mineralization accompanied by variable amounts of antimony (Fig. 3).

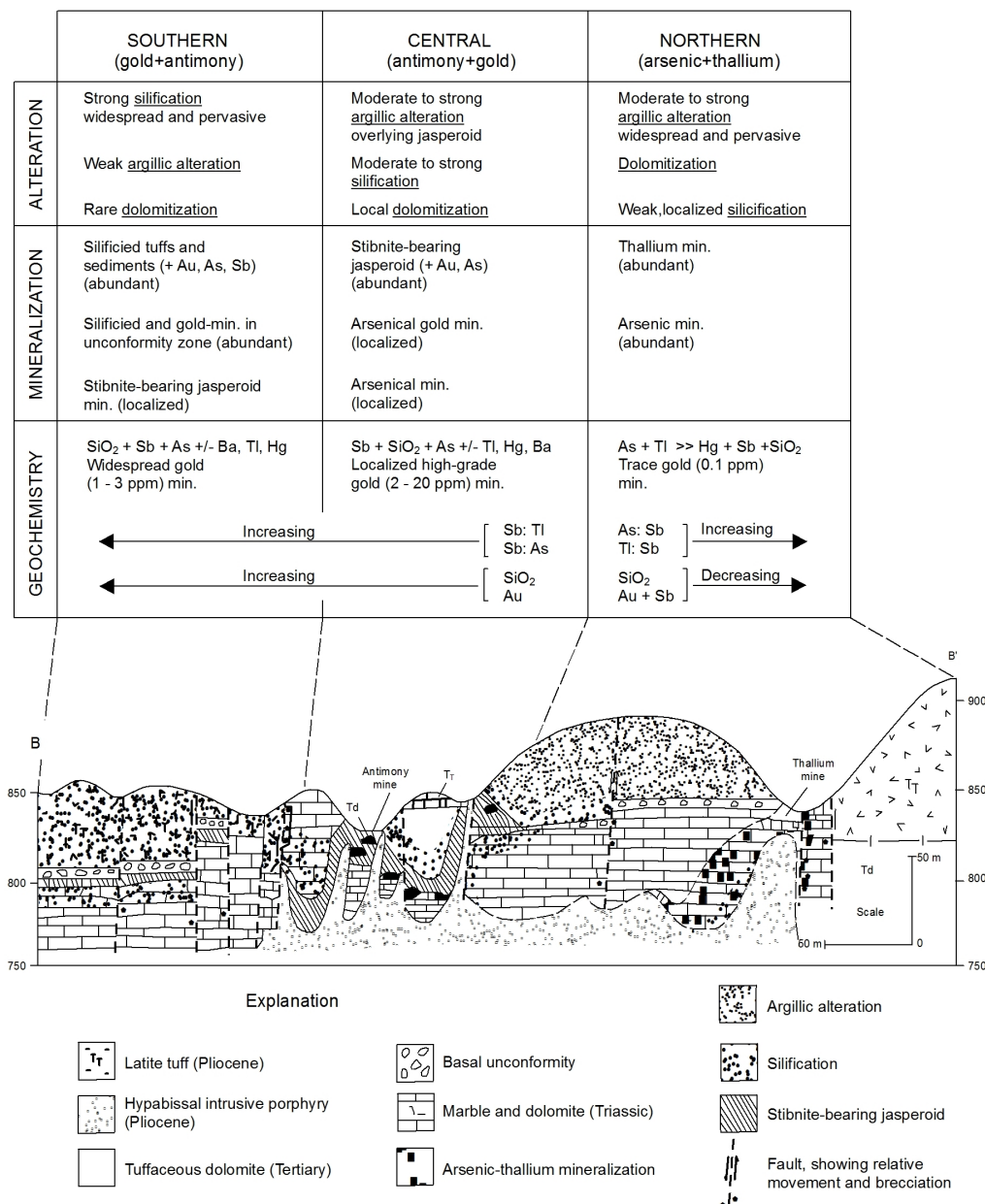


Fig. 3. Geological profile and mineral associations in Alšar deposit (Percival et al., 1994). Central part of the Alšar deposit.

Several ore bodies of variable size are revealed by three main adits at levels of 775, 799 and 823 m and including several sublevels and inclined shafts. Some diamond drillings were performed sporadically. The ore mineralization spreads from level at 852 m to beyond the level at 775 m. The length of mineralization exceeds 180 m and the width of the mineralized zone ranges from 20 to 50 m (Figs. 4 and 5).



Fig. 4. Panoramic view of the edit 823 in the central part of Alšar

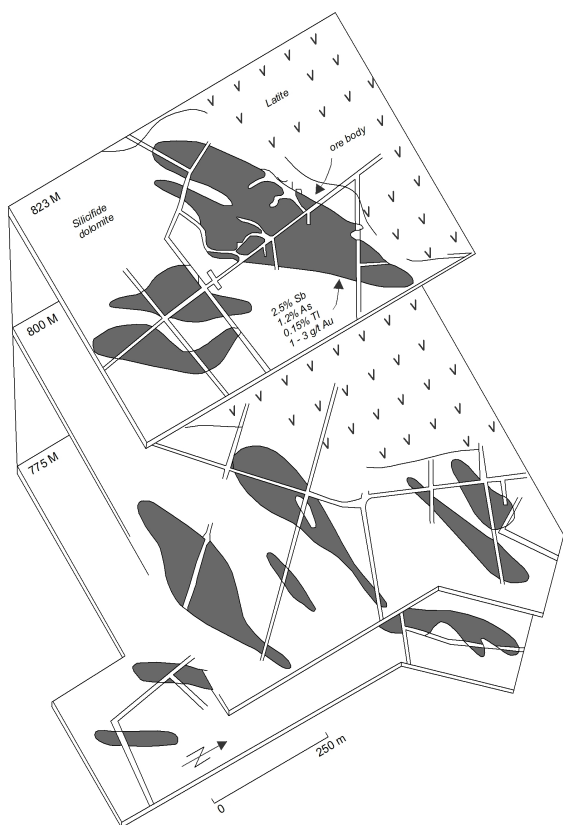


Fig. 5. Block diagram of the central part of the Alšar deposit

The ore reserves of proved, probable and possible categories are established at about 500,000 tons of 1.5% antimony, 2.2% arsenic, 0.1% thallium and 2 g/t gold. Table 1 shows the chemical composition of various types of ore.

Table 1

*Geochemical analyses of Sb-As-Tl mineralization from the central part of the Alšar deposit (by ICP-MS)*

No.	1	2	3	4	5
	%	%	%	%	%
Al	2,36	2,71	2,38	2,63	2,61
Fe	7,250	6,430	7,770	6,410	6,930
Ca	0,506	0,472	0,587	0,497	0,487
Mg	0,198	0,224	0,208	0,226	0,217
Na	0,071	0,074	0,077	0,071	0,071
K	0,946	1,09	1,01	0,99	1,04
Ti	0,103	0,129	0,107	0,124	0,123
P	0,048	0,045	0,048	0,045	0,046
Mn	0,020	0,015	0,021	0,015	0,017
As	0,818	0,789	0,815	0,802	0,805
Sb	0,437	0,382	0,426	0,385	0,400
Tl	0,187	0,175	0,191	0,175	0,180
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Cr	44	55	48	55	54
Ni	22	24	23	23	24
Co	8	8	8	8	8
Cu	12	18	15	14	14
Zn	<10	12,2	30,4	<10	<10
Pb	63	61	60	53	51
Cd	2,4	2,3	2,3	2,1	2,2
Sr	23	25	27	27	24
Ba	97	107	86	107	98
Rb	94	107	98	98	102
Cs	102	120	109	118	115
Li	80	80	78	82	82
V	49	52	51	50	50
Be	1,5	1,7	1,5	1,6	1,6
Mo	5,4	4,1	4,9	4,2	4,4
Ga	8,6	14,0	13,2	13,8	13,3
Ge	6,44	6,05	6,26	6,13	5,98
Se	5,59	5,11	5,93	5,45	6,21
Ag	1,33	3,49	2,98	3,53	3,56
Sn	3,62	3,74	3,47	3,44	3,25
Bi	0,64	0,32	0,42	0,28	0,47
Pd	0,46	0,41	0,46	0,42	0,37

1, 2, 3, 4, 5 – mineralized silicified dolomites with small crystals of stibnite

## MINERAL COMPOSITION OF ORE

The ore consists of numerous minerals, with stibnite, realgar, pyrite, marcasite being the most abundant minerals. These are accompanied by minor arsenopyrite, orpiment, native gold and sporadically by petzite, native gold, magnetite, bravoite and numerous thallium minerals such as lorandite, vrbaite, raguinite, picopaulite, pierrotite, parapierrotine etc. (the list of thallium minerals is still incomplete in the ore bodies) and then antimony-lead sulphosalts (boulangerite, falcmanite etc.), cinnabar and barite, among others.

**Stibnite** is the most significant antimony mineral. It occurs disseminated in the fine-grained micro-crystalline matrix of quartz. Sporadically thin veinlets of stibite are developed along fissures and thin fractures in the highly silicified rocks (jasperoids). In some drusies stibnite forms crystal aggregates. Locally, stibnite occurs in irregularly shaped fine to crystalline masses in jasperoid.

**Realgar** is usually deposited after stibnite. It occurs as crystals and crystalline aggregates filling thin fractures but sporadically it forms massive ore bodies of irregular shape. Host rocks are pervasively altered to fine-grained clay minerals and sericite mixed with limonite, jarosite, manganese oxides, gypsum and minor hydrothermal quartz (Percival and Radtke, 1994).

**Orpiment** is usually intergrown with realgar but in comparatively smaller amounts. It is often intermixed with argillic alteration but sporadically it forms large crystal aggregates.

**Pyrite, marcasite** and **melnikovite pyrite** are the most abundant sulphides, forming locally massive ore bodies, mostly of small size. The colloform structures are widespread.

**Pyrite** occurs as fine subhedral disseminated grains, often as large crystals and aggregates of coarse-grained crystals. Sporadically, pyrite and pyrite-quartz veinlets cut across the ground mass of microcrystalline quartz. The ground mass also contains fine crystalline arsenopyrite, stibnite and marcasite.

**Marcasite** is found mostly as framboidal masses and banded veins. It is a very abundant mineral in many jasperoid ores.

**Lead-antimony sulphosalts** occur in association with stibnite and are represented by falkmannite and fizelyte. They form after stibnite but

prior to the commencement of deposition of realgar and orpiment. They occur as elongated crystal aggregates along with quartz (Soufek et al, 1998).

**Thallium minerals.** Although thallium geochemistry and mineralogy of the central ore bodies of the Alšar deposit are insufficiently studied, it is known that these ore bodies contain high thallium concentrations. Several thallium minerals are so far identified.

**Lorandite** is the most common thallium mineral in the Alšar deposit (Krenner, 1894). It occurs in close association with realgar and less frequently with orpiment. It forms sporadically large aggregates and/or individual crystals. Precipitation of lorandite usually takes place after crystallization of realgar and orpiment.

**Vrbaite** occurs predominantly as small crystals with realgar and orpiment (Ježek, 1912, 1913; Krehlik, 1912, 1913). Aggregates of realgar, orpiment and vrbaite crystals of variable sizes are found in hydrothermally altered dolomite and tuffaceous dolomite. Its deposition follows precipitation of arsenic-sulphides.

**Raguinite** (Laurent et al., 1969) occurs in association with pyrite and as a pseudomorphose of picopaulite. Its position in the paragenetic sequence of mineralization is not quite clear. Raguinite is sporadically replaced by lorandite.

**Picopaulite** (Johann et al., 1970, 1975) is known in association with raguinite and realgar. It occurs in realgar with envelopes of raguinite.

Both raguinite and picopaulite are, as thallium minerals of the thallium-iron-sulphur system, closely associated with pyrite. It seems that raguinite and pyrite originated from a parent mineral, most likely picopaulite by adoption of sulphur. Raguinite occurs more frequently where lorandite is abundant and it is rare where realgar is dominant.

It is expected that other minerals from the thallium-iron-sulphur system will be found. Further investigations are needed to clarify the conditions of precipitation and the position of thallium-iron sulphides in the paragenetic sequence of mineralization in the central part of the Alšar deposit. At present, the critical factor governing the distribution of thallium in this system appears to be sorption of thallium in iron-sulphide gels, with isomorphism playing a secondary role. Some pyrite/marcasite contain 300 to 900 ppm of thallium.

**Parapierrrotite** (Johann et al., 1975) is the only mineral so far identified in Alšar from the thallium-antimony-sulphur system. It is associated with realgar but its crystals, up to a few mm in diameter, are sporadically found independent of realgar.

**Simonite** is the only mineral currently identified from the thallium-mercury-arsenic-sulphur system. It is very rare in the deposit and its position in the paragenetic sequence of mineralization is not clear.

**Rebulite** is a new thallium mineral discovered in the last decade. It occurs as dark-grey crystals with a metal lustre and brownish-red streak. It occurs in association with realgar, simonite and other thallium sulphosalts.

### Gold mineralization

Gold mineralisation occurs in the central and southern parts of the Alšar deposit. The epithermal ore is of disseminated replacement type. Percival and Radtke (1994) reviewed the principal characteristics of gold mineralization in the Alšar deposit.

Gold mineralization occurs in Mesozoic dolomite, in jasperoids along faults and within an unconformity between the pre-Tertiary age rocks and in micro-quartz veinlets, disseminations and silica replacement bodies in Tertiary tuffaceous dolomite and overlying Tertiary tuffs. Gold is very fine-grained (micron to submicron particles) and shows a strong association with introduced silica and antimony (Figs. 6 and 7).

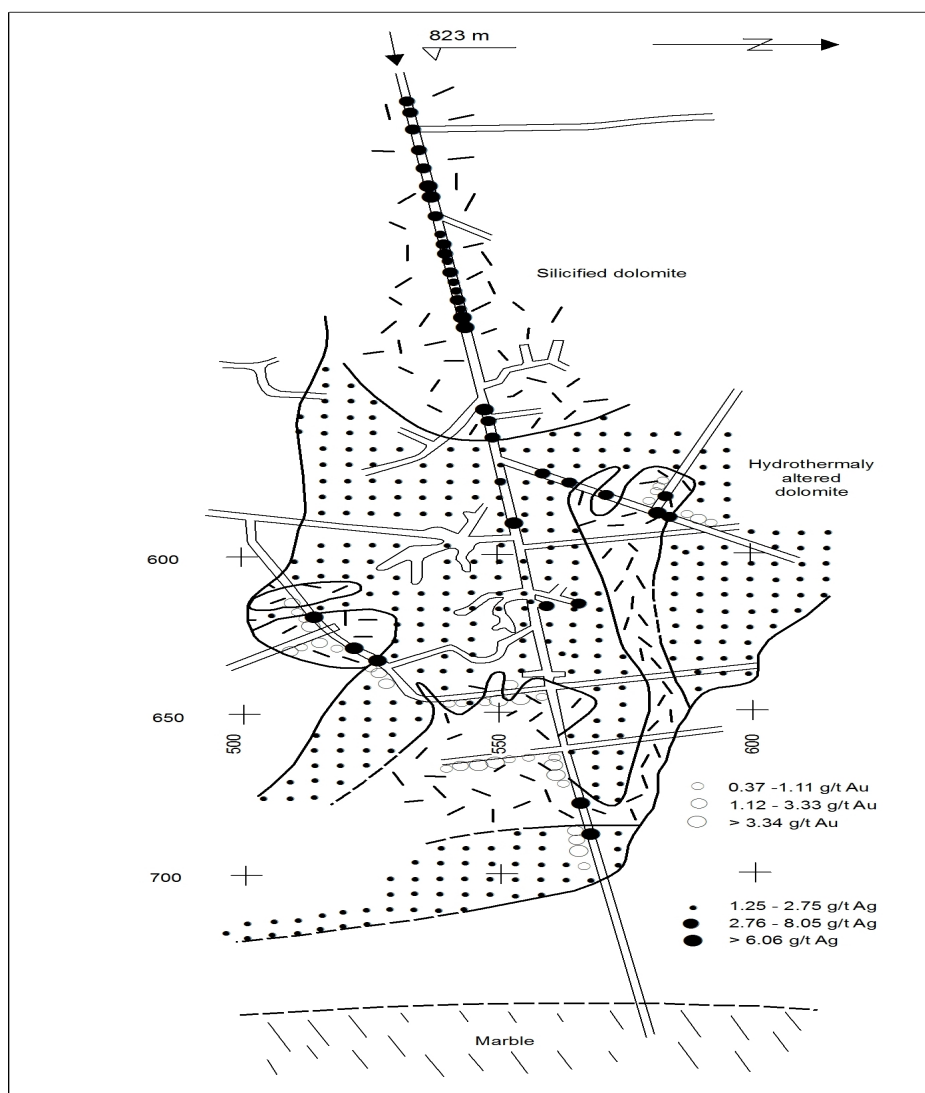


Fig. 6. Geological map of Edit 823 in the central part of Alšar with distributions of gold



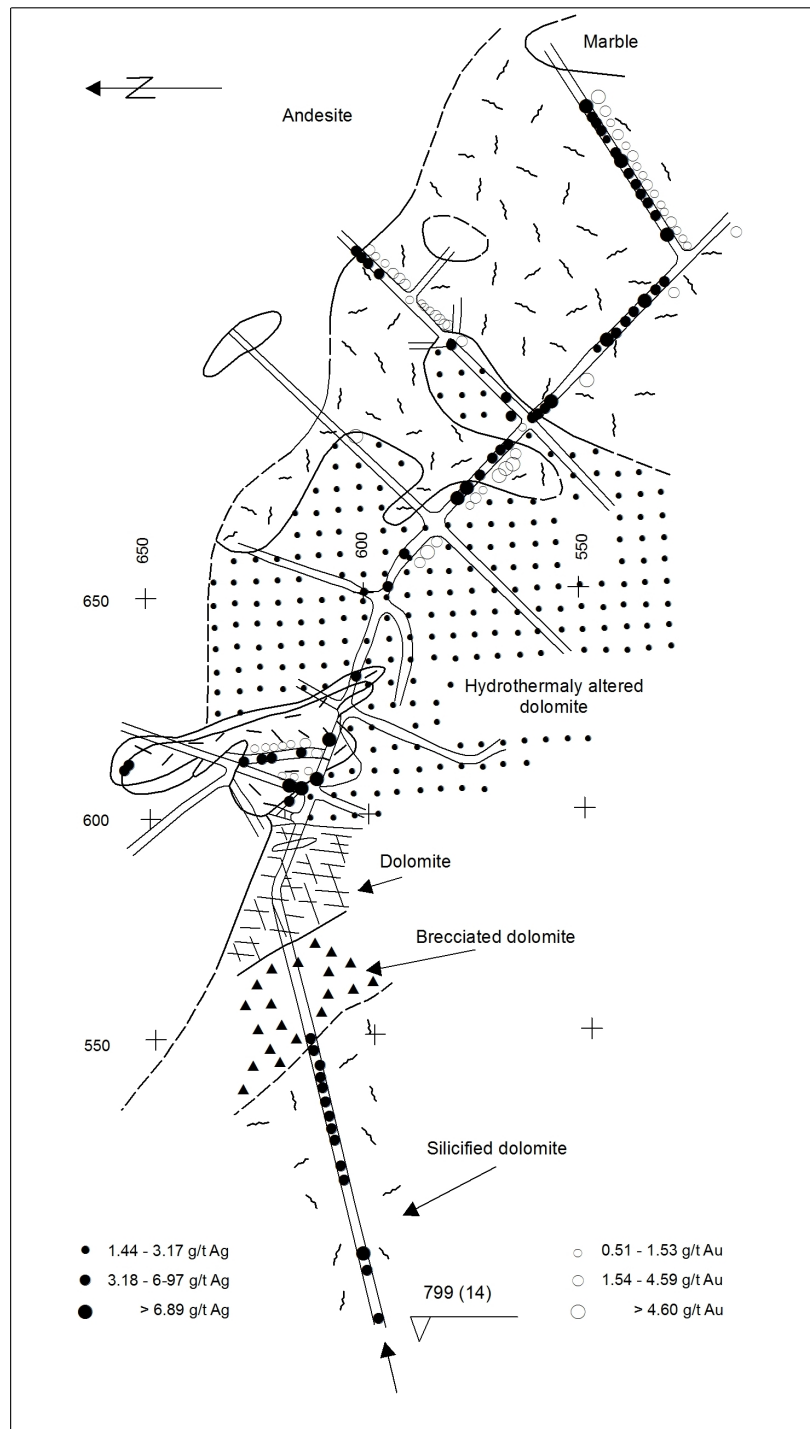


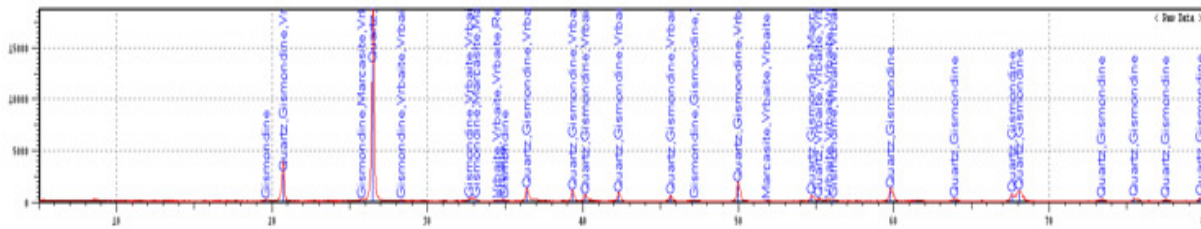
Fig. 7. Geological map of Edit 799 in the central part of Alšar with distributions of gold

### RESULTS OBTAINED AND COMMENT

The results obtained using the X-Ray Fluorescence method are shown on diffraction graphs in Figure 8. From these it can be observed that the following minerals dominate the central part of the

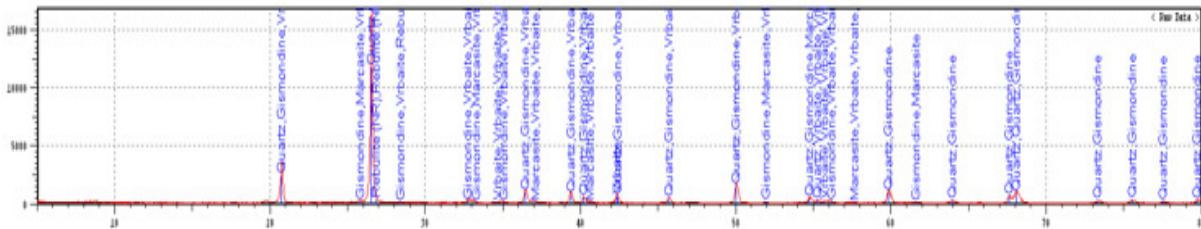
Alšar deposit, where sampling was performed: quartz, stibnite, marcasite, rebulite and gizmondine. These are the dominant minerals that occur in silicified dolomites (Fig. 8).

## Probe 1.



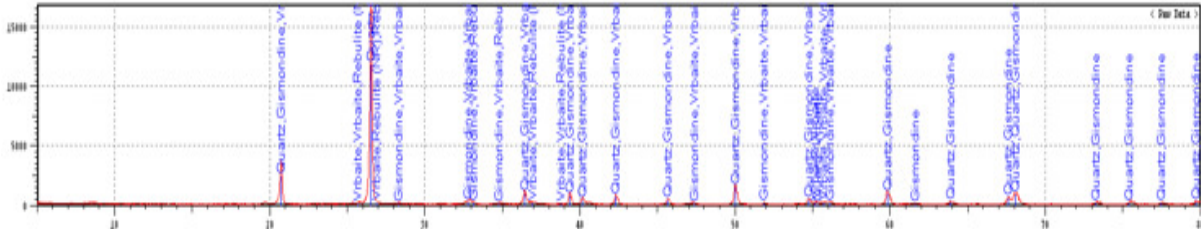
Quartz JCPDS 00 046 1045; Marcasite JCPDS 00 003 0795; Vrbaita JCPDS 01 071 2436; Gismondine JCPDS 00 020 0452; Rebulite JCPDS 01 072 1519.

## Probe 2.



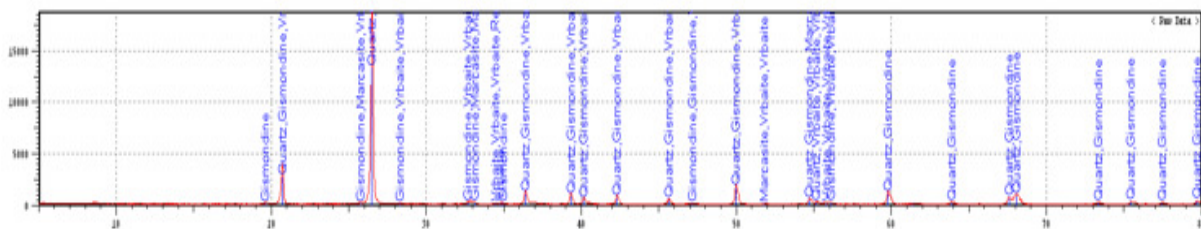
Marcasite JCPDS 01 089 2089; Vrbaita JCPDS 01 071 2436; Quartz JCPDS 00 033 1161; Rebulite JCPDS 01 072 1519; Gismondine JCPDS 00 020 0452.

## Probe 3.



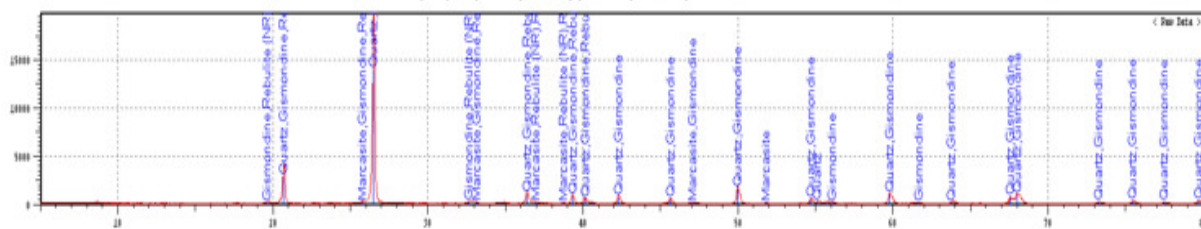
Quartz JCPDS 00 046 1045; Marcasite JCPDS 00 003 0795; Vrbaita JCPDS 01 071 2436; Gismondine JCPDS 00 020 0452; Rebulite JCPDS 01 072 1519.

## Probe 4.



Quartz JCPDS 00 033 116; Rebulite JCPDS 00 044 146; Marcasite JCPDS 01 088 2302; Vrbaita JCPDS 01 071 2436; Gismondine JCPDS 00 020 0452.

## Probe 5.



Quartz 00 033 116; Gismondine 00 020 0452; Rebulite 01 072 1519; Marcasite 00 003 0795; Vrbaita 01 071 2436.

**Fig. 8.** XRD analyses of samples of Sb-As-Tl mineralization from the central part of the Alšar deposit

## CONCLUSION

Several distinct types of mineralization occur in the central part of the Alšar deposit including:

– Mineralized brecciated zones developed along the contact between the subvolcanic intrusions and dolomite and/or tuffaceous dolomite or along shear zones in the carbonate rocks and/or silicified tuffs.

– 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.

– Mineralized systems of veinlets and fractures occur in the tuffaceous dolomite and the Triassic dolomite.

– Disseminated mineralization, mostly stibnite, pyrite/marcasite and gold occurs (a) as strata-bound 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 thallium-minerals.

– Geochemical analyses and investigations by XRF of the probe of Sb-As-Tl mineralization from the central part of the Alšar deposit made by ICP-MS indicated the Tl contents of 0.175–0.190 %. Investigation of this specimens by XRD technique indicated that no contents of the lorandite and Tl is presented in other Tl-minerals (vrbaite, rebulite, gismondine).

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## Резиме

**ГЕОХЕМИСКИ И МИНЕРАЛОШКИ КАРАКТЕРИСТИКИ НА ЦЕНТРАЛНИОТ ДЕЛ НА НАОГАЛИШТЕТО АЛШАР (РЕПУБЛИКА МАКЕДОНИЈА) СО ПОСЕБЕН ОСВРТ НА ИСТРАЖУВАЊАТА СО РЕНДГЕНСКА ДИФРАКЦИЈА**

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**Клучни зборови:** рендгенска дифракција; ребулит; марказит; кварц; гизмондин; врбаит; Алшар

Во централниот дел на наоѓалиштето Алшар постојат неколку видови минерализација, и тоа:

Зони од минерализирана бреча кои се развиле на контактот помеѓу субвулканските интрузии и доломитите и/или туфозните доломити или покрај раседните зони во карбонатните карпи и/или силифицираните туфови.

Масивни леки од реалгар се појавуваат во карбонатните карпи и преминуваат во штокверкна минерализација.

Масивна сулфидна минерализација, главно пирит/марказит, се појавува надолж стрмните раседни зони. Масивните јасписоиди кои содржат сулфиди се појавуваат спорадично само како мали парчиња.

Минерализирани системи на мали жилички или пукнатини се појавуваат во туфозниот доломит и тријаскиот доломит.

Дисеминирана минерализација, главно стибнит, пирит/марказит и злато, се појавува: а) како страта-баунд тела надолж контактот помеѓу базалниот дел на вулканоседиментниот туфозен доломит и/или туфовите и тријаските карбонатни карпи во основата, б) во силифицирани вулкански карпи (со варијабилни количини на аргилизација) и в) како ситно импрегниран пирит-марказит во изо-

билство и како стибнит во јаспидите, локално придружувани од арсен сулфиди и талиумови минерали.

Геохемиските анализи и истражувања со XRF на пробите од Sb-As-Tl минерализација од централниот дел на наоѓалиштето Алшар, спроведени со ICP-MS покажаа присуство на Tl од 0.175 до 0.190%. Истражувањата на овие примероци со примена на техниката на XRD покажаа дека воопшто не е присутен лорандит, а Tl е присутен во другите Tl-минерали (врбаит, ребулит, гизмондин).