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# ALLCHAR MINERAL ASSEMBLAGE

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Abstract. The paper is a summary of investigations carried out on minerals of the Allchar deposit. It discusses the Tl-As-Sb-Au mineral assemblage after detailed and intense research work.

Four types of mineralization have been distinguished based on the mineral assemblage present:

1. The first type is characterised by high content of iron and sulphur, but lower arsenic and thallium content. The pyrite-marcasite mineral assemblage is characterized by the presence of some quantities of arsenic-pyrite.

2. The second type is characterized by the high antimony and low iron and thallium content. Stibnite is the most common mineral in the group.

3. The third type is characterized by the high arsenic and sulphur and relatively low thallium content. Orpiment is the most common mineral in this group.

4. The fourth type of minerals is characterized by the high content of arsenic, sulphur, iron and thallium. This type of minerals is accompanied by the high content of manganese and zinc.

Key words: Allchar; Macedonia; mineral assemblage

#### INTRODUCTION

The Allchar complex Sb-As-Tl-Au deposit is one of the unique deposits in the world not because of its size, but mineral composition. It contains significant thallium concentrations that classify it as a unique deposit containing that metal. Besides economically significant antimony and arsenic concentrations, the Allchar deposit is the first Carlin-type gold deposit found in the Balkan Peninsula during the mid 1980's.

The latest mining activities started in 1881, and with some interruptions, lasted till 1913 (Janković, 1960). During that period mainly arsenic ore was excavated and exported to Thessaloniki, Greece and Germany. Small amounts were mined out in the outcrops of the deposit. There are no data about the amount of arsenic ore mined out at that time.

The mineral potential of arsenic in the deposit is estimated at some 15,000 tons (Ivanov, 1965). According to today's criteria arsenic is a harmful component that results from antimony processing.

The first results concerning the sulfide minerals from Allchar locality were published by Foullon, 1890, 1892, 1904; Hofmann, 1891; Pelikan, 1891; Goldschmidt, 1896; Hackman, 1897; Stevanovic, 1904).

During the end of the nineteenth (Vrba, 1894; Krener, 1895; Goldschmidt, 1899) and the beginning of the twentieth century (Jannasch, 1904; Loczka, 1904; Ježek, 1912, 1913a) the first thallium minerals were discovered (lorandite and vrbaite, respectively) as constituents of arsenic-antimony ore.

Exploration for antimony carried out from 1953 to 1957 and from 1962 to 1965 resulted in the discovery of significant reserves of low grade ore (Ivanov, 1965). However, high arsenic content in Sb-concentrations has precluded economic exploitation. The latest exploration for antimony was carried out in 1970–1973 (Ivanov, 1986).

Mineral potential of the Allchar deposit, both mined out and available ore, exceeds 20,000 tons of antimony with 0.5 % Sb as cut-off grade (Janković et al., 1997).

The name of the deposit pronounces as Allchar, being derived from the names Allatini (a bank institution, owner of the concession) and Charteau (a mining engineer who worked in the mine).

Special interest for thallium as possible solar neutrino detector (Freedman, 1976, 1979) gave a new impulse for systematical investigations of thallium mineralization in the north part of the Allchar deposit (i.e. the Crven Dol ore body). This was an international LOREX (LORandite EXeriment) Project aiming to establish reliability of the mineral lorandite from this deposit as thallium solar neutrino detector (Ernst et al., 1984; Pavićević, 1986, 1988, Morinaga, 1986; Pavićević and El Goresy, 1988; Palme et al., 1988; Pavićević and Korschinek, 1993; Anovski et al., 1993; Frantz et al., 1994; Gržetić, 1993; Hejl et al., 1993; Ivanovski et al., 1993; Lazaru and Stafilov, 1993; Balić Žunić et. al., 1993a, 1993b; Makovicky and Balić Žunić, 1993; Mihajlović, 1993; Mijatović et al., 1993; Petrov and Andonova, 1993; Petrov et al.,

Spatially the Allchar deposit is located along the western flank of the unstable Vardar zone and the Dinarides or rigid Pelagonian crystalline block on the west, about 50 km south-west of the town of Kavadarci in close proximity to the Greek-Macedonian border.

Mineralization is associated with a Pliocene volcano-intrusive complex of calc-alkaline suites, controlled by deep fractures striking mostly N–S and SW–NE.

This igneous complex formed on a basement composed predominantly of Triassic sediments, Jurassic ophiolite (gabbro-peridotites prevail) and Cretaceous sediments. 1994; Sotirovski and Boyer, 1993; Stafilov et al., 1993, 1995; Trajkovska et al., 1993).

Some adits as no. 21 have been re-opened to enable taking the samples. This activity lasted from 1987 through 1993. Later it was restricted to laboratory investigations.

The mineral potential of thallium in the Allchar deposit has been estimated at 500 tons (order of magnitude) (Ivanov, 1986).

The possible presence of gold in the Sb-As-Tl association at Allchar was initially suggested by different authors (Stafilov, 1985; Ivanov, 1986; Stafilov and Todorovski 1987). During the 1986–1989 period gold mineralization was systematically explored. The results of both field and laboratory studies showed that the geological, geochemical, mineralogical and hydrothermal alteration features are strikingly similar to those which characterize Carlin-type mineralization of the Western United States (Percival and Radtke, 1990; Percival et al., 1992).

Unlike the Carlin-type gold deposits in the Western USA, the Allchar mineralization is hosted not only by sediments, but volcanics as well.

It should be emphasized that the Allchar deposit is not fully explored and that the metallogenetic studies are not completed. The current investigations are still in progress.

For the results of previous studies of the Allchar deposit, the reader is referred to Ivanov (1965, 1986); Janković (1960, 1988, 1993); Percival and Boev 1990); Stieglitz (1990); Percival et al. (1992); Percival and Radtke (1994); Boev and Serafimovski (1996); Boev et al. (1993a); Rieck, 1993; Caubel and Galvier (2000).

#### REGIONAL GEOLOGIC SETTING

The terrain adjacent to the deposit is composed of several litho-stratigraphy members.

The wide vicinity of the Allchar deposit is characterized by complex tectonic relations in which N–S structures of deep fractures along the contact of the Vardar zone and the Pelagonian massif play an important role. Volcanic structures and subvolcanic intrusions of calc-alkaline magma are formed at their intersections with neotectonic fractures SW–NE. The age of subvolcanic intrusions in all parts of the Kožuf area is the same, the Allchar deposit intrusions belonging to the youngest phases (3.9 - 5.1 m.y.).

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All geological units, except those of the Pliocene shallow basin, demonstrate an elongation with north-south trend and are tectonically rather dislocated.

**Precambrian albitic gneisses** with sporadic amphibolite lenses belong to the oldest rocks in the wide vicinity of Allchar. Sporadic marble masses occur in the gneisses.

*Paleozoic schists*, phylites, locally cipolines, metasandstones, argilloschists and quartzites are not widespread.

*Triassic sediments* comprise a large portion of the terrain in the Allchar area. They occur in two basic facies: (i) as marbleized limestones and dolomites and (ii) claystones and sandstones with sporadic masses of diabases and local green schists.

Jurassic rocks are represented by diabasechert formations composed of limestones, sandstones, clayshists, quartzites, cherts sedimentary facies as well as strongly serpentinized gabbroperidotite complexes of harburgitic-dunitic composition. Small deposits with podiform chromite bodies have been found in the latter. Serpentinites also occur as separated narrow bands with tectonic borders on surrounding rocks. They appear in this area as a result of processes associated with diapirism. This is indicated by intensive tectonic fracturing as well as by the appeared dislocations in the western margin of the Vardar zone. *Upper Cretaceous* sediments are significantly spread in the vicinity of Allchar. They occur in several facies such as:

- Barremian-Albian conglomerates and

- Turronian limestones

These rocks make up the hanging-wall in the Ni-Fe Ržanovo deposit.

*Upper-Eocene* series consists of basal conglomerates covered by flysch sediments (alevrolites, clays, sandstones and limestone intercalations).

Pliocene lacustrine sediments and pyroclastites are wide spread in the vicinity of Allchar. Pliocene sediments consist of conglomerates and clayey-sandstone facies with local occurrences of marls. Small deposits of diatomaceous earths are occasionally noticed. Volcano-sedimentary suites with pyroclasts and clayey-sandstone sediments (Kojčov Rid north' of Allchar) are developed in individual Pliocene basins.

Quaternary sediments occur in the form of terraces, and as tuffs locally.

The volcano-intrusive complex of calc-alkaline rocks of Pliocene age is part of the wide Kožuf area. Its petrologic features are shown in detail by Boev (1988).

Latites, minor quartz latites and andesites (near Studena Voda) occur in the wide area of Allchar.

## LOCAL GEOLOGIC 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 Allchar deposit.

The quartz-sericite-feldspar schists are developed along the eastern flank of the deposit, whereas 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 to amount about 250 m.y. (Lepitkova, 1995).

# MINERAL ASSEMBLAGE OF INDIVIDUAL TYPES OF MINERALIZATION IN THE ALLCHAR DEPOSIT

Microscopic and X-ray spectral laboratory studies carried out on samples from the Allchar deposit determined the mineral assemblages as follows:

The pyrite-marcasite mineral assemblage hosts pyrite, marcasite and arsenopyrite. Pyrite is

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the most widespread and occurs as massive aggregates. Grains are 0.5 mm in size. It is closely associated with marcasite and arsenopyrite. Chemically, pyrite is relatively pure. However, low manganese and copper contents have been found. Arsenic content is high, reaching 5 % which is an indicator of the large activities of this element during the process of formation of the deposit. Taking in consideration the occurrence of arsenopyrite in association with pyrite makes arsenic content in pyrite logical.

Marcasite is less common. It can be found in the form of spheroids in silicified mass or as peripheral zones in pyrite. Grains vary from 0.005 to 0.1 mm in size. It contains lower amounts of element impurities compared to pyrite. Marcasite is characterized by the presence of low arsenic and antimony concentrations.

Arsenopyrite is not very common. Its discrimination from pyrite is in general based on colored dispersion in crossed nicols, which is blue to yellowish-brown.

Stibnite assemblage includes only mineral stibnite. It occurs in the form of fairly large crystals of  $2 \times 5$  mm in size. It possesses idiomorphic grain structure with individual grains connecting quartz aggregates with marcasite. This indicates that stibnite has been formed later compared to pyrite-marcasite assemblage. Stibnite is not associated with any other mineral. Significant concentrations of other elements in stibnite are not registered. Iron and copper are common impurities, whereas thallium occurs sporadically (Boev et al.,

1993b; Lazaru and Stafilov, 1993, 1998; Stafilov et al., 1995).

Realgar-orpiment-lorandite assemblage is rather variable. The assemblage was formed during the later stages of hydrothermal activity in the area.

Orpiment is the most common in the assemblage. It forms aggregates of massive texture occurring as large crystals of 10 to 15 mm in size. Small quantities of iron and copper occur as impurities (Boev et al., 1993b; Lazaru and Stafilov, 1993, 1998; Frantz et al., 1994; Stafilov et al., 1995).

Realgar forms individual aggregates or occurs in association with orpiment, lorandite and other thallium minerals. It occurs as large grains of 3 to 5 mm in size. Its composition is stoichiometric containing low quantities of iron and copper as impurities. Orpiment corrodes realgar indicating that realgar has been formed earlier than orpiment.

Thallium minerals in this assemblage are very common. The most common is lorandite occurring in grains of up to 5 mm in size. It occurs in association with both realgar and orpiment. Chemically it is relatively pure (Boev et al., 1993b; Lazaru and Stafilov, 1993, 1998; Frantz et al., 1994).

Minerals present at the Allchar deposit are given in Table 1.

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Minerals present at the Allchar deposit

	CONCRETE NO. 2 CONTRACTOR CONTRACTOR CONTRACTOR		
No.	Mineral	Formula	Crystallographic system
Elem	ents		
1	Gold Au		Cubic
2	Sulfur	S	Monoclinic/orthorhombic
Sulfi	des and sulfosalts		
3	Arsenopyrite	FeAsS	Monoclinic
4	Bernardite	TI(AsSb) <sub>5</sub> S <sub>8</sub>	Monoclinic
5	Cinnabar	HgS	Hexagonal
6	Jankovicite*	Tl <sub>5</sub> Sb <sub>9</sub> (AsSb) <sub>4</sub> S <sub>22</sub>	Triclinic
7	Lorandite	TIAsS <sub>2</sub>	Monoclinic
8	Marcasite	FeS <sub>2</sub>	Orthorhombic
9	Orpiment	As <sub>2</sub> S <sub>3</sub>	Monoclinic
10	Parapierrotite*	Tl(Sb,As) <sub>5</sub> S <sub>8</sub>	Monoclinic
11	Pararealgar	AsS	Monoclinic
12	Picotpaulite*	TlFe <sub>2</sub> S <sub>3</sub>	Orthorhombic
13	Pyrite	FeS <sub>2</sub>	Cubic/orthorhombic

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No.	Mineral	Formula	Crystallographic system
14	Raguinite	TIFeS <sub>2</sub>	Orthorhombic
15	Realgar	As <sub>4</sub> S <sub>4</sub>	Monoclinic
16	Rebulite*	$Tl_5Sb_5As_8S_{22}$	Monoclinic
17	Simonite*	TlHgAs <sub>3</sub> S <sub>6</sub>	Monoclinic
18	Stibnite	Sb <sub>2</sub> S <sub>3</sub>	Orthorhombic
19	Vrbaite*	$Tl_4Hg_3As_8Sb_2S_{20}$	Orthorhombic
20	Weissbergite	TlSbS <sub>2</sub>	Triclinic
21	Fangite	Tl <sub>3</sub> AsS <sub>4</sub>	Otrhorhombic
Oxid	les		
22	Arsenolite (or Claudetite)	As <sub>2</sub> O <sub>3</sub>	Cubic
23	Cervantite	Sb <sub>2</sub> O <sub>4</sub>	Orthorhombic
24	Goethite	FeO(OH)	Orthorhombic
25	Quartz	Quartz .	
26	Roméite	(Ca,Fe,Mn,Na) <sub>2</sub> (Sb,Ti) <sub>2</sub> O <sub>6</sub> (O,OH,F)	Cubic
27	Stibiconite	Sb <sub>3</sub> O <sub>6</sub> (OH)	Cubic
28	Valentinite	Sb <sub>2</sub> O <sub>3</sub>	Orthorhombic
Carb	onates		
29	Aragonite	CaCO <sub>3</sub>	Orthorhombic
30	Calcite	CaCO <sub>3</sub>	Hexagonal (rhombohedral)
31	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	Hexagonal (trigonal)
Sulfa	ates		
32	Barite	BaSO <sub>4</sub>	Orthorhombic
33	Dorallcharite*	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>	Hexagonal (trigonal)
34	Epsomite	MgSO <sub>4</sub> ·7H <sub>2</sub> O	Orthorhombic
35	Fibroferrite	FeSO <sub>4</sub> (OH)·5H <sub>2</sub> O	Trigonal
36	Gypsum	um CaSO <sub>4</sub> ·2H <sub>2</sub> O	
37	Melanterite	FeSO <sub>4</sub> ·7H <sub>2</sub> O	Monoclinic
38	Rozenite	FeSO4·4H2O	Monoclinic
39	Starkeyite	MgSO <sub>4</sub> ·4H <sub>2</sub> O	Monoclinic
Arse	nates		
40	Hörnesite	Mg <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	Monoclinic
41	Pharmacolite	CaHAsO <sub>4</sub> · 2H <sub>2</sub> O	Monoclinic
42	Picropharmacolite	Ca4Mg(AsO3OH)2(AsO4)2.11H2O	Triclinic
43	Unnamed new mineral*	Fe2Tl[(As0.85S0.15)O4]3.4H2O	
Molib	odates		

Allchar thallium minerals are marked in bold \* Thallium minerals present only at Allchar deposit

# MINERAL ASSAMBLAGE

# Elements

#### GOLD, Au

The presence of gold in the Sb-As-Tl association at Allchar was suggested by Stafilov, 1985; Ivanov, 1986, and Stafilov and Todorovski 1987. During the 1986–1989 period gold mineralization was systematically explored. Percival and Radtke (1990) and Percival et al. (1992) showed that the geological, geochemical, mineralogical and hydrothermal alteration features are similar to those, which characterize Carlin-type mineralization of the Western United States.

#### SULFUR, S

Sulfur forms a small bright yellow well developed crystals up to 1 mm. It is also found as earthy yellow masses. On the exposure to sunlight it is unstable and tends to become milky earthy.



Fig. 1. One of the crystal forms of sulfur

# Sulfides and sulfosalts

#### ARSENOPYRITE, FeAsS

Among marcasite and pyrite only a unique occurrence of arsenopyrite has been mentioned in the northern part of the As-rich deposit. H. von Foullon (1882) has reported this occurrence as small lustrous crystals embedded in massive orpiment.

#### BERNARDITE, TI(AsSb)<sub>5</sub>S<sub>8</sub>

Bernardite was found in only one of the numerous specimens that were collected by group of Czech mineralogists in 1975 and 1976. The name was given in honour of Jan Bernard, Czech mineralogist and metallogenist, who first recognized the new mineral and drew attention to it. Pasava et al. (1989) have published the work with detailed description of its physical, chemical and structural characteristics. It forms thick tabular crystals, which are usually smaller than 1 mm, the largest reported being 4 mm in size. The crystal faces are commonly corroded or striated and dull. The mineral is black with occasional dark red internal reflections and a red streak. No cleavage has been observed and fracture is subconchoidal to uneven. The mineral occurs in associations with orpiment and realgar. Its position in the general mineral sequence is unclear. Holotype specimens have been deposited in the Narodní Museum in Praha and in the Naturhistorisches Museum in Vienna.



Fig. 2. One of the crystal forms of bernardite

#### CINNABAR, HgS

Rick (1993) mentioned cinnabar as very rare mineral detectable only in polished sections as grains up to 150 micrometers. Some inclusions in realgar belong to cinnabar as well. Among the samples which were deposited in Croatian Natural History Museum in Zagreb there are single crystals of cinnabar up to 2 mm in size. These samples are the subject of recent study.



Fig. 3. One of the crystal forms of cinnabar

#### JANKOVICITE, Tl<sub>5</sub>Sb<sub>9</sub>(AsSb)<sub>4</sub>S<sub>22</sub>

A new sulfosalt mineral from the Allchar deposit has been described by Libowitzky et al. (1994). The crystal structure determination has confirmed that the As sites are partially substituted by Sb. The structure shows close similarities with those of rebulite. Named in recognition of Prof. S. Janković for his work on the mineralogy and geology of Allchar.

# LORANDITE, TIAsS<sub>2</sub>

Lorandite is world famous mineral described as the first thallium-bearing mineral. Since its first discovery in Allchar in 1884 (Krenher, 1894, 1895, 1897) its 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 more seldom. They show many different forms. Krenner (1895), Goldschmidt (1899) and Barić (1958) described up to 32 forms. Lorandite can easily be distinguished from realgar by its darker red color, its semimetallic luster 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 exceptionally single crystals up to 5 cm in size have been found. Lorandite is named after the Hungarian physician Lorand Eötvös (1848-1919).

Chemical composition of lorandite has been well established (Jannasch, 1904). The investigations in connection with the LOREX program have revealed some interesting features. The Allchar 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 cubic meters of ore with an average Tl content of 0.35 %. Microprobe analyses in the recent investigations show presence of Hg.



Fig. 4. Some of the crystal forms of lorandite

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# MARCASITE, FeS<sub>2</sub>

Marcasite appears as black botryoidal nodules. It is very dull, crumbly and (in the presence of moisture) altering to other minerals of iron sulfide type. It is often associated with realgar and stibnite containing rather high quantity of arsenic.



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#### ORPIMENT, As<sub>2</sub>S<sub>3</sub>

Palme at al. (1988) described orpiment as a stoichiometrically rather pure mineral, 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 luster faces are very rare. Orpiment usually forms fan-shaped aggregates or hemispheres, mainly having brownish yellow color and dull luster. The crystal size of a few mm is typical. The presence of lorandite near the realgar and orpiment zones is observed.



Fig. 7. Some of the crystal forms of orpiment



Fig. 8. Orpiment

# PARAPIERROTITE, Tl(Sb,As)<sub>5</sub>S<sub>8</sub>

Parapierrotite usually appears as single elongated crystals in cavities of massive realgar. The length of the crystals is usually about 3 mm, but exceptionally the size can reach up to 1 cm. (Johan et al., 1975). They are black with a semimetallic luster. The mineral is named on account of its relations with pierotite. Holotypes have been deposited in the mineralogical collection of École nationale supérieure des mines de Paris.



Fig. 9. Some of the crystal forms of parapierrotite

## PARAREALGAR, AsS

Pararealgar occurs as a result of decomposition of realgar, which has been exposed, to sunlight. The mineral appears as very tiny yellow coloured crystals.

# PICOTPAULITE, TIFe2S3

In the lorandite bearing zone of the deposit, especially in the zone of pyrite and raguinite, picotpaulite was found as inclusions mainly up to 0.5 mm. It is bronze colored but in polished section under reflected light it appears creamy white with very strong anisotropic character. Often it is at least partly replaced pseudomorphically by raguinite. Picotpaulite is rhombic, but the crystals are usua': y pseudohexagonal because penetration twinning on it is common (Johann et al., 1970). It is named after the French mineralogist Paul Picot. Holotypes have been deposited in the mineralogical collection of École nationale supérieure des mines de Paris.



Fig. 10. One of the crystal forms of picotpaulite

# PYRITE, FeS2

The pyrite itself is very unattractive, It has been the first crystallized sulfide mineral in Allchar being of high importance for the formation of some of the rare iron bearing thallium sulfosalts. Pyrite is responsible (as in the other Carlin-type deposits) for the precipitation of gold. It is mainly found as corroded grains and in the core of marcasite nodules.

#### RAGUINITE, TIFeS<sub>2</sub>

Raguinite has been named according to the French scholar Eugène Raguin (Laurent et al.,

1969). In the Laurent's paper raguinite has been described as pseudomorphs after an unknown species later described and named picotpaulite. Like picotpaulite it is found in the central zone of thallium ore body, associated with orpiment, realgar and lorandite. Raguinite crystals are elongated in the form of fibers. Such bundle of fibers has brilliant bronze color. Usually it is intimately intergrown with pyrite. In reflected light is a gray white to pinkish white. Mineral shows very strong polarization colors with a dominant orange color. Only small quantities of this mineral have been recovered to date. Holotypes have been deposited in the mineralogical collection of École nationale supérieure des mines de Paris.



Fig. 11. Some of the crystal forms of pyrite

# REALGAR, As<sub>4</sub>S<sub>4</sub>

Realgar was mentioned in the papers of Foullon (1892 and 1904) where its physical and chemical characteristics are described. It occurs as crystals of up to 2 cm in size. The crystals are elongated red coloured prisms which (exposed to light) decompose and transform to yellow pararealgar. It is worth mentioning that realgar is the host for mineral lorandite. Liquid inclusions can be found in some crystals (Beran et al., 1994).



Fig. 12a. Crystal forms of realgar







Fig. 13. Realgar with lorandite

# REBULITE, TI<sub>5</sub>Sb<sub>5</sub>As<sub>8</sub>S<sub>22</sub>

This mineral is named in honor of well known geologist Boris Rebula from Macedonia who has hardly worked on Allchar mineral characterization. The crystals of rebulite are dark gray with a metallic luster and a brownish red streak. They exhibit the dominant forms {100}, {001} and {111}. The faces of the zone [010] are striated. Well developed crystals up to 2 mm in size are described. Rebulite is associated with realgar and simonite. The identity of the studied by Balić Žunić et al. (1982) samples of rebulite was established by means of EDX analysis, and powder patterns were calculated according to the crystal structure. Allchar is the type locality for this mineral.



Fig. 14. Some of the crystal forms of rebulite

# SIMONITE, TIHgAs<sub>3</sub>S<sub>6</sub>

Engel et al. (1982) published the results of the crystal structure determination of a new sulfosalt mineral named simonite. The small orange-red crystals of simonite were found only as inclusions in rebulite. They have irregular shape with dimensions 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.

#### STIBNITE, Sb<sub>2</sub>S<sub>3</sub>

Stibnite was mined especially at the turn of 19<sup>th</sup> to 20<sup>th</sup> century. The entire production of manually upgraded ore (with an antimony content of 60 %; the Sb content of pure stibnite is 71.68 %) was sold to England to use in the hardening of lead and tin alloys. Stibnite occurs as groups of well-developed crystals in cavities of massive stibnite. Crystals of stibnite are elongated prizmatic with high luster. They reach a length up to 10 cm. The most attractive specimens of stibnite are often accompanied by sprinkled small realgar crystals on it.

# VRBAITE, Tl<sub>4</sub>Hg<sub>3</sub>As<sub>8</sub>Sb<sub>2</sub>S<sub>20</sub>

Vrbaite is a very rare sulfosalt which was noticed for the first time in 1903 by Wilhem Maucher (Ježek, 1912). He identified in small cavities in realgar existence of a new, as yet undescribed mineral and he analyzed major constituents of these samples: thallium, arsenic, antimony and sulfur. Later Ježek (1912, 1913a) described it as a new mineral and named it in honor of his teacher Karl Vrba (1845–1922).

Vrbaite occurs as dark gray minute crystals with a bluish sheen and semimetallic luster. Usually they are tabular or flat bipyramidal having a pale yellowish streak. In thinnest sections vrbaite is dark red translucent. Its good cleavage on {010} is usually observable and can be used for identification. Previously the chemical formula TlAs<sub>2</sub>SbS<sub>5</sub> or Tl(As, Sb)<sub>3</sub>S<sub>5</sub> has been proposed based on the results of the chemical analysis (Tl 29.52, Fe 1.85, Sb 18.34, As 24.06, and S 25.20 %) (Křehlík, 1912, 1913). More than 50 years later this composition was found to be incomplete. The results of microprobe work (Caye et al., 1967; Nowacki, 1968) have shown that Hg is major constituent of the composition leading to the now commonly accepted chemical formula: Tl4Hg3As8Sb2S20. Allchar is the type locality for this mineral. The crystal structure of this mineral was solved by Ohmasa and Nowacki, 1971.



Fig. 15. Some of the crystal forms of stibnite



Fig. 16. Stibnite



Fig. 17. Vrbaite

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Fig. 18. Crystal forms of vrbaite

## WEISSBERGITE, TISbS<sub>2</sub>

Rieck (1993) has reported for the first time weissbergite from Allchar, which is now the second known location for this mineral. Weissbergite was first described from the Carlin mine by Dickson and Radke in 1978. Rieck has identified weissbergite on a single specimen of realgar, in the form of elongated prismatic crystals with a maximum size of 0.5 mm. It is steel gray, and has a metallic luster, with deeply striated faces. Its well developed cleavage in four different directions helps to distinguish it from the other thallium sulphosalts.

#### FANGITE, Tl3AsS4

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This new mineral form rims around lorandite (El Goresy and Pavićević, 1988) and has so far only been identified using reflected light microscopy and microprobe analysis. Frantz et al. (1994) confirmed its chemical composition. Later Wilson et al. (1993) found the mineral with the same chemical composition in Mercur gold deposit in Utah, USA, giving a name fangite.

# Oxides

# ARSENOLITE (or CLAUDETITE), As2O3

Frantz et al. (1994) identified a mineral with the chemical composition  $As_2O_3$ . It has been described as a small vein between realgar grains. It is still unknown which of the two minerals (arsenolite or claudetite) with this composition ( $As_2O_3$ ) is present. The presence of both mineral forms is not excluded. Due to the small quantities that have been found this question is still open.

#### CERVANTITE, Sb<sub>2</sub>O<sub>4</sub>

Many authors have reported that yellow glassy coating appearance on stibuite crystals. These coatings have always been called "antimony ochre". Stieglitz (1990) has revealed that their major component in most cases is cervantite  $Sb^{3+}Sb^{5+}O_4$ , with a small subordinate amounts of roméite (Ca,Fe,Mn,Na)<sub>2</sub>(Sb,Ti)<sub>2</sub>O<sub>6</sub>(O,OH,F) and stibiconite  $Sb_3O_6(OH)$ .

#### GOETHITE, FeO(OH)

In the past these ubiquitous minerals from Allchar deposit have been considered to be a new mineral being consequently described as "allcharite" (Ježek, 1913; Cech and Johann, 1967). It appears like a dark brown to earthy masses and minute crystals. Pseudomorphs after pyrite crystals consist almost entirely of goethite.

## QUARTZ, $\alpha$ -SiO<sub>2</sub>

The well developed clear to milky crystals of quartz are found in the central zone associated with stibnite and realgar. Such up to 2.5 cm in size druzas are found sporadically. The crystal size usually does not exceed 2 mm. In most parts of the deposit quartz is also found in the form of chalcedony and jasper.



Fig. 19. Some of the crystal forms of quartz

# ROMÉITE, (Ca,Fe,Mn,Na)2(Sb,Ti)2O6(O,OH,F)

Roméite is an alteration product of stibnite. It forms glassy coatings on stibnite, which consist predominantly of cervantite Sb<sup>3+</sup>Sb<sup>5+</sup>O<sub>4</sub> as well as yellow powdery coatings.

#### STIBICONITE, Sb<sub>3</sub>O<sub>6</sub>(OH)

Stibiconite is found as earthly yellow to brown coatings and powdery masses in vugs within massive stibuite. In rare cases stibiconite forms pseudomorphs after stibuite.

#### VALENTINITE, Sb2O3

Foullon predicted the occurrence of this antimony oxide mineral and later (Foullon, 1890) proved its existence on material he received from a mine engineer. No further description of Allchar valentinite has been given by any other author.

# Carbonates

## ARAGONITE, CaCO3

Aragonite has been reported in Allchar's mineral paragenesis usually as white crusts consisting of fibrous tiny crystals. They are visually interesting when occurring in association with stibnite and realgar.



Fig. 20. One of the crystal forms of aragonite

# CALCITE, CaCO3

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.



Fig. 21. Calcite

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Fig. 22. Some of the crystal forms of calcite

# DOLOMITE, CaMg(CO<sub>3</sub>)<sub>2</sub>

The major host rock of the deposit is massive dolomite. Crystals have been found in cavities of the massive dolomite. They are usually brownist colored by iron-bearing weathering. Mostly the are small and do not exceed 1 mm in size. Dolo mite is partly or wholly replaced by silica by late hydrothermal processes.



Fig. 23. One of the crystal forms of dolomite

# Sulfates

#### BARITE, BaSO<sub>4</sub>

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Barite has been mentioned by Barić (1958) and Stieglitz (1990). In both papers it is pointed out that this mineral appears as platy, colorless clear to milky colored crystals to a maximum size of 6 mm. Although it has not been discussed in their papers, it is interesting to mention that the quantity of barium in this mineral is far a way from the value that is expected in Carlin-type ore deposits.

#### DORALLCHARITE, 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>

Dorallcharite is found in the oxidation zone of the ore body (Balić Žunić et al., 1993b, 1994). It appears as yellow earthy masses of submicroscopic crystals. This mineral is a member of the alunitejarosite family being isomorphous with jarosite  $KFe_3(SO_4)_2(OH)_6$ . 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.

#### EPSOMITE, MgSO<sub>4</sub>·7H<sub>2</sub>O

Epsomite appears in the form of the white fibrous aggregates. Stalactite forms of this mineral are also present inside of the ore deposit (Bermanec, 1999)."

#### FIBROFERITE, FeSO<sub>4</sub>(OH)·5H<sub>2</sub>O

Rieck (1993) has for the first time reported the presence of this mineral in Allchar paragenesis. He described fibroferrite as hemispheres of yellow fibers. It is associated with hörnesite (Mg<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O), rozenite (FeSO<sub>4</sub>·4H<sub>2</sub>O) and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) on altered host rock in the vicinity of realgar veins.

## GYPSUM, CaSO4·2H2O

Gypsum is spread on all types of ore and host rock. Single crystals are rather small with typical flat habit on {010}. In large quantity it appears as an efflorescence on wall rock and even on timbering. Stalactitic masses sometimes exceed 25 cm.



Fig. 24. One of the crystal forms of barite



Fig. 25. Epsomite with melanterite



Fig. 26. One of the crystal forms of gypsum



Fig. 27. Gypsum

#### MELANTERITE, FeSO4.7H2O

Melanterite is a typical post mining product, like rozenite. Highly altered parts of the host rock are traversing with melanterite. This mineral was found in Allchar for the first time by Barić (1958) who described green crusts and stalactitic aggregates without observing the crystals. In 1993, Zebec at al. (1993) published the result of measurement of three melanterites crystals. They are greenish – blue transparent crystals from 2 to 3 mm in size. In atmospheric conditions melanterite decomposes in rozenite (FeSO<sub>4</sub>·4H<sub>2</sub>O) by loosing three molecules of water.



Fig. 28. One of the crystal forms of melanterite

# ROZENITE, FeSO<sub>4</sub>·4H<sub>2</sub>O

It is found as white crusts of prismatic crystals or stalactitic aggregates throughout the deposit on altered host rock and ore in association with melanterite, hörnesite, gypsum and fibroferrite. Rozenite is in fact product of the decomposition of melanterite, pyrite and marcasite.

#### STARKEYITE, MgSO<sub>4</sub>·4H<sub>2</sub>O

Rieck (1993) has for the first time identified starkeyite as fibrous aggregates partly filling the space between the realgar crystals. The crystals are white with a silky sheen.

# Arsenates

### HÖRNESITE, Mg<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O

The firs report concerning this mineral belongs to Rieck (1993). Its small crystals (up to 50  $\mu$ m) are prismatic and elongated. They are usually aggregated to crusts and stalactites. It is associated with other efflorescent minerals. It is sometimes intimately intergrown with gypsum. Its identification can be confirmed only by means of chemical or X-ray analysis.

#### PHARMACOLITE, CaHAsO<sub>4</sub>·2H<sub>2</sub>O

Rieck (1993) has for the first time reported the presence of pharmacolite in this deposit. He described it as radiating acicular coating on realgar, orpiment and host rock. Single crystals are rarely observed.

# 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

Rieck (1993) has identified picropharmacolite, which occurs as dense coatings with a maximum thickness of 0.5 mm along fracture surfaces. The crystal sizes up to 50  $\mu$ m are bladed and give the specimen a silky white or colorless sheen.

# UNNAMED NEW MINERAL<sup>\*</sup>, $Fe_2Tl((As_{0.85}S_{0.15})O_4)_3 \cdot 4H_2O$

This mineral is found near pyrite globules, which are altered and partly or completely replaced

<sup>\*</sup> Formally it is incorrect to use the term "new mineral" as long as the species has not been accepted by the IMA Commission on New Minerals and Mineral Names.

by this new mineral, suggesting that it was formed through the alteration of pyrite by thallium – bearing weathering solutions. The sizes of the grains encountered varied from 30  $\mu$ m to over 100  $\mu$ m. In the course of reflected light investigations Frantz et al. (1994) discovered a phase with a radial structure. Microprobe analysis yielded the tentative stoichiometric composition that is given above.

# Molibdates

#### WULFENITE, PbMoO<sub>4</sub>

Wulfenite is the first discovered (Šoufek et al., 1998) lead bearing mineral in the deposit. Several authors have investigated the Pb content in Allchar minerals. According to Stafilov and Todorovski (1990) and Boev at al. (1993b) it is often present within the range of 0.3 to 10 ppm in the main sulfides. Wulfenite crystals were observed on one sample built of microcrystalline quartz. Such quartz aggregates fill cavities in stibnite – realgar ore body. Orange-yellow crystals of wulfenite up to 8 mm in size together with well developed crystals of realgar have crystallized over such microcrystals of quartz. Wulfenite is obviously the very late mineral in this part of ore body. The lead present in the wulfenite is due to a previous decay of U and Th and not as a result of transformations of <sup>205</sup>Tl to <sup>205</sup>Pb caused by neutrino interaction with Tl.



Fig. 29. Some of the crystal forms of wulfenite

#### CONCLUSION

The studies carried out on this mineral assemblage indicate that the Allchar deposit is a real challenge for investigation in the field of mineralogy. The total number of to nowadays discribed 44 minerals species in this paper does not mean that these studies have discovered all mineral assemblages present in the deposit. It is certain that further studies will discover new minerals.

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#### Резиме

#### МИНЕРАЛИ ОД АЛШАР

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Клучни зборови: Алшар; Македонија; минерали

Во трудот се сумирани резултатите од истражувањата на минералите застапени во Tl-As-Sb-Au рудиото лежиште Алшар. Најдено е дека во основа постојат четири типа минерални групации:

 Првиот тип се карактеризира со висока содржина на железо и сулфур, но писка на арсен и талиум. Пиритно-марказитната група на минерали се карактеризира со присуство на извесно количество арсенски пирит.  Вториот тип се карактеризира со висока содржина на антимон, но ниска на железо и талиум. Стибнитот е најзастапениот минерал во оваа група.

 Третиот тип се карактеризира со висока содржина на арсен и сулфур, но релативно ниска содржина на талиум. Најзастапен минерал во оваа група е аурипигментот.

 Четвртиот тип на минерали има висока содржина на арсен, сулфур, железо и талиум. Овој тип на минерали е проследен и со значително присуство на манган и цинк.