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**FACULTY OF NATURAL AND  
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# NATURAL RESOURCES AND TECHNOLOGY

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## SECONDARY MINERALS IN THE ALLCHAR ORE DEPOSIT, N. MACEDONIA WITH PARTICULAR REFERENCE TO SEM VIEW

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### Abstract

A remarkably large association of secondary minerals appears in the Allchar deposit, which is presented in detail in this paper. This mineral association is represented by the following minerals: Arsenolite,  $\text{As}_2\text{O}_3$ , Valentinite,  $\text{Sb}_2\text{O}_3$ , Cervantite  $\text{Sb}_2\text{O}_4$ , Goethite  $\alpha\text{-FeO(OH)}$ , Stibiconite,  $\text{Sb}_3\text{O}_6(\text{OH})$ , Roméite,  $(\text{Ca,Fe}^{2+},\text{Mn,Na})_2(\text{Sb,Ti})_2\text{O}_6(\text{O,OH,F})$ , Gypsum  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ , Starkeyite,  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ , Rozenite,  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ , Epsomite  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ , Melanterite,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Jarosite  $\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$ , Dorallcharite,  $(\text{Ti,K})_2\text{Fe}^{3+}_6(\text{SO}_4)_4(\text{OH})_{12}$ , Fibroferrite,  $\text{FeSO}_4(\text{OH}) \cdot 5\text{H}_2\text{O}$ , Pharmacolite,  $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ , Picropharmacolite,  $\text{Ca}_4\text{Mg}(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2 \cdot 11\text{H}_2\text{O}$ , Hornesite,  $\text{Mg}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ .

The paper shows microscopic photographs as well as photographs taken with a SEM microscope.

**Key words:** *secondary minerals, Allchar, SEM photos.*

### INTRODUCTION

The *Allchar* deposit belongs to a group of complex, polychrono-polygenetic volcanogenic-hydrothermal Sb-As-Tl-Au deposits. It is created in a heterogeneous geological environment, in connection with the complex physical and chemical processes of leaching ore elements from primary sources with hydrothermal solutions and their subsequent precipitation. Mobilization, transport and deposition of ore mineralization, as well as supergene transformations of primary minerals, were conditioned, partly accompanied by intensive pre-, syn- and post-structural-tectonic shaping of the terrain. As a result of the mentioned processes, more morphostructural types of ore bodies, different textural-structural varieties of ore, and associations of minerals and elements were created in the deposit (Fig.1).

The basic controlling factors of the spatial localization of the ore bodies of the Allchar deposit are lithological and structural. Ore bodies are found in intensively tectonized and hydrothermally altered carbonate rocks of Triassic age (dolomites and marbles), in the zones of their contact with igneous rocks of Tertiary age and accompanying volcanogenic-sedimentary formations (tuffaceous dolomites). The dominant facies of hydrothermal alterations are silicification and argillization, and decalcification and dolomitization are common [1, 2]. The hydrothermal alteration that took place in the final stages of volcanic activity of the Plio-Pleistocene age (andesites and younger latite intrusions) can tentatively be marked as the period of the beginning of the deposition of ore minerals in this area [3, 4, 5].

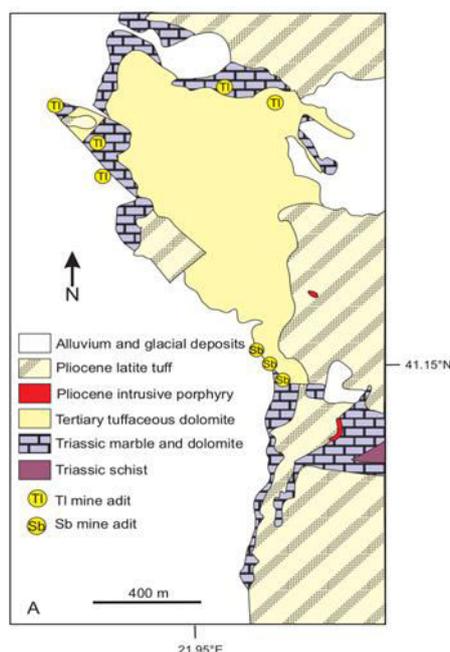


Figure 1. Geological map of Allchar deposit (Boev, 1997, modified by Palinkas S, 2018)

The time of formation of ore mineralization has not been fully studied. It is assumed to be related to the final phase of volcanic activity (the period of solidification of subvolcanic intrusions of calc-alkaline magma and extrusions of pyroclastic material), but before the overlying tuffites and lacustrine sediments. Judging by the results of the investigations carried out to date, the younger phase of volcanic activity took place in several subphases in the period from ~6.5 to ~1.8 Ma [6, 7]. Andesites and tuffs from the Crven Dol area were formed in the period 6.5 to 3.9 Ma, and tuffs from the Vitačevo and Rudina localities in the period  $5.1 \pm 0.1$  to  $4.31 \pm 0.2$  Ma. According to [2], the biotite ages of  $5.0 \pm 0.1$  and  $5.1 \pm 0.1$  Ma from blocks of the Vitačevo tuff are geologically significant and interpreted to date the age of initial Pliocene volcanism in the Allchar region. The latites from the Kojčov Rid locality were formed in the period  $4.8 \pm 0.2$  to  $3.3$  Ma. Experiments with amphibole from a subvolcanic latite body result in disturbed  $^{40}\text{Ar}/^{39}\text{Ar}$  release patterns and an age of  $4.8 \pm 0.2$  Ma. Biotite yield slightly varying ages ranging between  $4.6 \pm 0.2$  and  $4.8 \pm 0.2$  Ma. K-feldspar disturbed, staircase patterns with ages increasing from  $3.3 \pm 0.2$  to  $4.0$  Ma. The mineral ages of the subvolcanic latite body are interpreted, therefore, to monitor rapid cooling from ca.  $550\text{-}500^\circ\text{C}$  /amphibole/ through ca.  $300^\circ\text{C}$  /biotite/ to ca.  $250$  to  $160^\circ\text{C}$  /K-feldspar/ between  $4.8 \pm 0.2$  and  $3.3 \pm 0.2$  Ma.). Judging by the tests of the age of K-feldspar from the Rudina locality, the beginning of intense alteration of the surrounding mining rocks, and we assume the initial deposition of ore minerals, is related to the period  $4.31 \pm 0.02$  Ma.

The heterogeneous geological structure of the Allchar deposit terrain, the presence of various products of volcanic activity and complex, multiphase hydrothermal fluids, caused the zonal lateral and vertical distribution of basic (Sb, As, Tl and Au) and supporting elements of the ore association (Hg, Ba, Pb, Zn and Cu). In the northern part of the deposit, the predominant type of ore mineralization is As-Tl interspersed with Sb, locally Hg and Au. In the central part of the deposit, Sb and Au predominate, while As, Tl, less Ba, Hg and traces of Pb are found in variable concentrations. In the southern part of the deposit, gold mineralization prevails followed by Sb [1, 3, 8, 9, 10, 11].

The number of morphostructural types of ore bodies, together with the vertical and lateral zonation of the distribution of ore elements in the deposit (southern, central and northern parts of the deposit), indicate the complexity of the metallogenetic development of the wider area of the analyzed area. Its basic characteristics are the existence of a complex volcanic apparatus in the domain of the mineralization system of Pliocene age and pulsating hydrothermal activity of various physical and chemical characteristics in spatially separated parts of the hydrothermal system. Although the process of formation of ore mineralization is complex, it is generally possible to distinguish two mutually complementary genetic systems: (1) the system of the Central and Southern parts of the Allchar deposit and (2) the system of the Northern part of the *Allchar* deposit. The mentioned systems differ from each

other in terms of the environment of spatial localization, the prevailing controlling factors of the spatial position of the ore bodies, and the conditions of formation, while in the case of the primary sources of ore elements, sulfur, the origin of hydrothermal fluids, etc., have a number of similarities.

Primary sources of sulfur and useful components: The results of previous studies of sulfur isotopes ( $\delta^{34}\text{S}$ ) in antimonite, realgar, auripigment and marcasite from the Sb-ore of the Allchar deposit, which are located in areas of intense silicification and jasperoid, indicate enrichment with light isotopes.  $\delta^{34}\text{S}$  in antimonite varies from +0.35‰ to -5.6‰, in realgar -0.18‰ to -3.77‰, in marcasite from -0.67‰ to -6.84‰, while in auripigment it is -3.69‰. The obtained values suggest that the sulfur is predominantly of volcanic origin, but also that a part of it originates from the surrounding rocks of ore mineralization [17, 29].

The basic ore elements (Sb, As, Tl) come from the continental crust. Their primary source is calc-alkaline magma of Pliocene age, i.e., volcanics from which they were mobilized by hydrothermal solutions during their solidification [12]. A smaller part of ore elements originates from the surrounding rocks of the mine. According to the same author, lead isotopes also indicate origin from volcanic parent rocks.

*Origin and composition of hydrothermal solutions, mobilization of ore elements:* Hydrothermal ore-bearing solutions, from which the ore mineralization of the Allchar deposit was deposited, represented a mixture of waters of different origins. In addition to magmatogenic, meteoric waters played a significant role in their composition [16, 14]. The confirmation of the above is represented by the results of the study of oxygen and carbon isotopes in calcite from the Allchar deposit. In the analyzed calcites, partial enrichment with heavy C and O isotopes was determined ( $\delta^{13}\text{C}$  varies from +2.03‰ to +3.93‰, average +2.92‰, while  $\delta^{18}\text{O}$  ranges from +14.92‰ to 28.72‰).

Hydrothermal solutions in the initial stages of activity, during lateral-secretion leaching of ore elements from primary sources, were acidic in nature, with high sulfur fugacity. The former is evidenced both by the presence of native sulfur in the deposit and by pronounced solfatar activity. Microthermometric tests of fluid inclusions in realgar crystals indicated a temperature of homogenization of primary inclusions of 144-177°C. The salinity of the solution was 7.9-12.9 wt% NaCl, and the pressure in the fluids was about 1500 atm. [4]. Bearing in mind the complex mineral composition of the ore bodies, the observed paragenetic relationships of the ore minerals and their accompanying minerals, as well as the structural and textural characteristics of the ore, it can be assumed that the temperature of the hydrothermal solutions ranged from 280-250°C to 120°C. The thermal energy for movement was taken over by the ore-bearing fluids from the surrounding volcanics. The transfer of ore elements was carried out in the form of complex ions in acidic to weakly alkaline systems with low salinity, in an oxidizing environment.

*Environments and conditions for the transfer of ore elements:* The transfer of ore components (Sb, As, Tl, Au) to the place of crushing was made possible by the tectonic predisposition of the environment, i.e., the presence of numerous fissure-crack and fault systems, contact zones of vulcanites and surrounding rocks, as well as planes layers in the surrounding rocks. The transfer of ore components was carried out with solutions of low salinity, most likely in the form of complex ions (bisulphide complexes), partly also in the form of colloids, under weakly reducing conditions.

*Deposition of ore elements:* The most significant part of ore mineralization in the central and southern part of the Allchar deposit was deposited due to the cooling of hydrothermal solutions, then as a result of complex fluid-surrounding rock reactions, and due to secondary boiling. The extraction of ore minerals from the solution took place successively. In the first phase, pyrite with marcasite was deposited, in the second, arsenopyrite, antimonite and Sb-Pb sulfosalts were deposited, and in the final phase of activity from ore-bearing systems, realgar, auripigment and, finally, Tl-sulfosalts were deposited.

The temperature range for the formation of most ore minerals was 120-200°C. In local conditions, however, the temperature was even higher. Based on data on the presence of marcasite in Sb-ores from jasperoid zones and intense silicification, it is assumed that the gold mineralization with accompanying mineral association was deposited at a temperature of ~200°C.

Most ore minerals were mined at depths of up to 500 m from the paleosurface of the terrain. In the conditions of a reactive environment (dolomites, dolomite-volcanite contact), the vertical interval of mineralization was short, while in the conditions of a weakly reactive environment (silicified dolomites, tuffaceous dolomites, felsitic tuffs, argillization zones) it was up to 150-200 m. In the

northern part of the deposit (Crven dol), ore mineralization was deposited at shallower depths, in conditions of highly oxidizing environment and high fugacity of As and Tl. Other processes of depositing ore minerals (fluid mixing, etc.), although possible, were not of greater importance in the process of creating ore mineralization.

The deposition of ore minerals in the northern part of the deposit, which is the most fully studied, is the result of changes in the physical and chemical characteristics of hydrothermal fluids due to their interaction with carbonate rocks (mainly dolomites) and metasomatism. The deposition of ore minerals was preceded by the process of ankeritization of dolomite and argillization of silicified rocks (400°C, low pH values). It was followed by the extraction of a fine-grained massive mixture of siderite, pyrite and marcasite with a little Tl. In the next phase, which took place under oxidizing conditions, pyrite was extracted with low arsenic content, and then deposited a small amount of auripigment and realgar with a little antimony at a temperature of around 180 °C [15]. In the next phase, thallium minerals were deposited. After the deposition of the main phase of mineralization, a supergene transformation of the primary ore mineralization took place and the formation of numerous supergene minerals.

## **MATERIALS AND METHODS**

### **The Alshar's secondary minerals present**

The secondary minerals within the Alshar deposit are mostly sheltered in the northern part, the part of Crven Dol.

In the northern part of the deposit, which also encompasses the Crven Dol site, the predominant mineralization is that of As-Tl-Fe-S, rarely of Sb with traces of Au and Hg. It consists of:

- (1) Morphologically complex, massive realgar orebodies, localized in dolomites in the zone of contact with subvolcanic intrusions, as well as in brecciation zones;
- (2) Stratiform, band-type and vein-like orebodies of orpiment in tuffs and tuffaceous dolomites, localized in the lower levels of massive realgar orebodies;
- (3) Morphologically complex, impregnation-type Tl-As mineralization in carbonaceous rocks, mostly dolomites, and
- (4) Morphologically complex ore mineralization with supergene (secondary) arsenic minerals.

### **Applied methodology**

The coated samples were imaged on a Quanta 650F SEM, equipped with a backscattered electron beam detector (BSED) and a Bruker 5030 X-ray detector. The Esprit Quantax 1.9 EDS analysis system was used to determine the elemental composition of a particular substance. Point Analysis was used to characterize the samples under high vacuum, using an accelerating voltage of 15 kV and size 6. BSE images of selected fields were taken for SEM-based characterization.

## **SECONDARY MINERALS ASSOCIATION**

### **Arsenolite, As<sub>2</sub>O<sub>3</sub>**

The chemical composition of this mineral at the *Allchar* locality was determined in 1994 [12]. 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<sub>2</sub>O<sub>3</sub>) 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. (Fig.2)

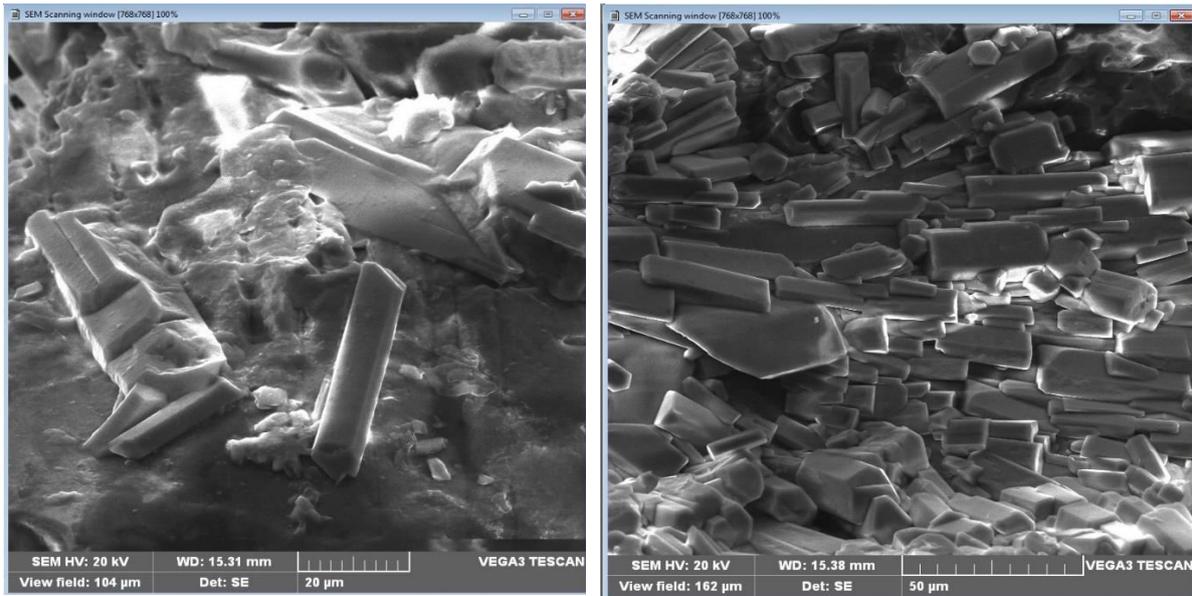


Figure 2. Arsenolite from Allchar under the SEM

### Valentinite, $\text{Sb}_2\text{O}_3$

The occurrence of this antimony oxide mineral was predicted in 1890 [16] and found in 1892 [17] after studying the material given by a mine engineer. No further description of *Allchar* valentinite has been given by any other author [18].

### Cervantite, $\text{Sb}_2\text{O}_4$

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,  $\text{Sb}^{3+}\text{Sb}^{5+}\text{O}_4$ , with small subordinate amounts of roméite  $(\text{Ca,Fe,Mn,Na})_2(\text{Sb,Ti})_2\text{O}_6(\text{O,OH,F})$  and stibiconite  $\text{Sb}_3\text{O}_6(\text{OH})$  [24]. (Fig.3)

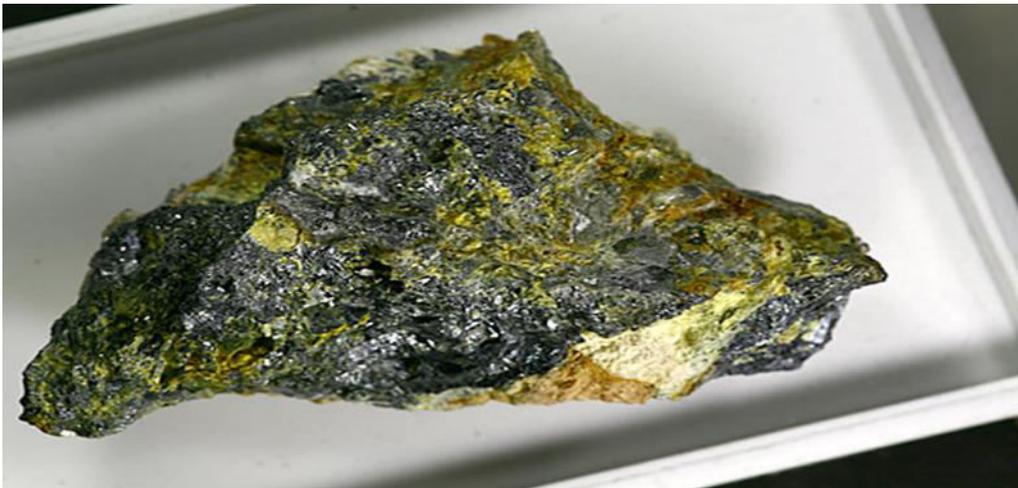


Figure 3. Cervantite from Allchar

### Goethite $\alpha\text{-FeO}(\text{OH})$

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 a new mineral being consequently described as “allcharite” [19, 20]. Pseudomorphs after pyrite crystals consist almost entirely of this mineral. (Fig.4).



Figure 4. Goethite from Allchar

**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 [21].

**Roméite,  $(\text{Ca}, \text{Fe}^{2+}, \text{Mn}, \text{Na})_2(\text{Sb}, \text{Ti})_2\text{O}_6(\text{O}, \text{OH}, \text{F})$**

Roméite forms glassy coatings on stibnite, which consist predominantly of cervantite  $\text{Sb}^{3+}\text{Sb}^{5+}\text{O}_4$  and yellow powdery coatings [21]. This mineral appears as an alteration product of stibnite.

**Gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$**

Nice gypsum crystals are found in the Allchar site, predominantly in its northern portion. Very nice 1m thick gypsum crystals of variable sizes (white to transparent) develop because of the large amount of sulfides in dolomites after rainfall. Gypsum at the *Allchar* 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 [18].



Figure 5. Gypsum from Allchar

**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 [18]. The crystals have white color with a silky sheen.

**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) [22]. Rozenite is the product of the decomposition of melanterite, pyrite and marcasite.

**Epsomite  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$** 

Beautiful present day epsomite crystals in the form of the white fibrous aggregates can be seen in the *Allchar* deposit [23]. 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.

**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 [24, 22]. 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 [22].

**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

**Dorallcharite,  $(\text{Tl},\text{K})_2\text{Fe}^{3+}_6(\text{SO}_4)_4(\text{OH})_{12}$** 

Dorallcharite appears as yellow earthy masses of submicroscopic crystals being found in the oxidation zone of the ore body [15, 25]. 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.



Figure 6. Dorallcharite from Allchar

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

This mineral in *Allchar* paragenesis has been described as hemispheres of yellow fibers [18]. It is associated with hornesite, rozenite and gypsum on altered host rock in the vicinity of realgar veins.

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

The presence of pharmacolite in this deposit was first reported in 1993 [18]. The mineral was described as radiating an acicular coating on realgar, orpiment and host rock. Single crystals are rarely observed.

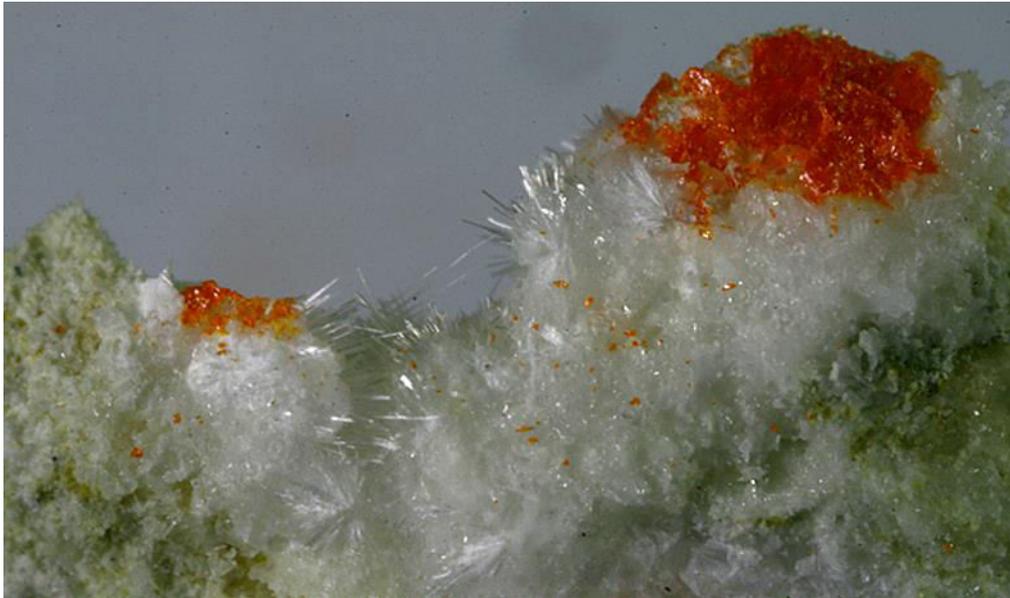


Figure 7. Pharmacolite from Allchar

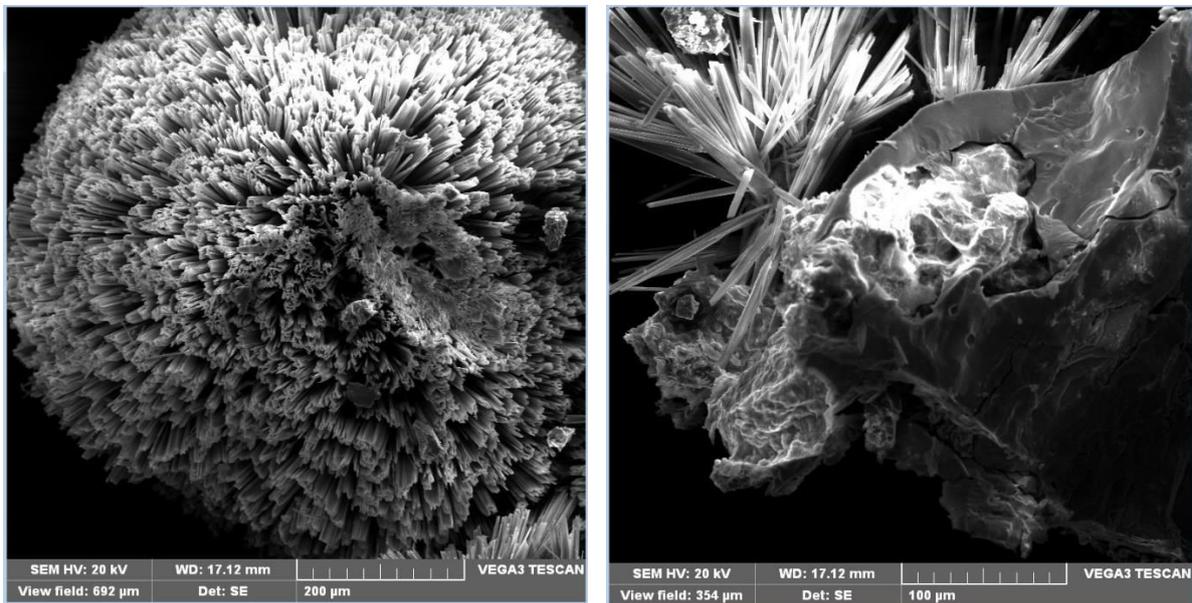


Figure 8. Pharmacolite from Allchar under the SEM

### **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 [18]. Crystal sizes up to 50 µm are bladed and give the specimen a silky white or colourless sheen. Occasionally, it appears in association of realgar and vrbaita.

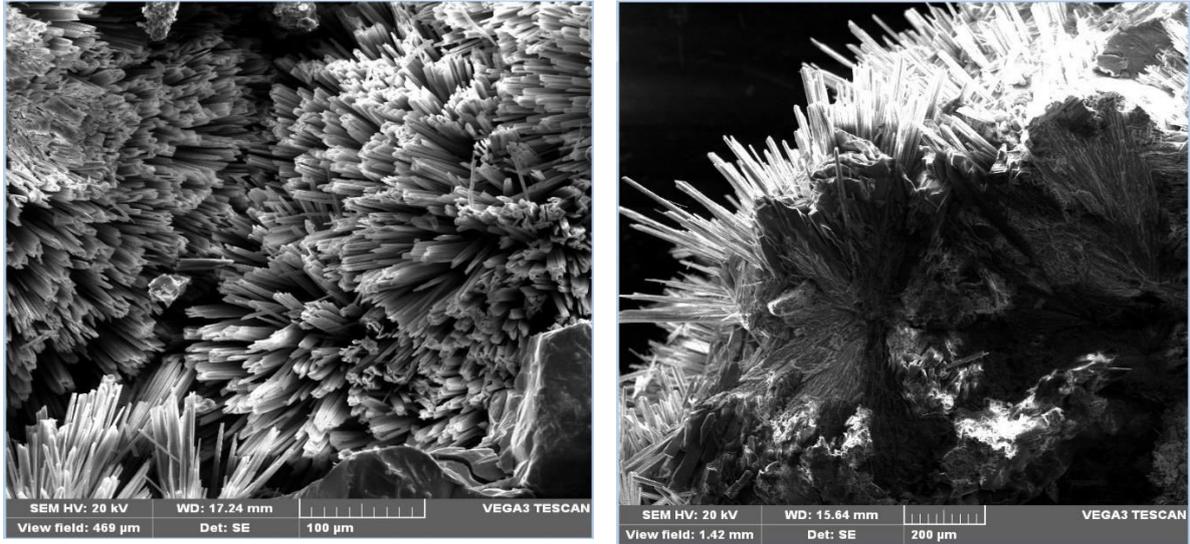


Figure 9. Picroparmacolite from Allchar under the SEM

### Hornesite, $Mg_3(AsO_4)_2 \cdot 8H_2O$

The crystals of hornesite are prismatic and elongated [18]. They are usually aggregated to crusts and stalactites being associated with other efflorescent minerals. It is sometimes intimately intergrown with gypsum.



Figure 10. Hornesite from Allchar

### CONCLUSION

In the Alshar deposit, especially in the northern parts, the Crven Dol area, numerous secondary minerals of arsenic and thallium appear.

The 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 (markasite 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 Allchar deposit, involving the following processes and products:

(1) Oxidation of iron and to some extent antimony, arsenic sulphides, and 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., sulphides into scorodite, arsenolithe 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.

(2) 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, local concentrations of residual sulphides.

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

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