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MINERALOGICAL AND CHEMICAL CHARACTERISATION ON STIBNITE FROM ALLCHAR LOCALITY, NORTH MACEDONIA

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Abstract

Crystalline stibnite occurrences in the Republic of Macedonia in several antimony deposits such as Allchar, Lojane and Krstov dol. The best stibnite crystals can be found in the central parts of the Allchar mine. Crystals of stibnite are thick to thin elongated prisms with vertical striations, lead gray color and high metallic lusters. Stibnite also occurs in columnar, granular, blended and compact habits. Cleavage is perfect on {010} and imperfect on {100},{110}. The density determined by pycnometer is 4.62 g/cm^3. Hardness is 2. The concentration of the oxides is: Sb:70,912-71,155%, S:27,166-28,166%. The following trace elements were also detected: As, Tl, V, Se, Ba, Ag, Cr, W, P. The unit cell parameters obtained using the main reflection lines of X-ray diffraction are: a = 11.24 Å, b = 3.84 Å, c = 11.34 Å, V = 490.43 Å^3, Z: 4.

Key words: *stibnite, Allchar, SEM-EDS, ICP-MS, XRD*

INTRODUCTION

Stibnite, described in 1832, is antimony sulfide, Its name comes from "stibium," the Latin word for antimony an element whose long history of medicinal uses can be traced back 3000 years. It is found in association with minerals such as realgar, orpiment, cinnabar, galena, pyrite, arsenopyrite, calcite, and quartz [1].The Allchar deposit is situated at the northwestern margins of Kožuf Mts, close to the border between Republic of North Macedonia and Greece. From the metallogenic point of view, the Allchar deposit belongs to the Kožuf ore district as part of the Serbo Macedonian metallogenic province. From the geotectonic point of view, ore mineralization is related to a Pliocene volcano-intrusive complex located between the rigid Pelagonian block in the west, and the labile Vardar zone in the east [2,3]. The district has been intensively mined for its antimony, arsenic and thallium resources beginning in about 1860. The Allchar deposit is of hydrothermal low temperature origin, genetically associated with the Pliocene subvolcanic dacite andcsitic intrusive. The age of the volcanic activity is about 7 to 5 million years [4]. Hydrothermal ore fluids containing large amounts of silica, antimony, iron, arsenic, thallium, barium, sulphur, mercury, and gold from silificied replacements, hypogene argillic stratigraphic horizons and disseminated replacements in both Mesozoic and Tertiary rocks are found. The dominant lithological members comprising the Kožuf ore district are the following: a complex of metamorphic rocks of Pre-Cambrian and Paleozoic age; the sediment rocks of the Triassic, Jurassic and Upper Cretaceous; a complex of sediments of upper Eocene age; the sediments and pyroclastic rocks of Pliocene age; the Quarternary sediments; as well as the magmatic rocks of various composition and age (metamorphozed rhyolites and pyroclastic rocks; serpentinized ultrabasic rocks; basic magmatic rocks; and the complex of volcanic rocks) [4,5]. A characteristic feature of ore mineralization in the region of the Allchar deposit is the presence of zones in the spatial distribution of chief ore components (Sb, As, Tl, Au) and the accompanying associations of elements. In the northern part of the deposit (Crven Dol), there is a prevalence of As-Tl mineralization accompanied with Sb, locally and traces of Hg and Au. In the central part of the deposit, the basic ore components are Sb and Au, accompanied with As, Tl, minor Ba, Hg and traces of Pb (the central part); whereas the southern part of the deposit is characterized with mineralization of gold accompanied with varying concentrations of Sb and As [6,7].

ANALYTICAL METHODS

For reliable characterization of the mineral species in our research following analytical methods were used:

SEM-EDS- Scanning electron microscopy VEGA3LMU, increasing 2 × 1000000, W-wire, voltage up 200 V to 20 kV, infrared camera, maximum sample size 81 mm height, 30 mm width. The standards used are as follows: O: SiO_2; Na: albite; Mg: MgO; Al: Al_2O_3; Si: SiO_2; P: GaP; Ca: wollastonite; Ti: Ti; Fe: Fe; Br: KBr. Results of SEM/EDS analyses of mineral phases demonstrated usefulness of this method for identification and characterization of mineral phases whose size is often below the resolution of an optical microscope.

ICP-MS. Chemical composition also is determinated with ICP-MS. This method provides a rapid and precise means of monitoring up to 50 elements simultaneously for minor- and trace-levels. The ICP-MS technique is widely recomended as versatile analytical method for multi element analyses. The sample solution is introduced into the system and is jonized through an introductory nebulizer. The plasma (ionized argon) produces temperatures close to 7.000°C, which thermally excites the outershell electrons of the elements in the sample.

XRD analyses were carried by conventional X-ray diffraction (XRD) techniques on bulk samples For the present analysis, X-ray diffraction system (Shimadzu) diffractometer, series XRD-6100, with Cu (1.54060 Å) radiation operating at 40 kV and 30 mA. The powdered sample was scanned over the 5– 80° range with step size of 0.02° and scanning speed of 1.2°/min. The analyzed material than is finely ground, homogenized, and average bulk composition is determined. The most intense registered maxima in the studied powder diagrams were compared with the corresponding diagrams from PDF-2 software. Unit Cell software [8] was used for calculation of unit cell data.

RESULTS AND DISCUSSION

For the study, four stibnite samples have been selected. Stibnite occur as ring radial aggregates with well developed elongated lead gray prismatic crystals. Macroscopic features on stibnite from Allchar locality are given in fig.1. During crystal growth, stibnite's planes of perfect, one-directional cleavage functions as "gliding" planes that account for its lengthwise striations and the slight curvature of its prisms. Because of physical and thermal stresses incurred during the growth process, this plane frequently displaces, or "glides", causing subsequent crystal growth to proceed along new axes. Repeated displacement creates new crystal-face edges that appear as stibnite's diagnostic, pronounced longitudinal striations.

Displacement also generates lattice stresses that cause stibnite prisms to curve, an effect that is most noticeable in longer prisms.

Stibnite's metallic luster is due to the weak metallic bonding between its molecular layers and the inability of its sulphur ions to completely shield its antimony ions. Metallic bonding creates a pool of free-moving electrons. The manner in which light interacts with these free electrons produces stibnite's metallic luster. Like all minerals with a metallic luster, stibnite is opaque, meaning that it reflects, but does not transmit, light. Weak metallic bonding explains both stibnite's softness (Mohs 2) and low melting point of 1015°F (546°C)—low enough to fuse in a candle flame.

As an idiochromatic, or self-colored, mineral, stibnite's silvery-gray color is caused by its essential elemental components and the nature of its crystal structure. Incident light striking the surface electrons is absorbed more or less equally across the visible spectrum. Light energizes these surface electrons, which return to their normal levels by releasing excess energy in wavelengths that we perceive as a neutral silvery-gray, with a subtle, but attractive, hint of blue.

This basic silvery-gray color is usually modified by tarnish and iridescence. Tarnish forms when microscopic particles of elemental antimony separate from the crystal lattice to create a thin film on the stibnite surface. Because of their disassociation from the pool of free-moving electrons, the metallic-bonding strength among these particles is decreased, and they reflect less light. Subsequently, the metallic luster is replaced by a dull, dark tarnish.

(sample 1)

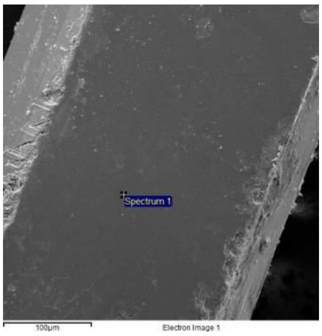
(sample 2)

(sample 3)

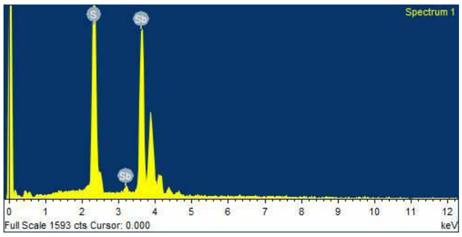
(sample 4)

Figure 1. Crystals of stibnite

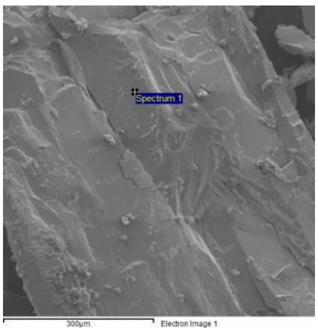
SEM image and EDX spectrum of stibnite are given in Fig. 2.



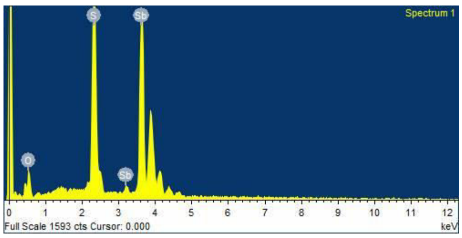
a) SEM image of stibnite (sample1)



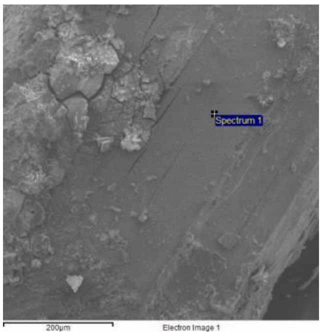
b) EDX spectrum of stibnite (sample1)



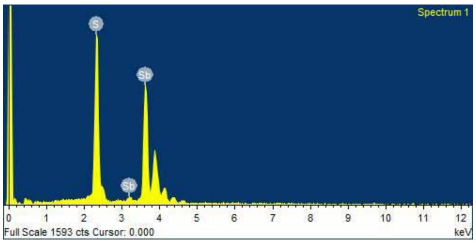
c) SEM image of stibnite (sample 2)



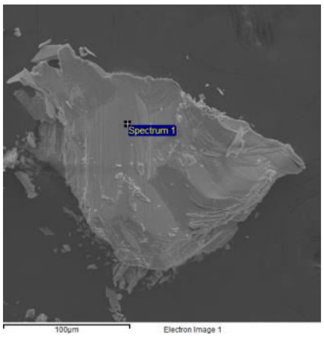
d) EDX spectrum of stibnite (sample 2)



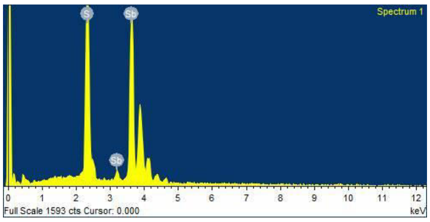
e) SEM image of stibnite (sample 3)



f) EDX spectrum of stibnite (sample 3)



g) SEM image of stibnite (sample 4)



h) EDX spectrum of stibnite (sample 4)

Figure 2. SEM image and EDX spectrum of stibnite from Allchar

Chemical composition of stibnite by ICP-MS is presented in Table 1.

Table 1. Chemical composition of stibnite from Allchar

Elements%	Sample 1	Sample 2	Sample 3	Sample 4
Sb	71.012	71.155	71.012	70.912
S	27.666	28.166	27.266	27.166
Al	0.119	0.103	0.118	0.253
Fe	0.038	0.053	0.048	0.010
Ti	0.313	0.301	0.303	0.303
Ca	<0.05	<0.05	<0.05	<0.05
K	<0.05	<0.05	<0.05	<0.05
Na	<0.05	<0.05	<0.05	<0.05
Mg	<0.05	<0.05	<0.05	<0.05
Elements mg/kg				
P	421	520	640	480
Cr	59.6	60.2	172	146
V	179	316	383	364
Se	26.9	18.5	24.8	57.2
Ba	363	373	327	394
As	488	681	1136	2071
Ag	28.1	17.5	15.9	19.5
Tl	8.41	5.68	20.66	15.07
W	30.0	7.3	48.7	9.4
Li	<10	<10	<10	<10
B	<10	<10	<10	<10
Co	<1	<1	<1	<1

Pb	<1	<1	<1	<1
Ni	<1	<1	<1	<1
Mn	<1	<1	<1	<1
Zn	<1	<1	<1	<1
Cu	<1	<1	<1	<1
Be	<1	<1	<1	<1
Bi	<1	<1	<1	<1
Th	<1	<1	<1	<1
Ge	<1	<1	<1	<1
Rb	<1	<1	<1	<1
Sr	<1	<1	<1	<1
Mo	<1	<1	<1	<1
Sn	<1	<1	<1	<1
Cd	<1	<1	<1	<1
Pd	<1	<1	<1	<1
U	<1	<1	<1	<1
Dy	<1	<1	<1	<1
Er	<1	<1	<1	<1
Eu	<1	<1	<1	<1
Hf	<1	<1	<1	<1
Ho	<1	<1	<1	<1
In*	<1	<1	<1	<1
La	<1	<1	<1	<1
Nb	<1	<1	<1	<1
Nd	<1	<1	<1	<1
Sc*	<1	<1	<1	<1
Sm	<1	<1	<1	<1
Tm	<1	<1	<1	<1
Y	<1	<1	<1	<1
Tb	<1	<1	<1	<1
Gd	<1	<1	<1	<1
Ga	<1	<1	<1	<1
Cs	<1	<1	<1	<1
Ce	<1	<1	<1	<1
Lu	<0.2	<0.2	<0.2	<0.2

Though stibnite is among the most predominant Sb-bearing mineral phases in most Sb deposits, little is known about the trace elements and their substitution mechanism in stibnite that are valuable to better decipher the genesis of Sb deposits. Results show that stibnite at Allchar contains measurable and : As, Tl, V, Se, Ba, Ag, Cr, W, P.

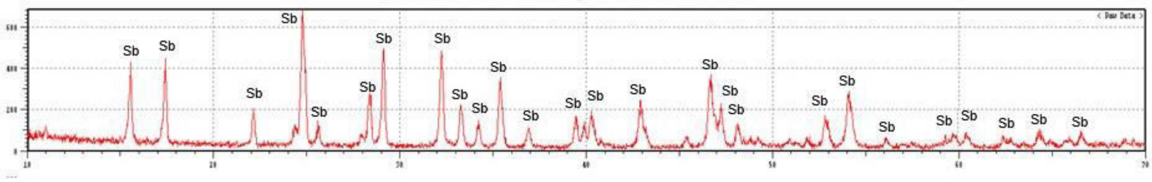
Other trace elementsare generally at concentrations of <0,2-1ppm.The relative enrichment of As and Tl indicate that the original Sb-bearing fluids for the Allchar deposit were likely enriched in these elements in the source region. Therefore, the differences in trace element composition in stibnite can be useful to discriminate between Sb deposit types.

Stibnite at Xikuangshan deposit contains measurable Hg and As (typically 10–100 ppm) while As, Cu, and Pb are the most abundant trace elements at Woxi deposit (generally 100–500 ppm). Other trace elements, including Au, Ag, Bi, In, Mo, Sn, Co, Cr, V, Zn, Ni, Ga, Ge, Rb, Sr, Pd, Cd and U, are generally at concentrations of 0.01–1 ppm [9].

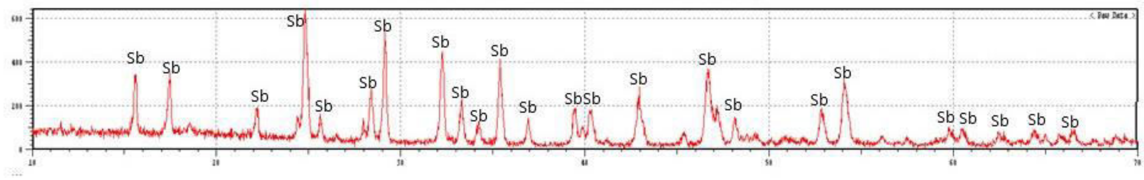
In the mineralogical literature, stibnite is usually stated to change by oxidation into kermesite and finally into valentinite or senarmontite. Another alteration product is described as antimony ochre, a term loosely applied to several minerals, viz. cervantite, stibiconite, and volgerite [10].

Most of the secondary minerals observed at the Stibnite Hill Mine are the product of the decomposition of stibnite. The four antimony oxide minerals found include kermesite, valantinite, cervantite and stibiconite. The first two are well crystalized minerals. Cervantite and stibiconite, which are also known as antimony ocher are poorly crystallized substances [11].

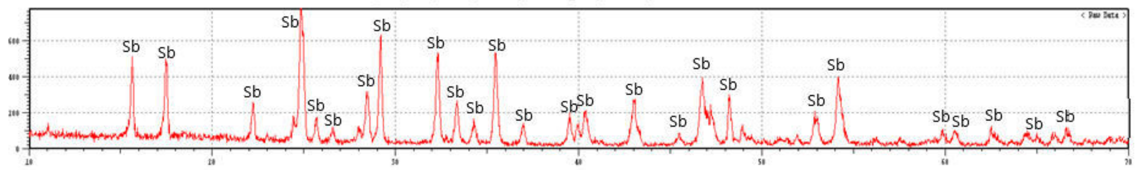
XRD patterns on investigated samples are given in fig.3. The most intense registered maxima in the studied powder pattern area compared with the corresponding maxima of stibnite ICDD 00 042 1393.



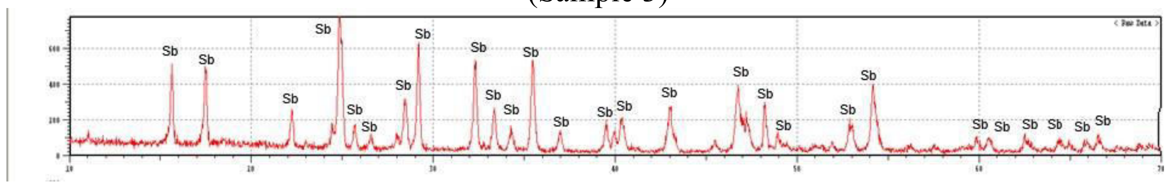
(Sample 1)



(Sample 2)



(Sample 3)



(Sample 4)

Figure 3. XRD pattern of the investigated stibnite from Allchar

The unit cell parameters obtained using the main reflection lines of X-ray diffraction are: a = 11.24 Å, b = 3.84 Å, c = 11.34 Å, V = 490.43 $Å^3$, Z: 4. In the crystal structure, Sb atoms in a trivalent state are distributed over two different crystallographic sites [12].

The crystal structure consists of parallel $(Sb_4S_6)n$ ribbon-like chains held together with the weaker intermolecular forces [13-15].

CONCLUSION

After summarizing the data collected in this research, we can confirm that the studied mineral samples are stibnite. The straightforward identification of the studied mineral samples was enabled by SEM-EDS, ICP-MS and XRD methods.

Crystals of stibnite are thick to thin elongated prisms with vertical striations, lead gray color and high metallic lusters. Stibnite also occurs in columnar, granular, blended and compact habits. Cleavage is perfect on {010} and imperfect on {100},{110}. The density determined by a pycnometer is 4.62 g/cm^3. Hardness is 2. The concentration of the oxides is: Sb:70,912-71,155%, S: 27,166-28,166%. Results show that stibnite at Allchar contains measurable As, Tl, V, Se, Ba, Ag, Cr, W, and P.

Results obtained by X-ray investigations are in good agreement with the ICDD cards 00 042 1393. The unit cell parameters obtained using the main reflection lines of the X-ray diffraction are: a = 11.24 Å, b = 3.84 Å, c = 11.34 Å, V = 490.43 $Å^3$, and Z: 4.

Stibnite is a fascinating mineral, and intricate clusters of interlocking, silvery-gray crystals are among its many interesting features.

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МИНЕРАЛОШКА И ХЕМИСКА КАРАКТЕРИЗАЦИЈА НА СТИБНИТ ОД АЛШАР, СЕВЕРНА МАКЕДОНИЈА

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Резиме

Кристали на стибнит се појавуват во повеќе наоѓалишта на антимон како што се Алшар, Лојане и Крстов дол. Најдобрите кристали на стибнит се наоѓат во централните делови на рудникот Алшар. Кристалите на стибнит се издолжени призми со оловно сива боја и висок метален сјај. Стибнитот се јавува и како зрнест и компактен. Цепливоста е совршена по {010}, а несовршена по {100},{110}. Густината одредена со пикнометар е 4,62 g/cm^3. Тврдината е 2. Концентрацијата на оксидите е: Sb:70.912-71.155%, S:27.166-28.166%. Добиените резултати покажуваат дека стибнитот од Алшар содржи мерливи концентрации на: As, Tl, V, Se, Ba, Ag, Cr, W, P.

Со добиените податоци од рендгенско дифракциони испитувања се пресметани димензиите на елементарната ќелија. Добиени се следниве резултати: a = 11.24 Å, b = 3.84 Å, c = 11.34 Å, V = 490.43 Å^3, Z: 4. кои се во потполна согласност со литературните податоци.

Клучни зборови: *стибнит, Алшар, SEM-EDS, ICP-MS, XRD*