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МАКЕДОНСКО ГЕОЛОШКО ДРУШТВО

ТРЕТ КОНГРЕС
на
Геолозите на Република Македонија

ЗБОРНИК НА ТРУДОВИ

-КНИГА 2-

Уредници:
Лепиткова, С. & Боев, Б.

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ПРЕДГОВОР

Геологијата како природна фундаментална наука има незаменливо значење за општеството и е оној камен темелник на кој се засновани голем број гранки од инженерството и индустријата.

Нејзиното значењето кај нас е многу јасно препознаено уште во далечната 1944 година, кога со одлука на Президиумот на АСНОМ е формиран Геолошкиот институт на НРМ, прва македонска геолошка институција.

Денес Македонското геолошко друштво како еден од главните промотори на геолошката наука во нашата земја, е пред нов предизвик, организирањето на Третиот Конгрес на геолозите на Република Македонија.

Организациониот и Научниот одбор на Третиот Конгрес, имајќи ја предвид долгата традиција на геолошката наука, но истовремено согледувајќи го актуелниот момент, одлучија носечките теми на Конгресот да бидат поврзани со:

- Геологијата и општеството,
- Фундаменталната геологија и
- Геологијата и економијата.

За овие теми во овој Зборник се публикувани вкупно 105 оригинални научни трудови, кои се подготвени од преку 350 автори и коавтори од поголем број на земји. Низ трудовите се елаборирани резултати од вредни и долготрајни истражувања на нашите и странските инженери и научни работници.

Од пристигнатите трудови може да се забележи поврзаноста на традиционалните истражни методи и примената на нови современи технологии и алатки при геолошките проучувања, вклучувајќи најсовремени теренски и лабораториски инструментални методи, системи за обработка, чување на податоци и следење на параметрите на животната средина. Се надеваме, дека прикажани ставови, размислувања и резултати ќе ги зацврстат досегашните знаења, и ќе се поттикнат идеи за значајни нови истражувања.

Затоа, Организациониот одбор искрено им се заблагодарува на сите автори, учесници и помагачи на Конгресот, кои сите заедно со пожртвуваноста овозможија овој Зборник да биде нешто со кое сите ќе се гордееме.

PREFACE

Geology as a natural and fundamental science is of great importance for the society and it is the foundation of many engineering and industry branches.

Its' importance in our country was clearly recognized in 1994, when the presidium of ASNOM reached a decision to establish a Geological institute of NRM, the first Macedonian geological institution.

Nowadays, the Macedonian geological society as one of the main promoters of the geological science in our country, has accepted a new challenge, the organization of the Third Congress of Geologists of Republic of Macedonia.

The Organizing and scientific committees of the Third congress, given the long tradition of the geological science, at the same time looking at its' current state, has decided that the main topics of the Congress are related to:

- Geology and society
- Fundamental geology and
- Geology and economy

There is a total of 105 original scientific papers published in these Proceedings, prepared by over 350 authors and coauthors from number of countries for these proceedings. Results from valuable and long investigations of our and the foreign engineers and scientific workers have been elaborated through the papers.

From the papers, it could be noted that there is a strong connection between the traditional investigation methods and the new contemporary technologies and tools in geological explorations, including the latest field and laboratory instrumental methods, systems for processing and data storage, and monitoring environmental parameters. We hope that, the presented views, considerations and results will strengthen the existing knowledge, and will encourage ideas for new significant research.

Therefore, the Organizing Committee would like to sincerely thank all the authors, participants and supporters of the Congress, who along with their devotion helped making us all proud of this Proceedings book.

Претседател на Организационен Одбор	**President of Organizing Committee**

Проф. д-р Соња Лепиткова

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LORANDITE AND ORPIMENTE FROM EDIT-25 NORTH PART OF ALSHAR DEPOSIT

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Abstract
This study presents research conducted on lorandite and orpiment taken from the Adit 25 in the northern part of the Allchar deposit using XRD, ICP-MS, SEM-EDS methods. From the research, it could be concluded that lorandite appears in big monocrystals (up to 1cm) with cherry color and can easily be split. Orpiment also appears in big monocrystals (from 2 to 5 cm). Lorandite always appears on an orpiment with a bit of dolomite basis. From the laboratory testing it can be concluded that those are very pure minerals with composition very near to the stoichiometric minerals.

Key words: lorandite, orpiment, Allshar

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 concen¬trations 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 (Janasch, 1904; Loczka, 1904; Jezek, 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., 1994; Sotirovski and Boyer, 1993; Stafilov et al, 1993, 1994; 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 systema-tically 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, 1968); 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).

METHODOLOGY

The mineralogical content of the collected samples from Edit 25 was determined using an X-Ray Siemens D 500 equipped with an automated computer and a Cu-monochromatic lamp working at 40 KV and 30 mA. Quantitative analysis of the mineral phases present was performed using the DIFRAC-11 software package and program support by EVAL and IDR.
The values given for the quantitative composition of the analyzed samples represent an average of 3 replicates. For QA and QC of the measurements referent materials and standards from various mineralogical compositions were used: BDS 17385/96 (standard for ore and ore concentrates for X-Ray diffraction quantitative phase analysis), ST SEV 3534-82 (SpS-quartz sand), ST SEV 2981-81 (KN-2, limestone), ST SEV 2980-81 (MpA-copper ore), USZ 47-2008 (granite “MGT-1”). In several cases standard addition method was applied by using some of the aforementioned RM and satisfactory values for the recoveries were obtained.
For the determination of the chemistry of mineralogical phase Cambridge-style SEM stubs using double sided carbon tape, and graphite coated to prevent charging. The coated samples were analyzed by Quanta 650F SEM, fitted with a back-scattered electron 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 particulate matter. Point Analysis was used to characterize the samples in high-vacuum mode, using an accelerating voltage of 15 kV and a spot size of 6. BSE images of selected fields of view were taken to examine SEM-based characteristics.
The trace elements were determined by the application of ICP-AES while the rest of the elements were determined by ICP-MS. The optimal parameters for both techniques are given in Table 1 and 2, respectively.

Table 1. Optimal instrumental conditions for the ICP-AES, Varian Liberty 110

Sample introduction						
atomizer			V-groove			
Atomizer chamber			Inert Sturman-Masters			
Peristaltic pump			12 rollers, 1 turn/min increment			
Conditions for the program						
Power of the plasma			1,0 kW			
Speed of the pump/rpm			25			
Flow ofArfor plasma			15 L/min			
Time for stabilization			30 s			
Flow of axial Ar			1,5 L/min			
Time for washing			30 s			
Pressure of the atomizer			200 kPa			
Time of lagging			30 s			
Background correction			dynamic			
Height of the plasma			Optimal according to SBR			
Conditions of elements						
Element	Wavelength/nm	Plasma height/mm	Slit/nm	Time for integration/s	Filter	Line of grating
Ca	396.847	20	0.02	5	1	1
Mg	279.553	20	0.02	5	6	2
Na	588.995	20	0.02	5	7	1
P	213.618	5	0.007	5	1	3
Fe	259.94	5	0.01	5	6	2
K	766.49	20	0.02	5	7	1

Table 2. The optimal instrumental parameters for the ICP-MS, Agilent 7500

Sample introduction			
Atomizer		PEEK, Babington - type	
Atomizer chamber		Glass, doublepass, temperature of the atomizer chamber 2^{o}C	
Injector of ICP torch		Quartz, 2.5 mm	
Conditions of the program			
Power of the plasma		1500 W	
Speed of the pump/rpm		0.1 rps	
Aux flow ofArfor plasma		1.0 L/min	
Carrier gas flowAr		0.9 L/min	
Sampler cone		nickel	
Skimmer cone		nickel	
Sample depth		7.4	
Points/mass		3	
Time for integration		0,3 s	
Total time for acquisition/ replicates		8 s	
Replicates		3	
Total time for acquisition/ sample		24 s	
Element/mass			
Element	m/z	Element	m/z
Li	7	Sr	88
Be	9	Mo	95
Al	27	Pd	106
Ti	48	Cd	111
V	51	Cs	133
Cr	53	Ba	137
Mn	55	Tl	205
Co	59	Pb	208
Ni	60	Bi	209
Cu	63	Th	232
Zn	66	U	238
Ga	69	Sn	120
Ge	72	Sb	121
As	75		

RESULTS AND DISCUSSION

Lorandite is world famous mineral described as the first thallium-bearing mineral. Since its first discovery in Allchar in 1884 (Krenner, 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.

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.

Chemical composition of pure lorandite and orpiment by ICP-MS are presented in the Table 3. In Table 4 and 5 are presented the chemical composition of pure lorandite and orpimente by SEM-EDS (Fig.1,2).

Table 3. Geochemical analyses of orpiment and lorandite from the edit 25 In Alshar deposit (by ICP-MS)

	Orpiment	Lorandite
	mg/kg	mg/kg
Tl	234	602999
As	**604620**	195996
Hg	<0,1	10
Sb	993	0,176
Li	<0,086	0,125
Be	<0,086	<0,054
Na	43	24
Mg	49	22
Al	74	7,8
P	6,32	1,72
K	<86	<54
Ca1	<86	<54
Ti	14,1	3,4
V	2,4	0,68
Cr	7,09	2,24
Mn	2,43	1,03
Fe	140	6,42
Co	0,15	<0,054
Ni	1,43	0,11
Cu	1,151799	0,170305
Zn	0,087378	0,1217
Ga	0,20	<0,054
Ge	0,09	<0,054
Se	3,5	0,95
Rb	0,25	<0,054
Sr	0,61	0,084
Mo	0,66	0,113
Pd	0,77	<0,054
Ag	0,110	<0,054
Cd	0,103	0,501
Sn	0,353	0,408
Cs	<0,086	<0,054
Ba	5,22	0,051
Pb	9,24	0,327
Bi	<0,086	<0,054
Th	0,251	<0,054
U	0,060	<0,054

Table. 4 Chemical composition of orpiment by the SEM-EDS

Orpiment SEM-EDS	
As %	S %
59.77	40.23
60.31	39.69
59.69	40.31
58.43	41.57
61.01	38.99
62.23	37.77
58.54	41.46
60.52	39.48

Table. 5 Chemical analysis of lorandite from edit 25 by SEM-EDS

Tl %	As %	S %
59.01	21.7	19.29
58.78	22.01	19.21
60.07	21.5	18.43
58.23	22.42	19.35

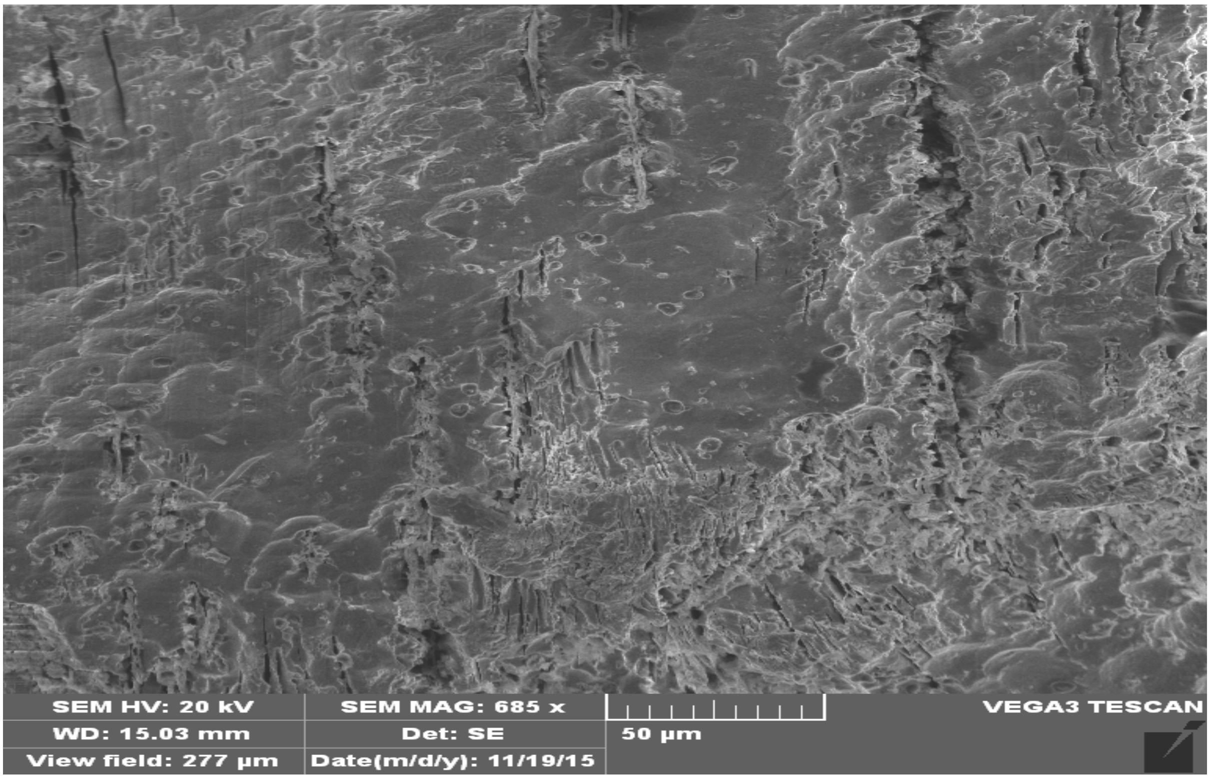

Fig. 1 *Orpiment from edit 25 in Allshar deposit under the SEM*

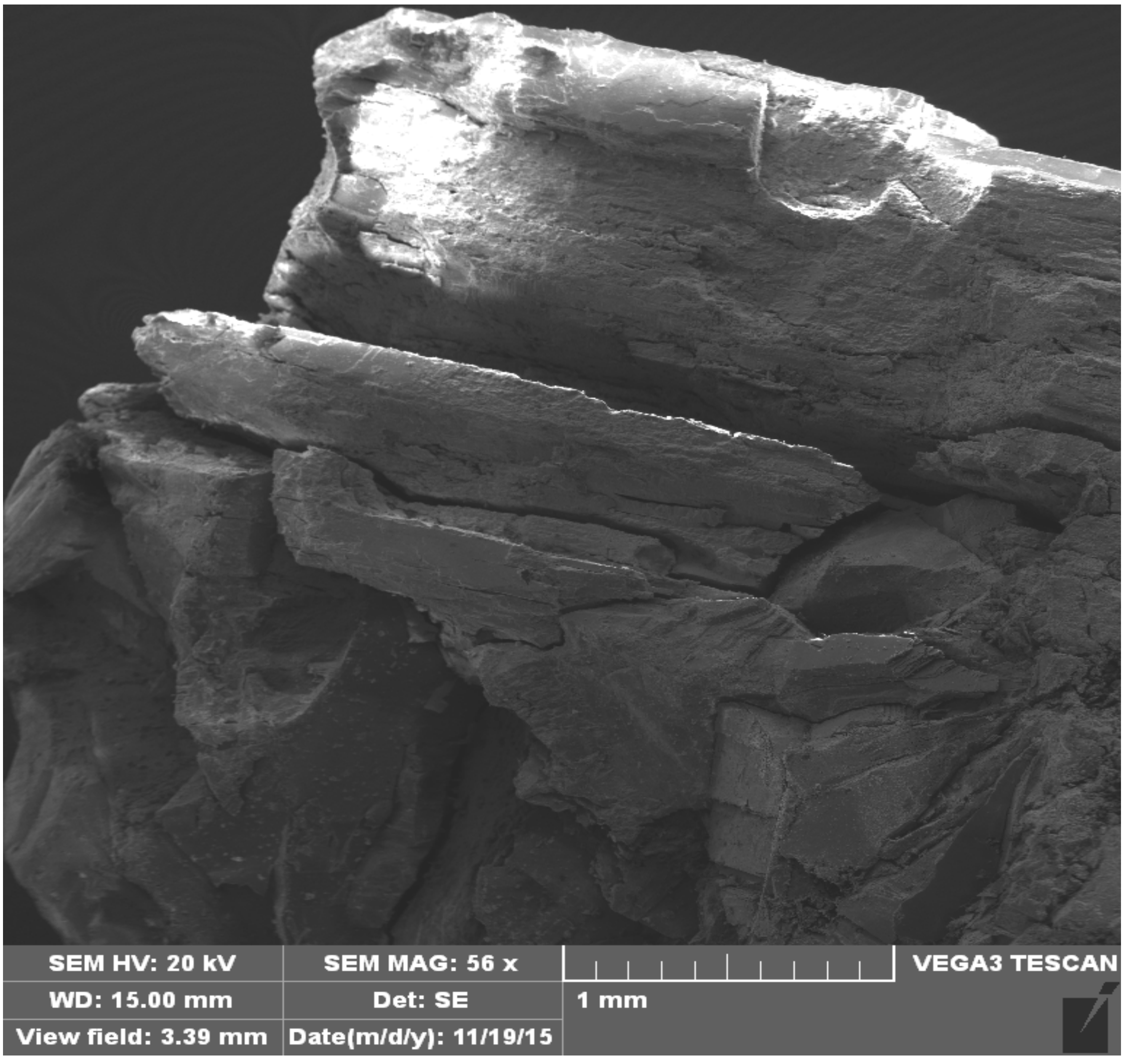

Fig. 2 *Lorandite from edit 25 in Allshar deposit under the SEM*

CONCLUSIONS

In the final sections of the Adit 25 in the Allchar deposit on 750 meters distance from the entrance there is a zone with hydrothermally altered dolomites with impregnated orpiment and lorandite occurrence (desiminated). The investigation on orpiment and lorandite samples using the ICP-MS and SEM-EDS methods suggest pure minerals with composition very near to the stoichiometric minerals.

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