

**Универзитет „Гоце Делчев“ - Штип, Македонија  
Факултет за природни и технички науки**

**University „Goce Delcev“, Stip, Macedonia  
Faculty of Natural and Technical Sciences**

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ФАКУЛТЕТ ЗА ПРИРОДНИ И ТЕХНИЧКИ НАУКИ**

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FACULTY OF NATURAL AND TECHNICAL SCIENCES**

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**THE CRVEN DOL ARSENIC-THALIUM MINERALIZATION  
IN ALSAR DEPOSIT IN THE REPUBLIC OF MACEDONIA****Ivan Boev<sup>1</sup>, Blazo Boev<sup>1</sup>**

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**Abstract**

This ore body lies in the northern part of Alsar. It was opened by two adits - No. 25 at the level 753 m on the western part, and adit 21 at the level 823 m on the eastern side. The mineralization is explored underground at three levels: 753, 802 and 823 m connected by two vertical shafts. The most significant mineralization occurs close to the entrance of adit 21 and the vertical shaft.

**Keywords:** *Crven Dol, Alsar, Thallium mineralization.*

**АРСЕНСКО-ТАЛИУМСКА МИНЕРАЛИЗАЦИЈА ВО  
НАОЃАЛИШТЕТО АЛШАР, ЦРВЕН ДОЛ, РЕПУБЛИКА  
МАКЕДОНИЈА****Иван Боев<sup>1</sup>, Блажо Боев<sup>1</sup>**

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**Апстракт**

Ова рудно тело лежи во северните делови на Алшар. Беше отворено со два хоризонтални отвори: No. 25 на ниво 753 m на западната страна и хоризонтален отвор 21 на ниво 823 m на источната страна. Минерализацијата е истражувана подземно на три нивоа: 753, 802 и 823 m поврзани со две вертикални окна. Најзначајната минерализација се јавува блиску до влезот на отворот 21 и вертикалното окно.

**Клучни зборови:** *Црвен Дол, Алишар, Талиумска минерализација.*

## 1. Introduction

The Alsar deposit consists of several ore bodies and numerous occurrences, each characterized by specific associations of metals and mineral assemblages (Boev, 1988) (Jankovic et al, 1977).

The Sb-As-Ti-Au mineralization occurs within a zone almost 3 km long and 200 - 300 wide.

### *Morphostructural types of mineralization*

Several distinct types of mineralization occur in the Alsar deposit including:

(i) Mineralized brecciated zones developed along the contact between the subvolcanic intrusions, with dolomite and/or tuffaceous dolomite or along shear zones in the carbonate rocks and/or silicified tuffs.

(ii) Massive lenses of realgar ore occurring in the carbonate rocks and grading into stockwork-type mineralization. Massive sulphide mineralization, mainly pyrite/marcasite occupies sporadically steeply-dipping fault/shear zones. Massive sulphide-bearing jasperoids occur sporadically only as small pods.

(iii) A Mineralized systems of veinlets and fractures occur in the tuffaceous dolomite and the Triassic dolomite.

(iv) Disseminated mineralization, mostly stibnite, pyrite/marcasite, gold occurs (a) as stratabound bodies along the contact between the basal portion of volcano-sedimentary tuffaceous dolomite and/or tuffs, and underlying Triassic carbonate rocks, (b) in silicified volcanics (with variable amounts of argillization), and (c) as abundant finely disseminated pyrite-marcasite and stibnite in the jasperoids, locally accompanied by arsenic sulphides and Tl-minerals.

Ore bodies occur most frequently as steep-dipping lenses, irregular in shape, sporadically as ore-shoots. The size and shape of these ore bodies depend on cut-off grades.

(v) System of thin, up to 10 cm wide, subparallel veins of orpiment are identified in the Crven Dol ore body at 800 m level (Fig.1).

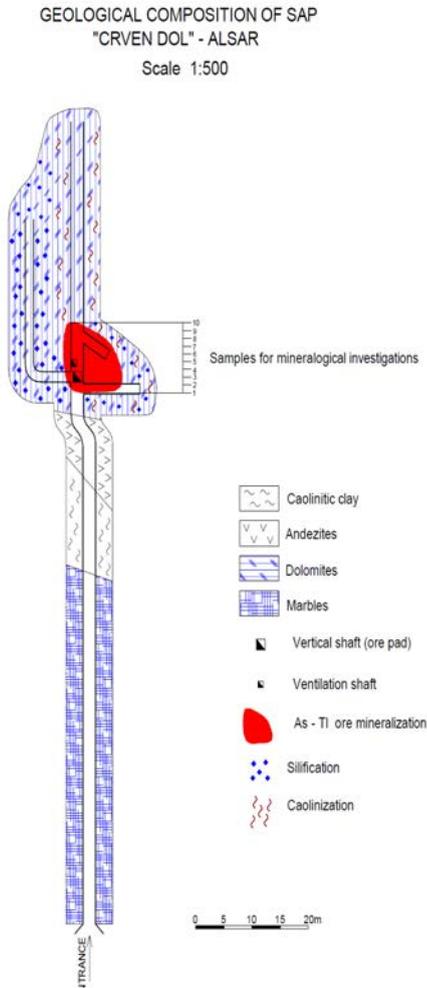


*Fig.1.* Panoramic view of Crven Dol (Photo : I.Boev)

*Сл. 1.* Панорамски поглед на Црвен Дол

## **2. Local geology**

Crven Dol is composed of carbonate rocks (dolomite and minor limestone /marble) (Table 1) intruded by a subvolcanic magmatic body (?) highly hydrothermally altered, so that its primary composition is extremely difficult to identify reliably (Fig.2).



**Fig.2.** Geological map of Crven Dol  
**Сл. 2.** Геолошка мапа на Црвен Дол

The rock contains phenocrysts of sanidine, quartz and biotite; the groundmass consists mostly of K-feldspar and quartz. It has been so far named as quartz rhyolite (Jankovic, Jelenkovic, 1994), andesite (Jelenkovic and Pavicevic, 1994) and rhyolitic tuff (Frantz, 1994).

**Table 1.** Instrumental neutron activation analyses of host rocks inside the Crven Dol orebody and comparison with a marble and dolomite outside from valley Crven Dol (Frantz et al., 1994)

element	a	b	c	d	e	f	g	h
%	marble	andesite	bulk	bulk	dolomite	dolomite	dolomite	marble
Mg	d.l	d.l	d.l	d.l	8.700	d.l	13.00	d.l
Ca	37.10	10.10	13.70	d.l	21.45	17.60	24.37	39.70
Fe	0.2260	2.890	9.130	21.10	0.1170	5.900	0.0253	0.0583
( ppm )								
Na	47.80	6230.0	98.70	75.30	103.0	62.20	83.50	41.30
Cl	d.l	d.l	d.l	d.l	<	<	51.00	d.l
K	229	18700	880.0	720.0	166.0	340.0	43.80	139.0
Sc	1.070	7.260	2.930	1.510	1.200	2.690	0.3700	0.2430
Cr	6.450	8.800	51.00	49.10	4.500	10.00	3.600	3.200
Mn	450	1220.0	11500	4350.0	392.0	5620.0	66.50	201.0
Co	1.440	5.810	1435.0	1470.0	0.4800	18.30	0.6700	0.2800
Ni	<	<	4340.0	4150.0	d.l	59.00	<	<
Cu	<	<	<	<	<	<	<	<
Zn	20.00	96.00	54.00	200.0	9.300	115.0	6.300	1.800
Ga	0.3200	18.60	<	<	d.l	d.l	d.l	0.1200
As	210	53.80	51600	82300	3040.0	36000	197.0	45.60
Se	13.20	<	d.l	2.500	<	<	<	<
Br	<	<	<	d.l	0.3900	d.l	0.3200	0.1230
Rb	<	127.0	<	<	<	<	<	1.100
Sr	68.00	285.0	<	<	70.00	90.00	41.00	116.0
Zr	d.l	200.0	d.l	<	d.l	d.l	d.l	<
Mo	0.8000	2.000	40.00	120.0	d.l	7.000	<	0.2400
Ag	d.l	d.l	d.l	d.l	0.6500	d.l	d.l	<
Cd	d.l	d.l	d.l	d.l	2.000	d.l	d.l	0.1600
In	d.l	d.l	d.l	<	d.l	d.l	d.l	d.l
Sb	1.370	<	16.70	32.80	0.1000	36.00	0.0640	0.9690
Cs	1.350	39.00	11.12	25.20	0.2000	7.060	0.0860	0.2900
Ba	11.00	1110.0	<	<	d.l	<	<	6.900
La	2.260	67.30	3.340	3.700	0.2500	3.250	0.2400	0.860
Ce	4.120	128.0	5.000	4.400	0.6500	5.100	0.2900	1.820
Pr	d.l	13.00	d.l	d.l	d.l	d.l	d.l	0.1300
Nd	1.400	51.80	d.l	d.l	0.3200	4.500	<	0.5600

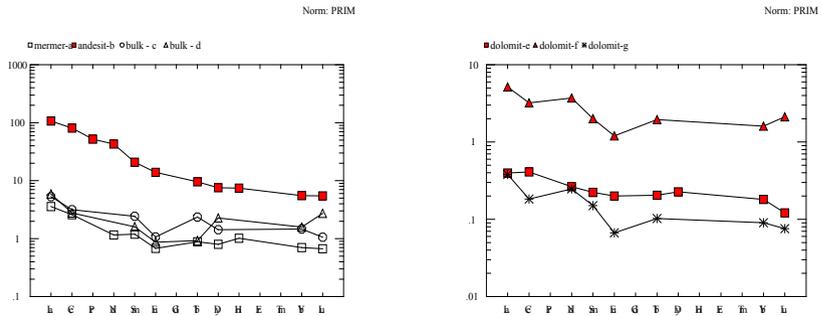
Sm	0.4750	8.310	0.9700	0.6400	0.0890	0.800	0.0660	0.1730
Eu	0.1020	2.090	0.1600	0.1300	0.0300	0.1800	0.0130	0.0302
Gd	d.l	0.1300						
Tb	0.0860	0.9300	0.2300	<	0.0220	0.1900	0.0130	0.0180
Dy	0.5280	4.990	<	<	<	<	0.0740	0.1200
Ho	0.1500	1.100	d.l	d.l	d.l	d.l	d.l	0.0280
Yb	0.3100	2.440	0.6500	<	0.0800	0.7100	0.0460	0.0760
Lu	0.0440	0.3680	0.0730	<	0.0080	0.1400	0.0052	0.0110
Hf	0.0760	6.100	<	<	<	0.0750	0.0130	0.0390
Ta	<	0.9100	<	<	<	<	<	0.0230
W	1.490	<	<	d.l	d.l	9.300	0.0630	0.9000
Ir	<	<	<	d.l	<	d.l	d.l	<
Au	0.0017	0.0020	<	d.l	1.098	0.0210	0.0897	0.0006
Hg	d.l	d.l	<	6.600	0.1400	2.900	<	0.2600
Tl	d.l	d.l	<	d.l	d.l	4500.0	<	d.l
Th	0.2430	61.50	<	<	0.0660	0.1900	0.0370	0.2700
U	0.6000	9.200	4.400	<	0.1300	3.970	0.0540	0.4500

d.l – detection limit

The rock contains phenocrysts of sanidine, quartz and biotite; the groundmass consists mostly of K-feldspar and quartz. It has been so far named as quartz rhyolite (Jankovic, Jelenkovic, 1994), andesite (Jelenkovic and Pavicevic, 1994) and rhyolitic tuff (Frantz, 1994).

Table 2 shows instrumental neutron activation analyses of host rocks inside the Crven Dol orebody. These data are important when analyzing primary sources of metals mobilized later and concentrated in the Crven Dol ore body. Thallium content in carbonate rocks and in tuffs as well (intrusive body ?) is very low, whereas arsenic content is high ( with the possibility that it originated from hydrothermal solutions). The LIL elements such as B, K, Rb, Cs, Ba and Sr are strongly enriched with regard to primitive mantle, particularly Cs (Frantz, 1994).

The REE spider diagram of the altered subvolcanic intruded body and surrounding marble and dolomite shows enrichment in LREE up to a factor 100 normalized to the CI- chondritic values (Fig. 3, Frantz, 1991).



**Fig.3.** Spider diagrams of samples inside and outside the mine from Crven Dol. Samples are normalized to C 1- chondritic values of Palme et al., (1981) from Frantz, (1991)

### 3. Mineralization

Three styles of low mineralization have been so far revealed, each with a distinct geochemical signature and mineral assemblage:

(i) **Massive realgar** ore grading into stockwork formed in dolomite near or along its contact with subvolcanic intrusions. Sporadically, high grade ore occurs in brecciated zone (Fig. 4).

This ore is open at the level 823 m and explored by short cross-cuts and shallow shaft. This ore body contains about 6.000 tones with 8 % As, 0.09 % Sb, 0.35 % Tl, 45 ppm Hg and 0.2 ppm Au. It is located approximately 30 m below the present surface.

**Realgar** is dominant mineral accompanied by pyrite and marcasite, minor orpiment and thallium minerals.

Realgar encloses lorandites and marcasites. It appears as crystals, often of large size, and as massive pods and lenses. It is usually intergrown with orpiment and it frequently hosts lorandite. In some places, realgar is found to cement “gel-marcasite”.



**Fig.4.** Masive realgar in edit Crven Dol (foto by I.Boev)

Table 2 shows major and trace elements of realgar within the orebody of Crven Dol (Frantz, et al., 1994).

*Native Ag* occurs sporadically in realgar (electrum).

*Orpiment* occurs in massive ore as small aggregates intergrown with realgar, but locally it forms plate crystals.

*Marcasite and pyrite* are widespread minerals. Collomorph textures are characteristic for both, particularly marcasite.

Marcasite occurs in crystal forms, but frequently marcasite grains are rounded. Some marcasite grains consist of a core, a thin rim and globules of an As rich composition (Frantz et al., 1994). Table 3 shows composition of marcasite from Crven Dol.

**Table 2.** Major and trace elements of realgar from Crven Dol, ppm (Frantz et al., 1994)

Element	Realgar
Fe %	<
As	57.33

Tl	<
Sb	0.00243
Na ppm	<
K	<
Sc	<
Cr	69.8
Mn	<
Co	<
Ni	d.l
Cu	d.l
Zn	<
Ga	<
Se	24.2
Mo	<
Cd	d.l
In	d.l
Cs	2.5
La	d.l
Sm	<
Eu	<
Yb	<
Lu	<
Ta	<
W	<
Hg	<
Th	<
U	<

d.l. - below detection limit,

&lt;

Weight . %	Core	Rim	Globules
As	-	-	71.73
Fe	47.59	48.20	24.64
S	52.81	51.80	3.63
Total	99.86	100	100.01
Formula			
As	-	-	2.17

Fe	1	1	1
S	1.933	1.870	0.25
Total	2.933	2.872	3.42
	FeS2		FeAs2

The As-rich globules, surrounding altered marcasite with cores of stoichiometric composition, containing 24.64 wt % Fe, 71.73 wt % As and minor S (3.64 wt %), are described by Frantz et al., (1994) as lollingite (Fe As ).

**Thallium minerals**

The massive realgar ore body of Crven Dol contains numerous Tl-minerals, some of them have been recently discovered. The list of Tl-minerals from Crven Dol is still incomplete.

**Tl - As - S system**

Lorandite TlAsS<sub>2</sub> (Krenner, 1884)

Bernardite TlAs<sub>5</sub>S<sub>8</sub> (Pasava et al., 1989)

Fangite Tl<sub>3</sub>As<sub>4</sub> (El Goresy/Pavicevic. 1988, Williamson, et al., 1993)

**Lorandite** is the most common thallium mineral.

Lorandite occurs in close association with realgar and less frequently with orpiment, locally with marcasite. It sporadically forms large aggregates and/or individual crystals.

The lorandite mineral from Crven Dol contains numerous trace elements (Table 4).

**Table 4.** Major and trace elements (ppm) in lorandite from Crven Dol (Frantz et al., 1994)

Elements	FP 11	FP 12	FP 13
Fe %	0.196	0.059	0.126
As	20.53	19.72	19.56
Tl	62.70	57.50	60.35
Sb	0.0379	0.0278	0.0258
Na ppm	40	<	37
K	<	<	<
Sc	<	<	0.046
Cr	15	20	23

<b>Mn</b>	48	9	58
<b>Co</b>	<	<	<
<b>Ni</b>	<	<	<
<b>Cu</b>	d.l	<	<
<b>Zn</b>	d.l	<	<
<b>Ga</b>	<	<	<
<b>Se</b>	<	<	<
<b>Mo</b>	<	8.6	<
<b>Cd</b>	d.l	d.l	<
<b>In</b>	d.l	<	<
<b>Cs</b>	d.l	d.l	d.l
<b>La</b>	<	<	d.l
<b>Sm</b>	<	<	<
<b>Eu</b>	<	<	<
<b>Yb</b>	<	<	d.l
<b>Lu</b>	d.l	<	d.l
<b>Ta</b>	<	<	d.l
<b>W</b>	d.l	<	d.l
<b>Hg</b>	1.4	<	d.l
<b>Th</b>	<	<	d.l
<b>U</b>	<	<	d.l

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Lead ( Pb )	from 0.5 to 2.0 ppm
Uranium ( U )	from 0.06 to 0.26 ppm
Thorium ( Th )	from 0.005 to 0.028 ppm

**Table 6.** Concentration of Pb, U, Th in lorandite from Crven Dol (Toldt., 1988) ( concentrations mg/g)

	Pb	U	Th
Crystal	0.79	0.039	0.0092
Small grains	2.02	0.150	0.0135

**Table 7.** Concentration of Pb, U, Th in realgar and orpiment from Crven Dol (Todt., 1988) ( concentrations mg/g)

	Pb	U	Th
Realgar	0.38	0.74	1.19
Orpiment	11.60	0.084	2.64

Todt (1988) has determined concentration values of Pb, U, and Th in a single idiomorphic crystal of lorandite from Crven Dol, and in small grains of lorandite. These analyses have revealed certain differences between them (Table 6).

Such concentration values of Pb, U and Th are small enough to be accepted for the LOREX tests. Since the concentration of U and Th in minerals intergrown with lorandite are also important, Todt (1988) found that the concentration of these crystal elements in realgar and orpiment are also acceptably low (Table 7).

Table 8, 9 and 10 show the concentrations of Pb, U, Th in some minerals such as lorandite, orpiment and realgar taken from underground mining workings in Crven Dol.

**Table 8.** Pb, U and Th concentrations of realgar at gallery I (823 m) ( Frantz et al., 1994)

Realgar	Number of grain	Weight (mg)	Pb (ppm)	U (ppm)	Th (ppm)	Level
Rea I	8	50.65	0.018	0.18	0.0017	
Rea II	5	98.70	0.213	0.28	0.0037	
FR 5	12	51.30	0.032	0.134	0.008	823/I/P21
FR 6	21	52.30	0.047	0.078	0.005	
FR 7	44	39.90	0.042	0.11	0.009	
FR 1	1	58.30	0.014	0.04	0.0018	
FR 2	1	152.60	0.0066	0.0017	0.0017	823/I/P21
FR 3	1	140.20	0.01	0.017	0.0058	
FR 4	1	47.00	0.08	0.007	0.002	

**Table 9.** Pb, U and Th concentrations of lorandite and orpiment from shaft ( 823 to 800 m ) ( Frantz et al., 1994 )

Lorandite	Number of grain	Weight (mg)	Pb (ppm)	U (ppm)	Th (ppm)	Level
PA 7	1	16.30	0.51	0.083	0.109	
PA 8 §	1	18.43	0.79	0.039	0.009	823 / 800
LI	1	13.04	1.79	0.186	b.l	
<b>Orpiment</b>						
A 1	1	42.21	0.41	0.0102	b.l	
A 2	1	21.11	0.207	0.092	b.l	823 / 800
<b>Orpiment</b>	1	13.44	11.60	0.084	2.64	

Lorandite	Number of grain	Weight (mg)	Pb (ppm)	U (ppm)	Th (ppm)	Level
Fl 1	1	42.20	0.552	0.686	0.0239	
Fl 2	1	70.10	2.024	0.174	0.0281	763/IV/P25
Fl 3	1	74.00	0.616	0.258	0.0057	
Fl 4	1	34.00	1.375	0.169	0.0099	
<b>Orpiment</b>						
FA 1	1	64.40	4.09	0.026	0.011	763/IV/P25
FA 2	1	166.10	0.072	0.092	0.0056	
FA 3	1	125.50	0.13	b.l	b.l	

b.l. - below detection limit

*Bernardite* occurs only locally as crystals of up to 1 cm in size. Its position in the general mineral series is not clear.

*Fangite* was discovered and preliminary described by El Goresy and Pavicevic (1988), but Wilson et al., (1993) found this Tl - As sulphosalt in the Mercur Au deposit, Utah and completed investigations necessary for its recognition as a new thallium mineral.

Fangite from Crven Dol resembles orpiment in its optical properties (El Goresy and Pavicevic, 1988). It was found as thin layers around lorandite, realgar and orpiment. It precipitated in the last mineralization episode, following crystallization of lorandite.

### Tl - Sb - As - S system

Only two minerals of this system have been identified in Crven Dol so far:

Rebulite  $Tl_5Sb_5As_8S_{22}$  (Balic-Zunic et al.1982)

Jankovicite  $Tl_5Sb_9(As,Sb)_4S_{22}$  (Cvetkovic et al.,1994; Libowitzky et al.,1995)

Jankovicite is one of the minerals from this system identified in Crven Dol. It is associated with coarse-grained realgar and minor stibnite, and very fine, globular pyrite.

Jankovicite displays some strong similarities to other Tl-Sb-As and Tl-Sb sulphosalts, such as rebulite and parapirotite, particularly to rebulite (Libowitzky et al., 1995).

Apart from the reviewed Tl minerals, Ribeck (1993) identified *weissbergite* ( $TlSbS_2$ ). It is not known whether this mineral was found in the Crven Dol orebody.

Detailed investigation on mineral assemblages of Crven Dol ore, carried out by Frantz et al., (1994) discovered a new mineral (?) iron-thallium arsenate ( $Fe_2Tl [(As_{0.85}S_{0.15})O_4]_3 \cdot 4H_2O$ ). It displays radial growth from a core (Fig. 70), and occurs locally as a colloform type filling fractures. This mineral is frequently associated with highly altered marcasite. Its chemical composition is shown in Table 11.

**Table 11.** Chemical composition of Fe-Tl arsenate ( EMP ) of adit 823 m of Crven Dol (Frantz et al., 1994)

	<b>Radial type</b>	<b>Colomorphic type</b>
<b>Fe ( % )</b>	18.36	17.20
<b>Tl</b>	29.27	26.63
<b>As</b>	37.16	39.28
<b>S</b>	4.13	4.03
<b>Total</b>	88.93	87.13
<b>Formula</b>		
<b>Fe</b>	1.31	1.34
<b>Tl</b>	0.56	0.71
<b>As</b>	1.65	2.25
<b>S</b>	0.28	0.29
<b>Total</b>	3.7	4.59

Composition	$Fe_2 Tl (As_{0.85} S_{0.15}) O_4 ) \times 4 H_2O$
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The very low sulphur and relatively low thallium contents, with high iron and arsenic concentrations and traces of other elements of around 0.1 wt % (e.g. Sb) indicate a secondary origin of this arsenate (Frantz et al., 1994).

(ii)- *Stratiform orpiment bands and veinlets in tuff/tuffaceous dolomite* are developed below the massive realgar ore body. They are revealed in gallery 800 m. Subparallel bands form a zone a few meters wide. Individual orpiment bands are mostly up to 1 - 2 cm wide.

Orpiment is the most abundant mineral and realgar is almost absent. Pyrite/marcasite disseminations round orpiment are widespread (Jankovic, 1993).

(iii) *Disseminated Tl-As mineralization in carbonate rocks*, mainly dolomite, is frequently found in Crven Dol, particularly in adit No. 25. Realgar, sporadically orpiment, Tl minerals and pyrite/marcasite are the main mineral constituents of this poor mineralization.

So far, this type of As-Tl mineralization has not been studied.

### **Secondary minerals**

Of the principal supergene minerals of Crven Dol the following have been identified so far: goethite, fibroferrite (Rieck, 1993), gypsum, hoernesite, picropharmacolite (Rieck, 1993), rosenite, starkeyte (Riebeck, 1993), jarosite, pharmacosiderite  $K_2(OH)Fe_4(AsO_4)_3(OH)_4 \cdot nH_2O$  and dor-allcharite (Balic-Zunic et al., 1993).

### **Some Genetic Aspects**

The hydrothermal system of Crven Dol includes As-Tl-Fe-S minerals, sparse Sb and barite, traces of Au and Hg, as well as minor silica. The same minerals are determined in the antimony mine in the central part of the deposit.

The process of mineralization took place in shallow depth, in a strong oxidation environment, under high arsenic and thallium fugacity; the period of the dominance of arsenic was followed by high concentrations of thallium decreasing gradually to the end of precipitation of primary mineralization.

A genetic model of the Crven Dol mineralization involves the following parameters:

*Ultimate source of metals.* Based on investigations of lead isotopes in ore metals (lorandite, realgar, orpiment) and volcanics, it is possible to constrain the geological history of the As-Tl minerals in Crven Dol (Frantz et al., 1994).

In conclusion, they suggest that lead in the hydrothermal phases was extracted from the neighbouring or basement rocks.

Since trace elements of investigated rocks in and near Crven Dol show that As- and Tl-contents of carbonate rocks are low, it appears that volcanics are the most probable ultimate source of ore metals, mobilized by hydrothermal fluids.

Isotopic composition of sulphur associated with realgar, orpiment and lorandite

from Crven Dol is characterized by values of  $\delta^{34}\text{S}$ , ranging from -1.7 to -5.7 ‰ (Table 52).

From these data it can be concluded that sulphide sulphur originated from a magmatic source. This is considered as an additional confirmation that volcanic rocks (quartz/lignite) are the ultimate source for thallium and other metals of the Crven Dol ore body.

- Composition of hydrothermal fluids. Hydrothermal solutions are characterized by high arsenic and thallium concentrations. They introduced into Crven Dol over 5.000 tons of arsenic, and about 20 tons of thallium, and small amounts of antimony and gold. Hydrothermal fluids were poor in silica.
- Temperature of metal-bearing solutions ranges from 280/250° and 120°C. Homogenization temperature of fluid inclusions in realgar is determined as 144 to 170°C (Beran et al., 1990).
- Salinity. Based on information from fluid inclusions in realgar, Beran et al., (1990) determined salinity to range from 7.9 to 12.9 equivalent wt % NaCl.

Some weak indications for the presence of hydrocarbon-bearing inclusions have been reported by Beran et al., (1990) for realgar. Hydrocarbon derives, very likely, from the Pliocene sedimentary basins in the vicinity.

- Mode of metals transport. Thallium and arsenic were transported most probably as complex ions by acid to slightly alkaline fluids of low salinity, and under oxidation conditions.
- Precipitation. Deposition of arsenic and thallium took place as the result of changes of geochemistry in hydrothermal ore-bearing fluids due to their interaction with host carbonate rocks (mostly dolomite) and replacement of host rocks. Several stages of precipitation are distinguished:

(i) Precipitation of ore minerals was predated by ankeritization of dolomite, and argillization of silicate rocks (kaolinization).

Temperature below 400°C, pH - low.

(ii) Precipitation of siderite, pyrite, marcasite as a fine-grained mixture (Balic-Zunic et al., 1993). The thallium content is low (0.5 %).

(iii) Precipitation of pyrite globules with low As contents.

High oxidation environment.

(iv) Precipitation of abundant realgar (i) accompanied by minor orpiment and realgar, locally very minor stibnite.

Temperature was about 180°C. Thallium contents started to increase. Due to high oxidation conditions, minor arsenolite was formed, and likely pharmacosiderite (Balic-Zunic et al., 1993).

(v) This is stage of the highest thallium concentrations resulting in deposition of lorandite, followed by precipitation in accordance with the decreasing of Tl activity by other thallium minerals (bernardite, fangite, jankovcite a.a.).

(vi) Stage of supergene development is characterized by

- strong oxidation environment,
- amorphous iron and manganese sulphate-arsenate such as pharmacosiderite, Mg-arsenate - hoernesite (with gypsum); absent or low thallium.
- thallium minerals of jarosite group formed under high Tl concentrations. Here belongs a new recently identified mineral dorallcharite (Tl, K) Fe (SO<sub>4</sub>) (OH) - Balic-Zunic et al., (1993).

Age of mineralization. Based on <sup>40</sup>Ar / <sup>39</sup>Ar investigations of sanidine grains separated from the subvolcanic intrusions, revealed by adit No. 21, total age of it was established as 4.2 ± 0.1 m.y. (Troesch and Frantz, 1992).

This age of intrusion represents most likely the age of primary As - Tl mineralization in the Crven Dol ore body.

#### 4. Conclusion

In the northern part of the deposit Alsar, 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:

Morphologically complex, massive realgar orebodies, localized in dolomites in the zone of contact with subvolcanic intrusions, as well as in brecciation zones;

Stratiform, band-type and vein-like orebodies of orpiment in tuffs and tuffaceous dolomites, localized in the lower levels of massive realgar orebodies;

Morphologically complex, impregnation-type Tl-As mineralization in carbonaceous rocks, mostly dolomites, and

Morphologically complex ore mineralization with supergene (secondary) arsenic minerals.

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