PLATE TECTONIC ASPECTS OF THE ALPINE METALLOGENY IN THE CARPATHO-BALKAN REGION
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GENERAL GENETIC MODEL OF THE ALSHAR DEPOSIT

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Intensive mining was carried out in the Alshar mine from 1980 to 1912 by Englo-French companies which had the concessions given to them by Turkish authorities. Arsenic and antimony were predominant ores that were mined and transported to Freiberg and other towns in Germany. Several minerals such as vrbaite (Jezek, 1903) and lorandite (Krener, 1884, 1885, 1889) were discovered in samples taken from railway cars in the Freiberg smelter at that time.

Important ore reserves of antimony with significant arsenic concentration were determined in the deposit after World War II (between 1958 and 1965). Exploration was completed in 1974.

Possible gold reserves were analyzed, but first detailed data was obtained during 1989 and 1990 (Percival et al. 1990). The large presence of thallium minerals in the Alshar deposit gave rise to the interest of many geologist in the issue of application of thallium minerals to solar neutrino detection. Geologists who worked on various issues related to the Alshar deposit are Boev and Lepitkova (1990), Boev and Percival (1990), Boev and Serafimovski (1990, 1993), Boev and Stojanov (1993), Ivanov (1965, 1986), Jankovic (1960, 1979, 1982, 1993, 1994), Jezek (1912), Locka (1904), Johan et al. (1970, 1975), Laurent at al. (169), Balik, Stafilov (1993), Pavicevic and Rakic (1991), Pavicevic and El Goresi (1988), Palme et al. (1988), Pasava et al (1990).

REGIONAL GEOTECTONIC AND METALLOGENIC SETTING

The Alshar deposit is located in the Kozuf metallogenic area (according to Ivanov, 1986) or the Kozuf - Aridea metallogenic area (according to Jankovic, 1993). This metallogenic area is situated within Mount Kozuf volcanic complex on both sides of Macedonian - Greek border.

Ore mineralization is related to the Pliocene volcano-intrusive complex which developed after tectono- magmatic processes in the unstable Vardar zone and the strong crystalline mass of the Pelagonian massif during the formation of the Kozuf - Kilkis transverse structure during Miocene - Pliocene (Boev, 1988). Mineralization includes Cu, Pb-Zn, and Au in the central parts (Alshar and Smrdliva Voda) and Sb, As, Tl, Au, and Ba (Alshar) (Fig. 1).

The Kozuf volcano-intrusive complex which is present as intermediary to acidic igneous rocks developed in a basement composed of Triassic sediments, Jurassic ophiolite formations (gabbro-peridotitic) and Cretaceous carbonates and clastic sediments. Magmatic activity took place during the Miocene - Pliocene (6.5 to 1.8 m.y.) (Boev,

Fig.1. Regional geological setting of the Alshar deposit (from, Ivanov, 1988 modified by Jankovic, 1994)

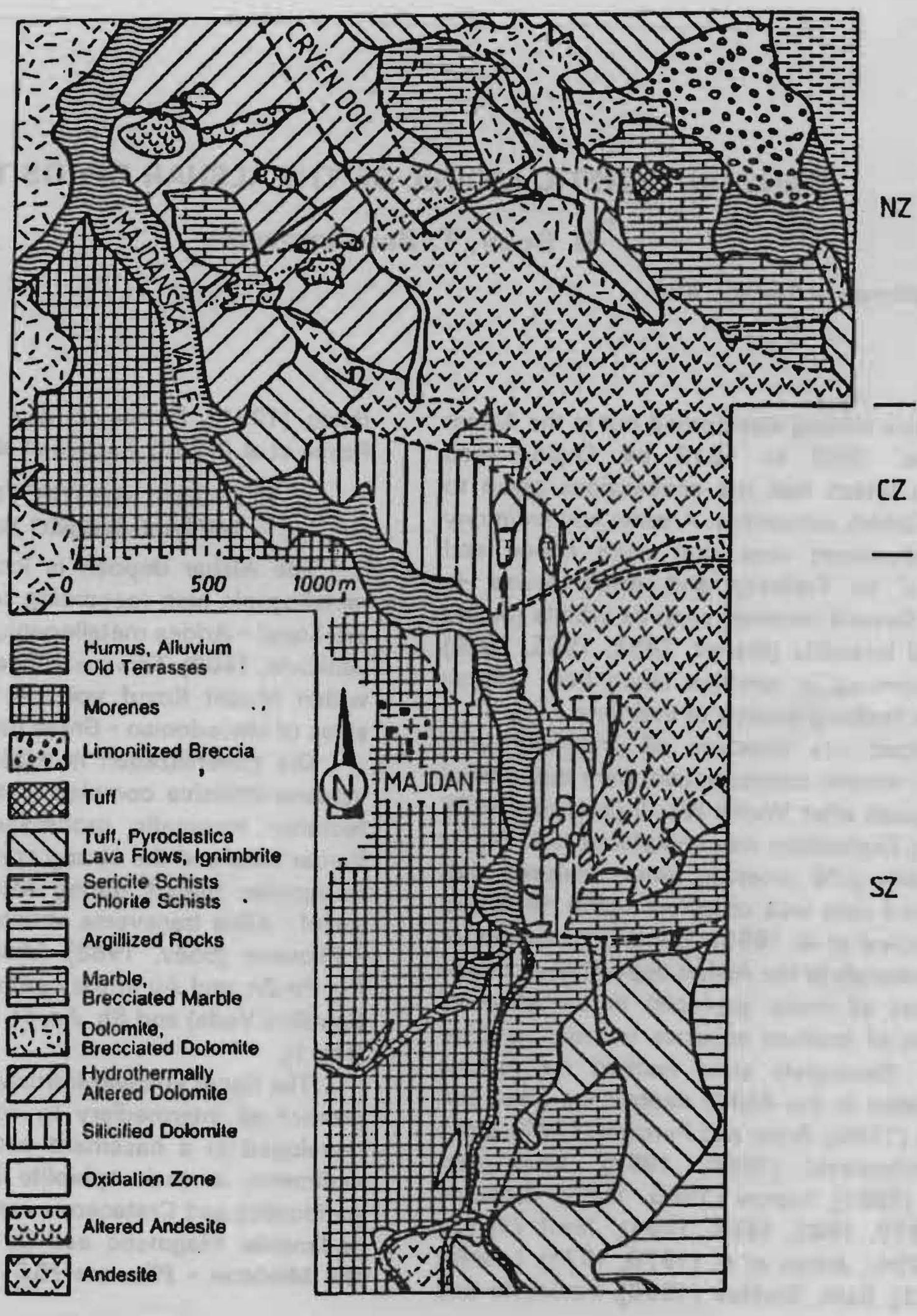

Fig. 2. Geological map of the Alshar deposit (Ivanov, 1986, modified by Boev, 1990)

1988, Kolios, 1980). Rocks are dacite-quartzlatitic to trachy-rhyolitic mainly enriched in LIL elements (Boev, 1988). Extrusive magmatic activity was intense and represented by various types of tuffs, breccias and lacustrine volcanic-sediments. The intrusive phase of the magmatic activity is represented by subvolcanic bodies which were entirely hydrothermally altered by later hydrothermal processes.

GEOLOGIC STRUCTURE OF ALSHAR DEPOSIT

The geologic structure of the Alshar deposit consists of rocks of different composition and age. They belong to the following geologic lithostratigraphic complexes (Fig. 2).

1. A complex of Pre-tertiary sedimentary and metamorphic rocks (dolomites, marbles and schists)

2. Tertiary (?) carbonate and Pliocene volcanic rocks and pyroclasts DOLOMITES are widespread in Alshar deposit. They are one of the environments in which metasomatic processes took place during the hydrothermal activity (the processes of deposition of ore- bearing materials).

The series of dolomites is probably the oldest stratigraphic unit in the geology of Alshar and underlies the marbles. One determination of the age carried out by fission tracke method gave value which corresponds to the Triassic (250 m.y.) (Lepitkova, 1995).

Correlation between marbles and dolomites

Table 1: Chemical composition of volcanic rocks from Alshar

	1	2	3	4	5	6
SiO_2	57.28	57.43	61.90	62.30	61.17	65.50
TiO_2	0.72	0.77	0.70	0.65	0.53	0.58
Al_2O_3	17.29	17.41	17.80	18.01	15.91	16.45
Fe_2O_3	5.60	5.84	4.60	4.80	4.68	3.43
FeO						
MnO	0.06	0.08	0.10	0.09	0.04	0.10
MgO	1.89	1.60	1.30	1.39	1.24	1.49
CaO	4.42	4.23	4.72	4.30	3.37	3.84
Na_2O	4.01	4.10	4.01	3.61	3.82	2.33
K_2O	5.60	5.70	4.30	4.10	0.24	3.50
P_2O_5	0.57	0.51	0.50	0.50		0.24
H_2O	2.30	2.30	0.85	0.88	4.77	6.79
SUM	99.74	99.97	100.78	100.63	98.31	98.97

1, 2 latites
3, 4 trachytes
5, andesites, 6, dacites

are present as normal stratigraphic relationships. Dolomitic series is represented by greysh-white to dark middium to small-grained crystalline dolomites. Iron oxides deposited in fracture systems and gave dolomites yellowish colours.

MARBLES are widespread in Pre-tertiary rocks. They are present as grey-white to white, in places bluish marble built of calcite grains of 0.5 mm in size. Marble mainly occurs as massive rocks but bedded in some parts. They are intersected by later white calcite veins in several places. The marble unit occurs as uncontrolled wrench fault blocks unevenly underlying the Tertiary rocks almost all over the area. The contact between marbles and tuffs in the south of the area is present as a mineralized irregular plane.

SCHISTS occur in two stripes of Triassic rocks along the eastern part of the Alshar area. Stratigraphic relationships between the schists and other Triassic rocks are not clear. Schists are silvery-grey to dark grey in colour. They consist of of quartz, sericite, feldspar and some chlorite. They possess lepidoblastic structure and pronounced schistosity with folding in some places.

The series of DOLOMITE-TUFFACEOUS SEDIMENTS is probably of Tertiary age. It unconformably overlies the Mesozoic basic rocks in the northern and western parts. They consist of dark- white to dark grey dolomites which contain variable amount of volcanic ash or tufaceous material. Hydrothermal alteration can be seen in part of the series which resulted in the yellowish to reddish colour of the rocks. They appear as banded sedimentary rocks and are very common. The relationships between the series and other members of the geologic structure in the field are not clear, but in one place (north of the part which contains antimony) volcano-sedimentary nature can clearly be noticed. The massive tuffaceous dolomites contain local intercalated sequances of small-grained tuff, volcanic ash and glass. The intercalations are several centimeters thick.

Most of the Alshar deposit is covered by tuffs of Tertiary age. The sequence of volcanic pyroclastic material consists of volcanic ashes, real volcanic tuffs, tuffaceous breccias and lacustrine tuffaceous materials. The material is part of the large Pliocene volcanic sequence in Mount Kozuf massif. Studies on petrochemical features of tuffaceous material indicate that its composition is consistent with latite delenitic volcanic material. The contact between the series of tuffs and the Tertiary tuffaceous dolomites and Pre-Tertiary rocks is represented by a noncomformable zone which can clearly be distinguished in the field. The zone which is 2 to 10 m thick is a mixture of unsorted detritic material with fragments of various size. Most probably there is normal stratigraphic sequence between the series of tuffaceous dolomites and that of tuffs due to the nature of volcanic activity. In many places the contact zone underwent mineralization processes which points to inception of ore mineralztion phase and the age of mineralization processes in Alshar. The tuffaceous series consists of volcanic rocks of various size and volcanic ashes. Occurrences of real lacustrine tuffs can be seen in several parts of the terrain (particularly in the southeast). They are thin layers with intercalations of clayey material.

VOLCANIC ROCKS

Volcanic rocks are widespread because the Alshar deposit is situated in the large Mount Kozuf complex. Two phases of volcanic activity in which volcanic rocks developed can be distinguished.

The first is older and probably of Miocene age (latest investigations carried out on individual relict materials from the Crven Dol site such as plagioclase determined age of 12 m.y. by the Ar/Ar method, Frantz, 1994). Subvolcanic bodies in the shape of dikes formed in several sites such as Alshar, Dudica etc. but were completely transformed and distroyed by later hydrothermal activity. Only in some places relicts of this old phase can be seen.

The second volcanic phase is younger and belongs to Pliocene. Most of the volcanic rocks formed in this phase are fairly fresh and favourable for detailed petrographic investigation. This volcanic phase is characterized by large explosion event in which a vast complex of pyroclastitic rocks built of tuffs, tiffaites and ignimbrites was formed. Products of the younger Pliocene volcanic phase covered the products of the older volcanic phase, whereas hydrothermal solutions completely transformed it. Based on detailed petrographic-petrologic investigation carried out in the terrain several types of volcanic rocks such as latites (trachyandesites), trachytes, andesites and dacites were determined (Fig. 3) (Table 1)

STRUCTURAL CHARACTERISTICS

Alshar deposit is situated on the Alshar - Radovish structure which has a NE - SW strike. This regional structure is clearly seen on satellite scanograms. It does not end in the Alshar deposit but continues to neighbouring Greece. Most of the Kozuf volcanism emerged along this structure and the Kozuf - Kilkis transverse structure from Miocene - Pliocene to Pleistocene.

Alshar deposit is located on the crosscut between this strucure and those with NNW - SSE to N - S strike and separate the Pelagonian block from the Vardar zone.

The structure with strikes N - S strike along the Majdanska Reka and those with NNW - SSE and NE - SW strikes can easily be distinguished. Most of them, however, can not be seen easily because they are covered.

The basic criteria in distinguishing these structures are the intensive hydrothermal alterations which took place along large discontinuities. Analysis of stratigraphic relationships between individual series and those of the relief and morphology of the Alshar block can also help to distinguish them.

ORE MINERALIZATION (TYPE AND BASIC CHARACTERISTICS)

Alshar deposit consists of several bodies and occurrences characterized by specific association of elements and minerals. It is the only depost which contains economic concentrations of thallium, antimony, arsenic and gold.

Thallium content ranges from 0.1% to 0.3% in some parts. The content of antimony amounts to 2.5%, whereas arsenic to 1.5%.

It should be mentioned that gold is not distributed uniformly. The largest gold presence was detemined in the so called jasperoid zones (in the south of the deposit where it amounts to 3 ppm).

Based on association of elemnts the following mineralization styles can be determined:

1. The first type is characterized by high Fe and S but low As and Tl concentrations.
2. The second type contains high Sb but low Fe and Tl concentrations.
3. The third type contains high As and S but low Tl concentrations.
4. The fourth type contains large amounts of As, S, Fe and Tl.

Several distinct morphostructural mineralization types can be distinguished as well.

1. Mineralized brecciated zones developed either along the contact between the subvolcanic

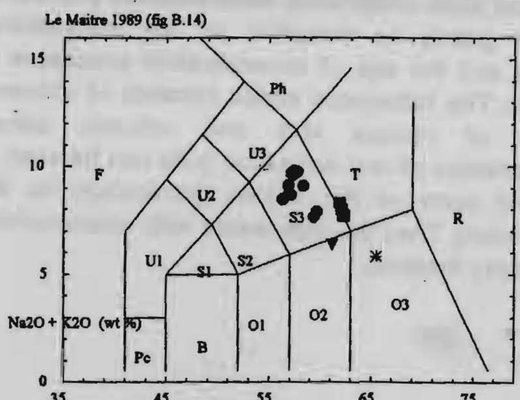

Fig. 3: Classification of volcanic rocks from the vicinity of Alshar (La Maitre, 1989)

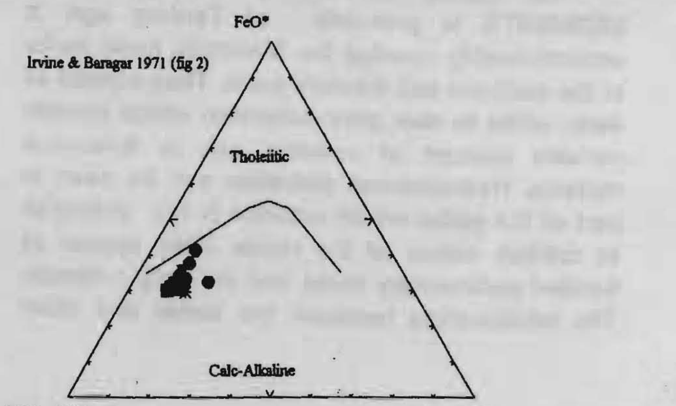

Fig. 4: Na_2O+K_2O-MgO-FeO diagram for the volcanic rocks from the vicinity of Alshar (Irvine and Baragar, 1971)

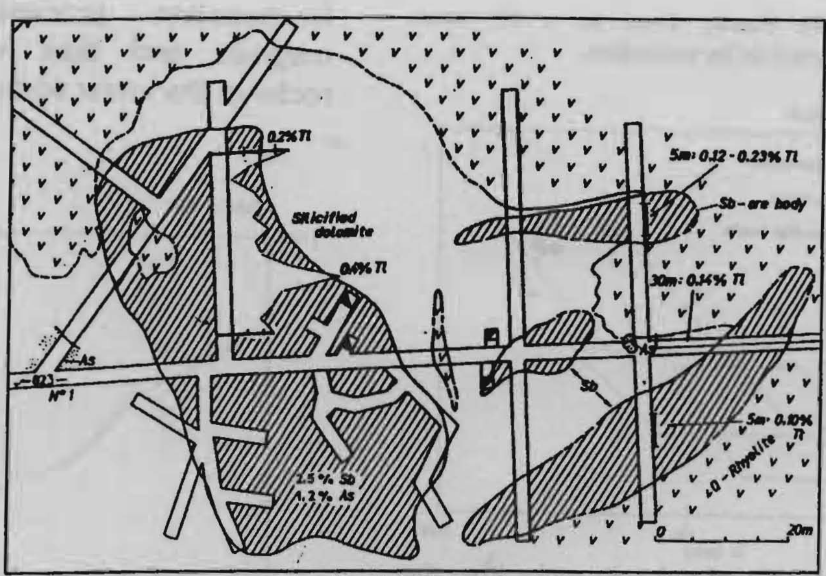

Fig. 5: Morphology of ore bodies in Alshar deposit (Geol. zavod. Skopje)

intrusions and dolomites, dolomitic tuffs or along fractured zones in carbonate rocks.

2. Massive sulphide mineralization (predominantly realgar) in carbonate rocks which passes into stockwork- disseminated.

3. Mineralizaed system of veins and fractures which occur in Tertiary tuffaceous and Triassic doomites.

4. Bedded sulphide mineralization in tuffaceous dolomites.

5. Impregnated mineralization (predominantly antimony) in which pyrite, marcasite and gold occur as

a. bedded bodies along the contact part of the volcanosedimentray series (tuffaceous dolomite or tuffs) and Triassic carbonate rocks,

b. in silicified volcanics and jasperoids.

ASSOCIATION OF MINERALS

The ore bodies in Alshar consist of a large number of minerals (primary and secondary). However, mineral composition of the deposit has not been investigated in detail particularly the primary (thallium) and the secondary.

Mineral paragenesis determined so far consists of: aragonite $CaCO_3$, arsenolite As_2O_3, arsenopyrite FeAsS, baryte $BaSO_4$, bernardite $TlAs_5S_8$, calcite $CaCO_3$, Cervanite Sb^{3+}, $Sb^{5+}O_4$, cinabarite HgS, dolomite Ca $Mg(Co_3)_2$, fibroferite $FeSO_4$ $(OH)\cdot 5\cdot H_2O$, goethite $FeSO_4(OH)\cdot 5\cdot H_2O$, gold Au, gipsum $CaSO_4\cdot 2\cdot H_2O$, hornesite $Mg_3(AsO_4)_2\cdot 8\cdot H_2O$, lorandite $TlAsS_2$, marcasite FeS_2, melanterite $FeSO_4\cdot 7\cdot H_2O$, orpiment As_2S_3, parapierotite $Tl(Sb,As)_5\cdot S_8$, pararealgar AsS, farmacolite $CaHAsO_4\cdot 2\cdot H_2O$, picotpolite $TlFe_2S_3$, picropharmacolite $H_2Ca_4Mg(AsO_4)_4\cdot 11\cdot H_2O$, pyrite FeS_2, quartz SiO_2, regenite $TlFeS_2$, realgar As_4S_4, rebulite $Tl_6Sb_5As_8S_{22}$, romeite (Ca, Fe, Mn, $Na)_2$(Sb, Ti $)_2O_6$(O,OH, F), rosenite $FeSO_4\cdot 4\cdot H_2O$, simonite $TlHgAs_3S_6$, starceite $MgSO_4\cdot 4\cdot H_2O$, stibiconite $Sb^{3+}Sb_2^{5+}O_6(OH)$, stibnite Sb_2S_3, native sulphur S, valentinite Sb_2O_3, vrbaite $Tl_4Hg_3As_8Sb_2S_{20}$, falcamanite and fiselite.

GENETIC ASPECTS

Based on data available obtained by investigation carried out by Boev, Serafimovski, 1992 and Jankovic, 1993 some aspects of the genesis in Alshar can be mentioned. Detailed information on the genesis of this low temperature hydrothermal deposit can be obtained by further field and laboratory investigation.

ORIGIN OF MAGMA

Data on this issue, particularly on origin of magma which formed the volcanic rocks of Kozuf, can be found in the papers of Boev (1988). Data indicates that magmatic sources are located in the border zone between continental crust and the upper mantle. The isotope $^{87}Sr/^{86}Sr$ ratio supprts this assumption.

Further investigation carried out by Lepitkova (1995) proved the assumptions given by Boev. Namely, the values determined for the isotope $^{87}Sr/^{86}Sr$ ratio are ithin 0.708568 and are very close to those that Boev (1988) gave about the volcanic rocks of Mount Kozuf.

Diagram 6 shows that data plot in the continental plate basalts or the so called within plate basalts.

Chemistry of magmas related to continental rift zones is conditioned by heterogeneity of mineral and chemical composition of the source located in the mantle, the degree of partial melting, depth of melting, amount of magma which came to the surface etc. The main problem in the study of continental magmatism is estimation of the role of the mantle in the genesis of primary magmas.

Most probably the genesis of the volcanic rocks from the vicinity of Alshar and those in Mount Kozuf can be interpreted as within the evolution of the Vardar zone as a rift zone, repeatedly occurred in its evolution.

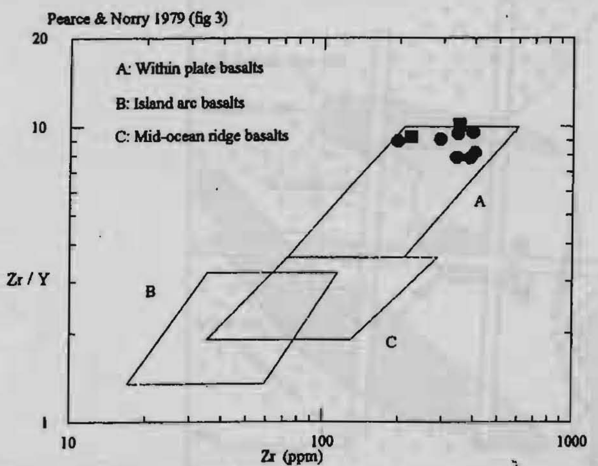

Fig. 6: Relashionship of volcanic rocks from the vicinity of Alshar to individual geotectonic zones (Pearce and Norry, 1979).

Table 2: Rare Earth in volcanic rocks from Alshar (in ppm)

La	70.8	78.5
Ce	140	157
Nd	50	63.
Pr	7.5	7.8
Sm	8.13	8.54
Eu	1.7	1.71
Tb	0.68	0.69
Dy	3.56	3.80
Ho	1.1	1.4
Yb	1.85	1.84
Tm	0.28	0.32
Lu	0.28	1.84
Hf	5.14	5.93
Ta	0.84	0.82
W	4	3.2
Th	31	34
U	9.1	9.7

Data related to the presence of REE in volcanic rocks in the vicinity of Alshar (determined as latitic rocks) (Table 2) shows that there was fairly large enrichment in rare earths and points to the processes of geotectonic evolution in the area. The enrichment in light earths relative to heavy rare earth differentiates the continental formations from toleitic basalts and makes them similar to alkali volcanic rocks from the continental rift zones. Poorly pronounced minimum of europium (Fig. 7) as well as the better pronounced minimum in Dy point to the fractionation processes in primary magmas and their contaminations by rocks of the lower and upper crust.

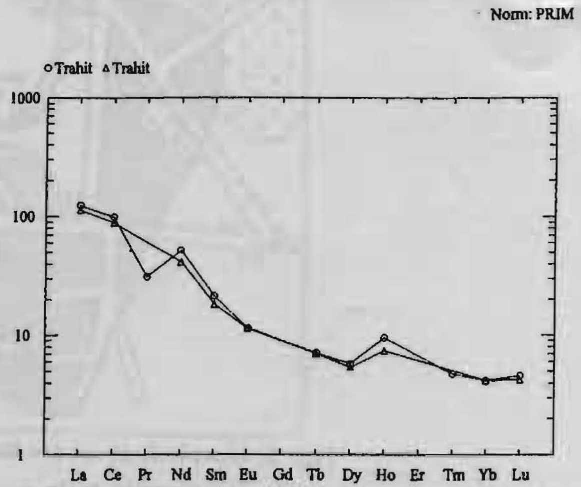

Fig. 7: Element distribution of rare earths in volcanic rocks from Alshar

1. Source of Ore Metals

Based on isotope composition of lead (Frantz, 1992) it can be inferred that lead in hydrothermal solution originates from surrounding igneous rocks. Antimony, arsenic and thallium can have the same origin, their ultimate source being calc-alkaline magma which produced the large volcanic complexes in the area. Ultimate gold source is not clear but it can be assumed that it was mobilized from the surrounding ultramafic rocks.

Isotope values of sulphur in sulphide minerals from Alshar range from +0.351 to -5.601 (Serafimovski, Boev, 1992). This data points to a unique source and endogene origin (Table 3).

Origin of ore-bearing solutions

Origin of ore-bearing solutions can not be judged on direct measurements and investigations but must be reconstructed according to direct exploration and investigation. In order to get information about the origin of ore-bearing solutions it is necessary to know the origin of waters. It was considered that juvenile waters have great influence on hydrothemal solutions. Today examination on isotopic composition of H/D, O, C etc. have determined that waters participating in hydrothermal solutions also have other origin (conatic, meteoric water etc.).

Results of examinations on isotope composition of $^{12}C/^{13}C$ and $^{16}O/^{18}O$ in calcite from Alshar deposit indicate certain fractionation, particularly enrichment in heavy isotope of oxygen but impoverishment in the same isotope with carbon which points to the high participation of meteoric waters in the composition of hydrothermal ore-bearing fluids from which ore mineralization developed in Alshar deposit.

Table 3: Isotope composition of sulphur in sulphide minerals of Alshar

No	Probe	Mineral	δS^{34} %	Variation S^{34} %
1.	14564	stibnite	+0.351	+0.351 do -5.601
2.	14565	stibnite	-0.337	
3.	14566	stibnite	-0.419	
4.	14567	stibnite	-4.728	
5.	14568	stibnite	-5.600	
6.	14569	stibnite	-1.750	
7.	14571	stibnite	-5.220	
8.	14576	stibnite	-3.560	
9.	14572	realgar	-1.640	-1640 do -3.770
10.	14573	realgar	-3.770	-
11.	14574	orpiment	-3.690	-
12.	14570	marcasite	-6.840	

Composition and temperature of solutions

Fluids are composed of large amounts of antimony, arsenic and thallium. Over 6.000 tonnes of antimony, 6.000 tonnes of arsenic and about 180 tonnes of thallium were deposited in ore bodies determined so far (gold content has not been determined yet). Large silica contents were also brought to several parts of the deposit by hydrothermal solutions.

Tempertaure in ore-bearing fluids ranges from 280/250 and 120°C or a little higher. Homogenization temperature of fluid in realgars from Crven Dol was determined from 144 to 170°C (Beran, 1990).

Based on data about fluid inclusions it can be inferred that salinity of solutions ranged from 7.9 to 12.9 equivalent weight units per sodium chloride. Beran (1990) mentions the presence of possibile hydrocarnonate composition of fluid inclusions in realgar from Crven Dol, but data seems to be insufficient.

Metalliferous hydrothermal fluids were acidic at the beginning of their development with high sulphur fugasity. The small occurreneces of native sulphur and traces of solfatara activity point to acidic hydrothermal fluids in Alshar.

Transportation and Deposition

Thallium together with antimony and gold were probably transported as complex ions (bisulphides) from acidic to slightly alkaline fluids of low salinity and reduction conditions.

Deposition of metals as sulphides and sulphosalts was probably due to saturation due to temperature decrease and change in chemical properties of solutions in interaction with surrounding rocks (mixing with other fluids is not important in the case of Alshar but should not be neglected).

The role of secondary boiling in deposition of ore-bearing metals in Alshar has not been defined. Hydrothermal fluids probably boiled at temperatures from 120 to 160°C and shallow depths (lower than 500 m) releasing vapour, CO_2 and H_2S which resulted in an incresae of pH value and ore deposition. This certainly needs further investigations.

Deposition of mineralization in Alshar is closely related to lithogeochemical features of the environment through which ore-bearing fluids passed. Entering reactive lithologic environments such as dolomite, would result in rapid deposition of ore mineralization due to interaction with hydrothermal fluids. In this manner dolomite was a barrier for the deposition of mineralization for acid hydrothermal fluids with free sulphur ion. Ore bodies formed in such processes are characterized by short vertical interval and are located in close proximity to the contact with intrusive magmatic bodies. Alternatively strongly silicified dolomites, volcanics and tuffs were environments which were slightly reactive to ore- bearing fluids. Such environments made possible fast movement of ore-bearing fluids along fault structures and brecciated zones. Deposition of mineralization in such environments took place in an area of hundreds of meters. Ore bodies mainly occur in the shape of elongated lenses of disseminated mineralization located close to magmatic intrusions. In these two environments depositon of ore took place in conditions of pyrite stability.

Alshar deposit did not develop by a single hydrothermal system and based on available knowledge it can be inferred that at least two major hydrothermal sub-systems existed.

A sub-system in the central and south part of the deposit (antimony and aresenic ore bodies).

This hydrothermal system includes Au, Sb, As, Tl, Hg, Ba and traces of Ag, Pb, Cu, Zn, as well as increased silica contents of various mineral types deposited in different periods of hydrothermal processes. Deposition of iron sulphides from coloid solutions was followed by deposition of arsenopyrite, antimony-lead sulphosalts, auripigmentum, realgar and thallium sulphosalts. The place of gold deposition and its relationship to other sulphides has not been investigated. Ore bodies developed from-poly phase solutions in a time period of several cycles.

The Crven Dol sub-system consists of As, Tl, Fe, S mineralization with traces of gold and mercury with minor silica minerals. Ore bodies formed in dolomites and volcanics along the contact with sub-volcanic intrusive bodies. Some small ore bodies developed by rapid ejection of large amounts of ore-bearing components from the hydrothermal systems which resulted in development of massive realgar ore. Vertical extension of mineralization is from 20 to 30 m.

It can be said that common features of both sub-systems are:

- poly phase mineralization and impulses of ore-bearing solutions due to fractionation,
- coloform textures, particularly with iron sulphides and their gradual enrichment in arsenic, antimony and thallium locally.

Events Accompanying the Development of Mineralization

Separation of the main mineralization mass did not put an end to all phases of hydrothermal ore mineralization. There were certain events which accompanied the final ore mineralization in the deposit. They are halos of scattering, hydrothermal altrations and zonal distribution.

Halos of scattering

Large number of elements occurring in incresaed concentrations have been established in, above and round the major ore bodies with Sb, As, Tl etc.

The geochemical association of elements in the vicinity of Alshar was defined by distribution of elements such as: arsenic, antimony, thallium, mercury, gold, silver, barium, lead, zinc and copper. This association of elements is characetristic of low temperature (epithermal) deposits of arsenic, antomony and gold.

Distribution of these elements in different lithologic alteration styles is inadequate. Analyses show that the contents of individual elements amount to 700 ppm As, 50 ppm Sb, 6 ppm Hg, 27 ppm Tl, 50 ppm Zn and 20 ppm Pb. Cu amounts to 50 ppm, whereas Ba to 250 ppm.

Selenium content is relatively low and amounts to 5 ppm. It should be mentioned that nickel and cromium contents are relatively high and amount to 100 ppm and 400 ppm respectively. The high nickel and chromium contents are due to high assimilation of these elements from ultrabasic rocks located close to the deposit. Gold content in the deposit varies depending on the mineralization style. It is highest in the so called jasperoids or silicified tuffs where it amounts to 3 ppm.

Alteration of surrounding rocks

Alteration of different degree and intensity is very common during hydrothermal processes of ore mineralization. Investigation has proved that alteration of rocks in Alshar deposit was versatile and took place in a large area.

Silification in the central and south parts was the most important hydrothermal alteration. It appears as quartz veins, stockwork or jasperoids (silicified tuffs). Silification is represented by microcrystalline quartz which either disseminates or completely replaces primary rocks.

Argillitization is also very common. It is located in Tertiary tuffs and igneous rocks and parts of tuffaceous dolomites. It is characterized by large presence of clay materials developed as a result of feldspar transformation. Occasionally it is represented by several meters thick clayey zones. This means that there is a complete replacement of primary rocks by secondary clayey materials. These secondary clays contain occurrences of hydrothermal quartz and sulphide minerals such as pyrite and marcasite. Alterations are zonal starting from a silicified core which laterally grades into argillitized rocks. The alterations are mixed locally.

Rocks also underwent calcitization which was post-ore and can be seen as veins or large calcite aggregates.

Sericitization is another hydrothermal alteration which took place in the area. It can hardly be distinguished because it occurs in association with argillitization.

Chloritization took place in some places. It occurs in femic minerals of primary volcanic rocks and tuffs.

Apart from hydrothermal alterations, the phenomena of supergene mineral transformation can be distinguished as well. They are due to

- iron sulphide oxidation
- argillitic alteration due to influence of sulphuric acid which forms at the expense of sulphide minerals
- alteration of primary volcanic and other rocks due to climate factor.

Oxidation of sulphide minerals took place extensively in the whole area and resulted in occurrence of yellowish and brown limonite and jarosite. The occurrence of powdery limonites and ochers as well as manganoan oxides in association with clayey products mark the structural mineralization zones. Sulphide arsenic and stibnite minerals oxidate in yellowish green arsenates and yellowish oxides.

Occurrences of so called green rocks can easily be distinguished in several places in the field developed as a consequence of strongly pronounced alteration.

Ore Mineralization Zoning

The major metals present in the Alshar

deposit are Sb, As, Tl, Fe and Au accompanied by minor Ag, Hg and Ba as well as traces of Pb, Zn, and Cu. The spatial distribution of these metals and concentration indicate certain zonality.

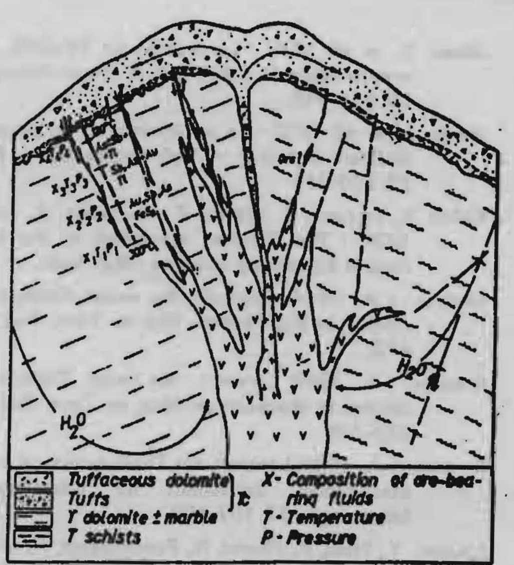

Fig. 8: General model of the mettalogenic environment of the Allchar deposit (Jankovic, 1990)

In the north a zone rich in As and Tl but poor in Au and Sb was distinguished.

In the central part a zone which contains the largest concentration of Sb was distinguished. The zone is located in the so called jasperoids in which besides antimony there are increased As, Au and Fe concentrations.

In the south a zone with the largest Au was distinguished. The concentrations of other metals such as Sb and As are very low. Gold mineralization is located within the series of silicified tuffs and dolomites.

Successive Order in Tectonomagmatic and Ore-bearing Processes

Information presented so far leads to the conclusion that development of Alshar deposit was a complicated and long process closely related to the Mio-Pliocene tectonomagmatic and mineralization phase.

In general, the hydrothermal phase of the occurrence of Alshar deposit began with high temperature alteration phase followed by ore mineralization phases. Hydrothermal alteration intensively affected silicates, carbonates environments and mixed silicate-cabonate parties. Hydrothermal alterations are present as silification, sericitization-argillitization-kaolinization etc. The intensity of alteration in surrounding rocks varies, but it can be said that in some parts of the deposit they were so stong that the primary rock was completely destroyed.

Ore mineralization began by separation of minerals of the high temperature sulphide paragenesis represented by arsenopyrite, pyrite, melnikovite, marcasite, maucherite etc. Most of the minerals in this sulphide phase developed from geo- mixutres which is indicated by their structures and presence of malnikovite. At the beginning development of ore minerals in this paragenesis took place along crackle-joint areas. Later metasomatic processes played the major role when intensive thrusting of carbonate minerals, first of all marcasite (seen as massive marcasite bodies), pyrite, melnikovite etc.

After separation of minerals from the first minerlaization phase a change in physical and chemical conditions took place (temperature and presure drops) favourable for the formation of ore minerals of the second phase in which dominate stibnite accompanied by falcmanite, phizelite, pyrite etc. Precipitation of stibnite took place mainly in void joint spaces predominantly along silification zones and carbonate environments. Fairly quiet conditions of crystallization and favourable environment of precipitaion of ore minerals in hydrothermal solutions made possible formation of large stibnite crystals of over 10 cm. in size. During intramineralization tectonic phases part of stibnite was fractured, brecciated and additionally cemented mainly by realgar which was a product of later mineralization phase.

The third mineralization phase is characterized by massive separation of As - Tl minerals such as realgar, auripigmentum, lorandite, vrbaite, alsharite, picopolite etc. Separation of these minerals took place mainly in intensively hydrothermally altered carbo-carbonate environments with prevailing metasomatic mineralization processes.

The hydrothermal phase ends with relatively low temperatures by separation of baryte, calcite, native sulphur, calzedony etc.

Supergene conditions are characterized by development of large number of minerals with low extensity and intensity. Such are valentinite, senarmonite, cermesite, servantite, epsomite, melanterite, gypsum, Fe - hydoxides etc.

It can be inferred that in terms of conditions of development, the environment of deposition, association of elements and minerals, and the relation to Pliocene magmatism Alshar deposit belongs to hydrothermal volcanogene deposits formed of highly differentiated hydrothermally solutions at relatively low temperatures (below 200°C) mainly in epithermal phase of hydrothermal phase. Mineralization partially formed by filling of empty crackle - joint spaces and a large part by metasomatosis in carbonate environments which were previously hydrothermally altered. Three mineralization styles formed in this manner: vein, disseminated and metasomatic.

Based on available knowledge it can be said that metasomatic ore bodies are widespread although in the part of the deposit with predominant stibnite minerlization.

REFERENCES

Balic, T.Z., Stafilov, T., 1993 : Distribution of thallium and the ore genesis at Crven Dol locality in Alshar International Conference On Solar Neutrino detection Skopje, 1993

Beran, A., Gotzinger, M., Reick, B., 1990 : Fluid inclusions in realgar from Alshar International Symposium on Solar Neutrino Detection, Dubrovnik, 1990

Boev, B., 1988: Petrolo{ki, geohemiski i vulkanolo{ki karakteristiki na vulkanskite karpi od Ko`uf Planina , Doktorska disertacija, [tip 1988.

Boev, B.,Lepitkova, S., 1990 : Petrological features of the volcanic rocks from the vicinity of Alshar, Macedonica Geologica, 1990

Boev, B., Percival, T., 1990 : As-Tl-Sb-Hg-Au-Ba-Mineralization Alsar District, Yugoslavia : A Unique type of Yugoslavian ore deposit International Symposium on Solar Neutrino Detection, Dubrovnik, 1990

Boev, B., Serafimovski, T., Petrov, S., 1990 : Hidrotermalni promeni vo del od nao|ali{teto Al{ar, XII Kongres na geolozite na Jugoslavija, Ohrid, 1990.

Boev, B., Stojanov, R., Denkovski, G., 1993 ; Geology of the polymetallic deposit Alshar, Macedonia, Geologica Macedonicva, 1993

Boev, B., Serafimovski, T., Milosavlevic, B., 1993 : Trace elements in some minerals from Alshar deposit, Macedonica Geologica, 1993

Frantz,E., 1994: Minerologische, geohemische und isotopengeochemishe Untersuchungen der As-Tl sulfide in der Lagerstatte von Allchar. Doctor dissertation, Mainz, 1994.

Ivanov, T., 1986 : Allshar the richest ore deposit of Tl in the world Proc. "The feasibility of the solar neutrino detection with 205 Pb by geochemical and accelerator mass spectroscopical measurements" GSI-86-9 Darmstad.

Jankovic, S., 1960 : Allgemeine Characteristika der Antimon Erzlagerstatten Jugoslawiens., N.Jb.Miner. Abh. 94.

Jankovic, S., 1979 : Antimony deposits in the Southeastern Europe. - Zav. Geol. geof. istr., A 37:25-48, Belgrade.

Jankovic, S., 1988 : The Allchar Tl-as-Sb deposit, Yugoslavia, and its specific metallogenic features. - In : Nolte, E., et Pavicevic, M., (ets): Solar Neutrino Detection, Proceed. Int. Conf. on Solar Neutrino Detection, with Tl 205 and Related Topics, North-Holland, Amsterdam, p. 286.

Jankovic, S., et Jelenkovic, R., 1990 : General metallogenic features of thallium mineralization in the Alsar deposit. Int. Simp. on Solar Neutrino Detection with Tl 205. Yug. Soc. Nukl. Elem. Part. Phys., Dubrovnik, pp. 32-35 (abstract).

Jankovic, S., 1993 : Metalogenic features of the Alshar epitermal Sb As Tl Au deposit. N. Jb. Miner. Abh. 166, 25 41 Studgart,1993.

Jezek, B., 1912 : Vrbait, ein neues Thallium Mineral von Allchar in Macedonian. - Z. Krystallogr. 51: 3, 365-378.

Johan, Z., et all 1970 : La picotpaulit TlFe2S3, une novelle espece minerale. - Bull. Soc. fr. Miner. Petrog. Cristallogr. 93: 544-549.

Johan, Z., et all 1975 : La parapierrotite, un nouveau mineral thallifere d Alchar. - Tschermarks Miner. Petrogr. Mitt. 22: 200-210.

Kolios, N., inocenti, F., Maneti, P., Paccerillo, A., et Guliano, O., 1980 : The Pliocene volcanism of the Voras Mts. (Central Macedonia, Greece). - Bull. Volc.

Krenner, J. A., 1984 : Lorandit, ein neues Thalliummineral von Allchar in Macedonien. Mat es Term Tud Ertesito, 12, 473.

Krenner, J. A., 1985: Lorandit , ein neues Thalliummineral von Allchar in Macedonien. Mat. es Term Tud Ertesito, 13 258-265.

Krenner, J. A., 1989: Lorandit, ein Thalliummineral von Allchar in Macedonien. Zeitscheift fur Kristallographie und Mineralogie, 27, 107-109.

Laurent, Y., Picot, P., Pierrot, R., Permingeaut, F., and Ivanov, T., 1969: La raguinite, $TlFeS_2$, une novelle minerale et le probleme de l allcharite. Bulletin de la Societe francaise de Mineralogie et Cristallographie, 92, 38-48.

Lepitkova, S., 1995 : Petroloski karakteristiki na vulkanskite karpi od okolinata na naogalisteto Alsar so poseben osvrt na izotopite na olovoto, Mag. Teza, Stip, 1995.

Locka, J., 1904 : Chemische Analyse des Lorandit von Allchar in Macedonien und des Clandetit von Szomolnok in Ungarn Z.Krist. Miner. 39: 520.

Palme, H., Pavicevic, M.K., Speittel, B., 1988 : Major and trace elements in some minerals and ore from Crven Dol, Alshar, Solar Neutrino Detection, Proceed. Int. Conf. on Solar Neutrino Detection, with Tl 205 and Related Topics, North-Holland, Amsterdam, 314, 319.

Pasava, J., Petlik, F., Stumpfl, E., Zemann, J., 1989 : Bernardite, a new thallium arsenic from Allchar, Macedonia, with a determination of the crystal structure, Miner. Mag. 53, 531-538

Pavicevic, M., 1986 : Lorandite from Allchar as solar neutrino geochemical detector. Proc. "The feasibility of the solar neutrino detection with 205 Pb by geochemical and accelerator mass spectroscopical measurements" GSI-86-9 Darmstad.

Pavicevic, M., El Goresy, A., 1988 : Crven Dol deposit in Allshar : Mineralogical investigation, chemical composition of Tl minerals and genetic implications. Solar Neutrino Detection, Proceed. Int. Conf. on Solar Neutrino Detection, with Tl 205 and Related Topics, North-Holland, Amsterdam, 297-300.

Pavicevic, M., Rakic, S., 1991: Investigation of Allshar lorandite, composition by EMPA and PIXE. Port. Miner, 59. Bh.1.150-151, Stuttgart