UNESCO
IGCP Project No 356

PLATE TECTONIC ASPECTS OF THE ALPINE METALLOGENY IN THE CARPATHO-BALKAN REGION

PROCEEDINGS OF
THE ANNUAL MEETING
SOFIA, 1996

Volume 1

University of Mining and Geology "St. Ivan Rilski", Sofia

IGCS UNESCO

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Volume 1, pp. 63-74

GENETIC MODEL OF THE BUCHIM PORPHYRY COPPER DEPOSIT, REPUBLIC OF MACEDONIA

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Abstract

The paper presents data about geology, geochemistry, structure and genesis of the Buchim copper which has numerous specific features. The basic characteristic in the deposit is the relationship between porphyry mineralization to Tertiary subvolcanic intrusions of latitic and latitic-andesitic composition. Intrusion of these rocks took place in Oligo- Miocene (24 to 27 m.y.) during the period of intensive tectonic-magmatic and mineralization processes. Primary copper mineralization is located around magmatic cross-cuts (0.3 % Cu, 0.3 to 0.5 ppm Au). Its development was preceded by intensive hydrothermal alterations of surrounding rocks.

Investigation of processes which resulted in the occurrence and spatial distribution of porhyry mineralization in the Buchim deposit was carried out by a general genetic model of development of ore deposits by these complicted hydrothermal porhyritic systems. The genetic model includes origin of magma, ore metals and hyrothermal solutions, physo- chemical features of solutions, separation of components as well as occurrences which followed the formation of ore mineralization. The paper gives new data about isotopic and investigations of gas-liquid inclusions, rare elements and elements of rare earths, mineral associations, types of alteration etc.

INTRODUCTION

The Buchim porphyry copper deposit is situated in the bordering area between the Serbo-Macedonian massif and the Vardar zone. In terms of its metallogeny it belongs to the Lece - Chalkidi metallogenic zone. Its spatial location and conditions of development are very similar to the Gerakario deposit in Greece and can be correlated with other porphyry deposits in the Lece - Chalkidi zone which are not in close paragenetic-genetic relationship with the small subvolcanic- volcanic intrusions of the Tertiary calc-alkaline magmas such as the Tulare, Borov Dol, Vathi, Pontokerasia and several other deposits. Only Buchim is in the process of exploitation. Its annual production amounts to 4 000 000 tonnes of ore with mean content of about 0.3 % Cu and 0.35 ppm Au. In terms of its output and ore reserves determined (approximately 100 m.t.) it is a small porhyry deposits. It should also be mentioned that this is a characteristic of all porphyry deposits determined in the bordering area between SMM and the Vardar zone or the Lece - Chalkidi zone. Estimated reserves do not exceed 100 to 150 million tonnes of low grade ore with accasional occurrences of gold and silver and molybdenum locally.

LOCATION OF THE BUCHIM DEPOSIT

The Buchim deposit occupies the northern parts of the Buchim - Damjan - Borov Dol ore district or the south parts of Buchim ore field. Spatially it belongs to the Buchim block which as a smaller structural-tectonic unit belongs to the Serbo-Macedonian massif.

The deposit is situated 10 kilometers west of the town of Radovis (about 120 SE of Skopje) close to the village of Buchim. The mine is connected to the Stip - Radovis main road by 3.5 km asphalt road. In terms of its geomorphology the vicinity of the deposit is characetrized by slightly corrugated relief with Vranjak - peak 783 m as the most striking part.

EXPLORATION AND INVESTIGATIONS CARRIED OUT

Exploration in the Buchim deposit and its vicinity dates before World War II as evidenced by old activities (level entries) found in the western parts of the Central Del ore body. Bulgarian and Italian experts made several shallow adits (down to 10 m) but no technical data has been found.

Systematic exploration of copper mineralization in the Buchim area started in 1955 by the geologic staff of the Zletovo Mine. Geologic exploration included 4 drill-holes to 800 m in depth. Data from exploration drill-holes gave mean copper content of 0.35 % Cu (Bogoevski and Srdjanovic, 1955) and was considered as unimportant at that time. Further exploration was carried out from 1960 to 1962 by the staff of Geoloski Zavod in Skopje. Exploration drill-holes gave mean content of 0.3 % to 0.4 % Cu which coincided with earlier data.

Detailed exploration was carried out in 1966 and 1971. Data analysis was completed by the end of 1971 and a detailed report was given by Culev et al. in 1972. Based on data about the amount and quality of mineral raw material a technical - economic study and investment programme for putting the mine into production were made by the American firm Mc Kee and later by Rudarski Institute from Belgrade. The mine started production in 1979 and has been in operation since then. It is the only copper deposit in the Lece - Chakidiki zone in operation.

Mineralogic, petrologic, structural-geologic and metallogenic investigations were also carried out. The most extensive are those of Ivanov (1966, 1982), Petkovic (1968, 1984), Velickovic (1974), Markovic (1974), Djordjevic, Karamata (1976), Mudrinic and Petkovic (1974), Blecic (1974), Zaric (1974), Culev (1976), Pavicevic and Rakic (1982), Cifliganec (1982, 1987, 1992), Hrkovic (1985), Stojanov and Serafimovski (1990), Serafimovski (1990, 1993), Boev et al. (1992), Cifliganec et al. (1994) et al.

GEOLOGIC COMPOSITION OF THE DEPOSIT

Geologic composition of the Buchim deposit consists of Precambrian metamorphic (gneisses, micaschists and amphibolites) and Tertiary rocks (Fig. 1).

Gneisses are the most common lithologic members which are the most favourable lithologic environment for the deposition of ore mineralization. Several alternating varieties of gneisses are determined according to their mineral composition: biotitic, amphibole-biotitic, micas, metasomatic etc. Augengneisses and augen-banded gneisses are very common varieties. Amphibolitic lenses and amphibolitic schists also occur within the series of gneisses. Tertiary magmatic rocks are present as several latitic subvolcanic-volcanic crosscuts and andesite-latites around which three ore bodies are lineated (Fig. 1) which points to direct relationship of the magmatism and mineralization in the deposit. Apart from mechanical dislocations individual cross-cuts are charactrized by hydrothermal altrations.

Spatially and paragenetically porphyry copper mineralization is related to latites and latite-andesites. They occur as small subvolcanic intrusions (dikes and necks) distributed NNW - SSE and NE - SW along fault structures. They are volcanic rocks with pronounced holo to hipocrystalline porphyritic structure and massive texture. Phenocrystals are represented by intermediary plagioclase, potassium feldspar (sanidine) and femic minerals (hornblende and biotite). The groundmass is holo to hipocrystalline and comprises 56 to 66 % of the total rock mass. The age of the rocks ranges from 27.5 to 24.5 m.y. (Stojanov and Serafimovski, 1990).

STRUCTURAL CHARACTERISTICS

The central parts of the Buchim block or the vicinity of the deposit consists mainly of low grade compressive structures present as folds and foliation planes in metamorphs. Part of these structural forms probably represent product of processes which led to folding during the phase of intruding of Tertiary magmatic structures in subvolcanic level. Based on data reported by Cifliganec (1987) obtained during field observations fold shapes do not indicate direct relationship to mineralization, whereas foliation in gneisses is in close relationship to the shape of the Centralen Del ore body. In addition to compressive structures, disjunctive structures controlling the spatial distribution of magmatism and mineralization in the area also comprise part of the structure in the Buchim block. The disjunctive succession mainly consists of lower fractures, fracture zones and various crackled systems.

These fault structure most often have NNW - SSE and NNE - SSW trends and intersect forming knots which served as supply channels for magmatism and mineralization. These processes are clearly pronounced in the vicinity of Buchim and the Kalapterovci - Crn Vrv - Kosevo strike where latitic and trachyrhyolitic subvolcanic facies are mainly related to the intersection zones.

Fracture zones in the area are present as rupture systems of NW - SE strike, ocassionally E - W with intensive mylonitization along them as well as occurrences of areas with schistosity. Such relatively well pronounced fracture structures are revealed in the Buchim open pit.

Joint rupture systems are intensively developed in close proximity to dike intrusions and most commonly have a periclinal dip relative to their central parts. They are mainly shear , tension and relaxation joints the most common being shear joints and relaxation joints in terms of their mineralization.

A particular feature in the structural-morphostructural composition of the Buchin block is the absence of morphologically pronounced structural forms such as volcanic domes, calderas et al. as well as the presence of smaller size ring structures (several hundreds of meters to 1,5 km in size) developed as a result of dike intrusions into subvolcanic level. These volcanic structures, according to Petkovic et al. (1986) are similar to those of the ore bodies in the tectono- magmatic

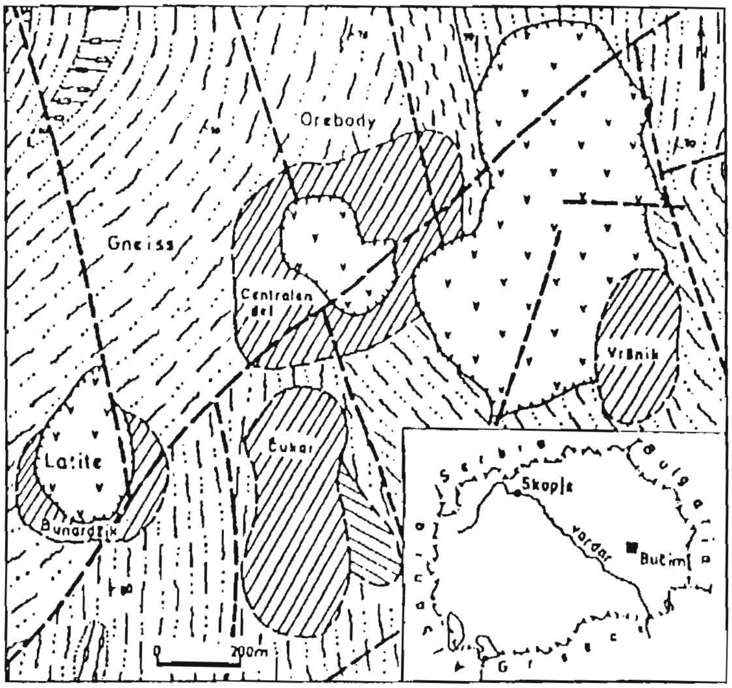

Fig.1. *Geological map of the Buchim deposit*

structures (in the dikes).

Morphostructural analysis determined such type of structures in the vicinity of the Buchim deposit and in the vicinity of Kalapetrovci, Crn Vrv and Kosevo.

Cicular-elliptical compressive ring-like structure of about 1.3 km in diameter with slight NE - SW extension was discovered by airplane imagery analysis north of Cukar (peak 678) in the area of the Buchim ore body. It is formed due to tectono-magmatic processes and conditioned by mechanical intrusion of latite dike into subvolanic level (Serafimovski, 1990).

Typical small size circular-concentric ring-like structures (several hundreds of meters in diamter) developed in the intersection of activated faults in which latitic dikes intruded the subvolcanic level were determined in the area of Bunardzik and Vrsnik. The rim parts of these structural forms consist of gneisses and the central parts consist of latitic crosscuts. Detailed geological investigations determined that with respect to their mineralization the areas round the dikes are particularly interesting.

TYPE OF ORE MINERALIZATION AND MORPHOLOGY OF ORE BODY

Based on data of detailed geological exploration copper mineralization was determined in an area of 1.5 - 2 km to 300 m in depth. It is located in four ore bodies: the Centralen Del, Bunardzik, Vrsnik and Cukar ore bodies (Fig. 1) of which the Centralen Del ore bodies is the most important. The presence of three types of copper

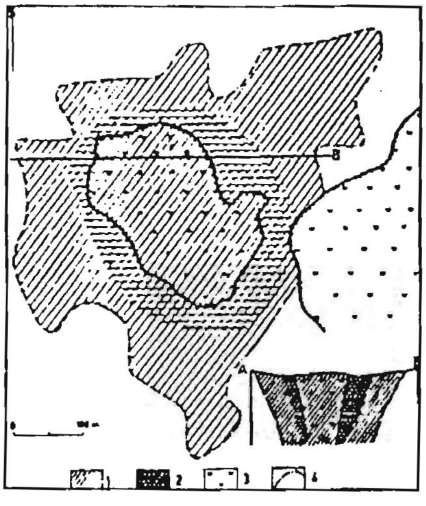

Fig. 2 *Geologic plan and cross-section through the Centralen Del ore body, Buchim deposit (Cifliganec, 1987); 1,2. Ore-body; 3. Andesite; 4. Outline of ore body*

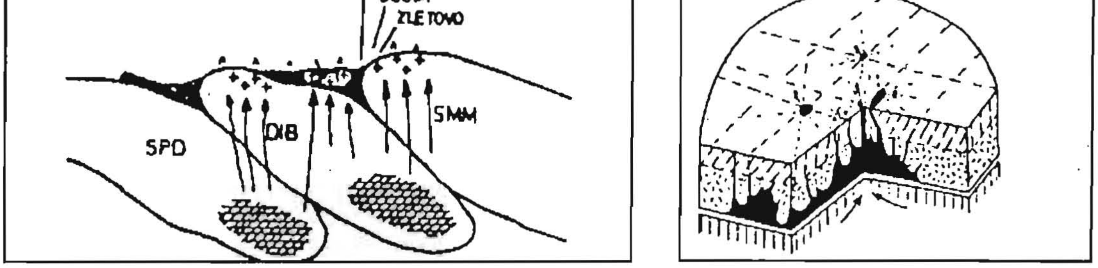

Fig. 3: *Origin of parent magma in the Buchim deposit*

mineralization is particularly interesting: primary (Centralen Del and Bunardzik) supergene or mineralization related to oxidation-cementation zone (Cukar) and mixed (Vrsnik) (Fig. 1). It should be pointed out that the primary sulphide mineralization played the major role in production of copper.

The Central ore body, formed round latite dike, is a typical example of primary copper mineralization. Ore mineralization mainly developed in gneisses, but round the latite cross-cut (Fig.1). The ore body has the shape of inverse cut cone and morphologically follows the volcanic body (Fig. 2). Based on the morphological classification of porphyry copper ore bodies given by Krivcov (1983) belongs to the firts group of so called conformable ore bodies (Cifliganec, 1987). The ore body (including the latite dike) is about 500 m in diameter with vertical interval of ore mineralization of over 250 m. The mean copper content amounts to 0.3 % Cu with about 0.35 g/t Au and 1 g/t Ag. The major ore mineral is chalkopyrite accompanied by pyrite, magnetite, hematite, cubanite, valerite, native gold, bornite and in trems of the mode of occurrence, mineral composition, association of elements etc. the ore mineralization in the Bunardzik, Cukar II and Vrsnik ore bodies is very similar to that in the Central ore body. Difference can be seen only in the Cukar ore body.

The Cukar ore body is a typical example of supergene mineralization in the deposit. It is characterized by increased amounts of copper but low ore reserves. The major ore minerals are chalkosine and coveline always accompanied by pyrite, tenorite, rarely native copper, malachite, azurite etc.

It is sheeted-like ore body or elongated lens about 400 m long and 200 m wide with N - S strike. The thickness of preserved oxidation-leach zone does not exceed 60 m. It should be mentioned that the ore body does not exsist any longer because it was mined out.

GENETIC MODELLING

Interpretation of the evolution of porphyry copper deposits from complex hydrothermal systems requires a lot of analysis and solving open issues. Interpretaion by genetic modelling which makes possible recontruction of cetrain genetic processes based on measured data has become very important in recent times. Such interpretaions can be found in the papers of Smirnov (1976), Ovtchinikov (1976), Jankovic (1981, 1990), Krivtsov (1983), Mitchel and Garson (1984), Ohomoto (1986), Makaev (1986), Cifliganec (1987,1993), Sotnikov et al. (1988), Serafimovski (1990, 1993) et al.

A general model which considers ore components from their ultimate source (the source of origin) to the place of deposition can be accepted for interpretation of conditions for the development of the Buchim poprhyry copper deposit. The development of the deposit will be studies through the following issues:

- origin of the magma
- origin of the ore metals
- origin of ore-bearing solutions
- physico-chemical conditions for ore-bearing fluids
- deposition of ore components
- occurrences which accompany the formation of ore deposits

This paper gives a brief account of all these on the example of the Buchim porphyry copper deposit.

ORIGIN OF MAGMA

Data about petrochemical composition reported in the works of Karamata (1974), Jankovic and Petkovic (1974), Jankovic (1977), Karamata and Djordjevic (1980), Knezevic et al. (1989) determined that magma ensuing volcanogene-intrusive complexes of the Serbo-Macedonian metallogenic province, to which the region of Buchim belongs, developed by partial melting of the deep parts of continental crust underthrusted by collison of continnetal blocks in depths where by fracture opening magma penetrated into upper levels (Fig. 3).

Recent data reported in the works of Boev et al. (1992) and Serafimovski (1990, 1993) based on isotopes of $^{87}Sr/^{86}Sr$ (0.706633 - 0.706928) as well as contents of rare earth elements (REE), Table 1 point out that magmas ensuing the volcano-intrusive rocks in the vicinity of Buchim and its surrounding developed by mixing of material from the continental crust and upper

Table -1. Contents of rare earth elements in intrusive and volcanic rocks of the Buchim deposit (ppm)

	71	70	72	73	74
La	10	66	98	69	88
Ce	18	160	190	150	170
Sm	4.6	9.5	10	8.9	5.5
Eu	2	3	3	2	2
Tb	1	1	1.1	1	0.5
Yb	5	2	2	2	2
Lu	0.5	0.2	0.2	0.2	0.2
Suma	41.1	241.7	304.3	233.1	268.2
Eu/Sm	0.4	0.31	0.33	0.22	0.36
La/Yb	2	33	49	34.5	44

71. Intrusive rock with granitic character from Buchim
70. Intrusive rock with dioritic character from Buchim
72. Latite from Vrsnik; 73. Latite from Central part
74. Trachyte from Crni Vrv

mentle in the areas of their contact parts. The content of microelements and elements of rare earths point to the great similarity with rock types formed in active continental margins (Boev et al. 1992).

ORIGIN OF ORE METALS

The issue of origin of ore metals and mechanism of concentration during development of hydrothermal deposits is of particular importance not from the aspect of interpretaion of genetic process but also with respect to determinetion of their spatial distribution. The issue of primary source of metals has always been interesting to the investigators of mineral resources.

In geological literature some investigators consider that ore metals originate from the upper mantle, whereas others that sources should be looked for in surrounding rocks. Today the assumption of polygene origin of ore metals is very common: Jankovic (1972, 1981), Ovtchinikov (1976), Krivtsov (1983), Ohmoto (1986), Bogdanov (1987), Serafimovski (1993) et al.

Results from stable isotope examinations are used today in order to get more accurate information about the origin of ore metals. Examination of isotope composition of sulphur in sulphide minerals points to the origin of this element and directly to the group of elements which make up the hydrothermal deposits.

Examination of isotope composition of sulphur from the Buchim deposits was carried out on ten pyrite samples (Mudrinic and Petkovic, 1974).

Analysis of the results of isotopic composition of sulphur (S) in pyrites indicates that the amount of ^{34}S is conformable with very narrow variation intervals for all three ore bodies (Table 2), but with slight enrichment in heavy isotopes $\delta^{34}S$ with respect to meteoric.

The variation $\delta^{34}S$ for the whole Buchim deposit ranges from +0.16 to +2.53 ‰, whereas mean content amounts to +1.06 %. It is obvious that there is difference in the variation in $\delta^{34}S$ between individual ore bodies, but when one analyses mean values the differences get smaller so that the mean content of $\delta^{34}S$ for the whole ore

Table - 2. Isotopic composition of sulphur in pyrite of the Buchim ore deposit

Ore body	horizont	$^{32}S/^{34}S$	$\delta^{34}S$ ‰
CUKAR	630	22.164	+2.53
CUKAR	630	22.216	+0.16
CUKAR	630	22.197	+1.02
C.DEL	605	22.186	+1.52
C.DEL	605	22.211	+0.42
C.DEL	605	22.205	+0.70
VRSNIK	650	22.220	+0.00
VRSNIK	650	22.212	+0.38
VRSNIK	650	22.180	+0.80
VRSNIK	650	22.174	+2.09

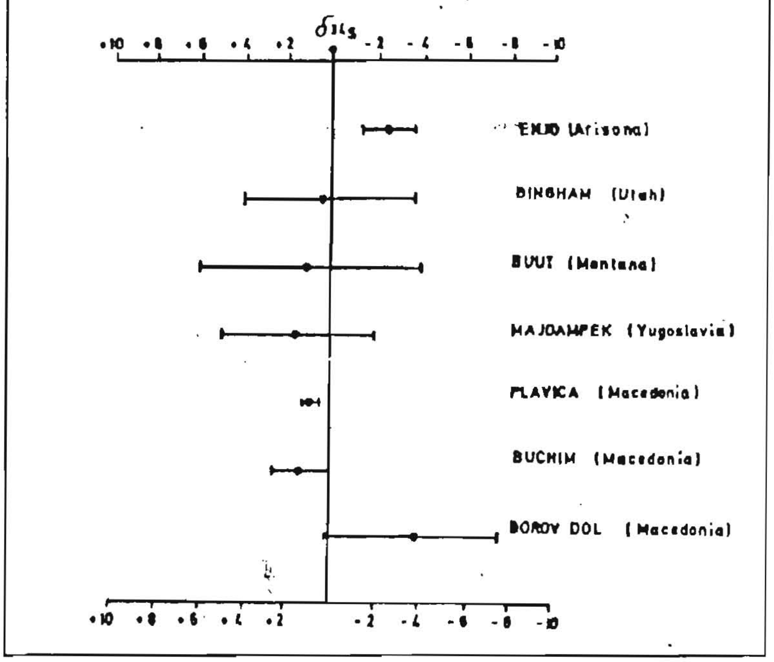

Fig. 4 *Diagram of the isotpic composition of sulphur ($\delta^{34}S$) in individual poprhyry copper deposits*

body becomes closer to the value of $\delta^{34}S$ for individual ore bodies.

Obviously, the narrow interval of $\delta^{34}S$, in our data is due to the homogene environment and the same physico-chemical conditions of development of sulphide paragenesis in all three ore bodies. The occurrence of certain difference in the values of $\delta^{34}S$ between ore bodies is due to slight difference in differentiation during ore solution movements from the commmon sources and the change of physico-chemical factors (first of all temperature).

Variations in the value of $\delta^{34}S$ in pyrites of all three ore bodies points to endogene origin of sulphur in pyrite.

In terms of Ryle and Ohmoto's (1977) classification and the results obtained for the values of $\delta^{34}S$, the deposit under consideration can be classified as first group in the interval from0.0 to 0.5 ‰ $\delta^{34}S$. Ohmoto and Rye (1979) indicate that deposits belonging to the first group are related to felsite igneous rocks. Sulphur in the deposit is of magmatic origin, and was either taken during liberation from silicate solutions or sulphur was mobilized from sulphides in the volcanic rocks.

It is very interesting to compare isotopic composition of sulphur (S) of Yugoslav porphyry deposits to the lagest porphyry copper deposits in the world where proximity of the amount of $\delta^{34}S$ is obvious (Fig. 4).

Origin of copper in the Buchim deposit is most probably related to primary igneous intrusives. Since igneous bodies - dikes and small stocks or "small intrusions" were too small for mobilization of hydrothermal convective systems the copper amounts that we find today in ore bodies of the Buchim deposit, the sources of copper should be looked for in the deeper parts or large igneous bodies.

We should also bear in mind that part of copper could have been mobilized from serpentinites lying in the basement and/or from the area in which primary igneous complex intruded. This possibility is particularly interesting if we bear in mind the fact that neogene calc-alkaline igneous complexes in the Serbo-Macedonian province are poor in copper (particularly compared with the Bor Cretaceous magmatism - Karmata, 1974).

ORIGIN OF HYDROTHERMAL ORE SOLUTIONS

The issue of origin of hydrothermal solutions, first of all water in them, has always attracted experts working on deposits of mineral raw materials.

When we talk about origin of hydrothermal solutions, we must first study the origin of water which is the major component in the composition of hydrothermal solutions basic material for transportion of all components in the hydrothermal solution.

It was considered that water in hydrothermal ore-bearing solutions is of magmatogene origin. However, recent exmaninations of various phenomena, particularly isotopic analyses of $^{18}O/^{16}O$ and D/H ratios indicate that origin of water in hydrothermal solutions must be related to other sources as well.

Based on our knowledge it can generally be

Table 3: Isotopic composition of $\delta^{13}C$ (PDB) and $\delta^{18}O$ (SMOW) in calcites from the Buchim pophyry copper deposit

No	Sample	Mineral	$\delta^{13}C$ ‰	$\delta^{18}O$ ‰
1	F.B.555/570 C.Del	calcite	-10.43	+17.60
2	F.B.555/570 C.Del	calcite	-7.76	+22.55
3	E.B.540/555 C.Del	calcite	-6.90	+18.93
4	E.B.540/555 C.Del	calcite	-6.38	+20.46
5	E.B.540/555 C.Del	calcite	-5.76	+21.43
6	E.B.540/555 C.Del	calcite	-3.84	+19.74
7	E.B.540/555 C.Del	calcite	-4.00	+22.70
8	E.B.540/555 C.Del	calcite	-6.42	+17.06
9	E.B.540/555 C.Del	calcite	-	+21.41
10	E.B.615/630 Cukar	calcite	-10.83	+13.98

inferred that greater amount of water in hydrothermal solutions originated from the surface of the earth. It is assumed that meteoric water penetrated into deeper parts of earth's crust. Development of convection system took place during penetration and at the very contact of meteoric water with water from inner parts of the crust when the difference in temperature between penetrating and existing water in the depth amounted to 200° C.

Determination of origin of water in hydrothermal solutions relies mainly on data from oxygen and carbon fractionation.

Isotopic compositions of carbon $^{12}C/^{13}C$ and oxygen $^{18}O/^{16}O$ in calcites of ore parageneses were determined on the axample of the Buchim deposit. Results of the probes are shown in Table 3.

The Table shows that although only a small number of examinations were carried out, there is continuity in obtaining results which undoubtedly point out the fractionation and change in carbon and oxygen primary compositions.

The variation of $\delta^{13}C$ ranges from - 3.84 to -10 10.83 ‰ which points to the pronounced carbon fractionation and enrichment in light isotope. This is characteristic of high temperature calcites in which, according to Rye et al. (19,74) changes in composition of carbon isotopes can be interpreted by decrease in oxidation potential of hydrothermal solutions and the increase of CH_4 part in them which results in carbon fractionation.

The variation of oxygen $\delta^{18}O$ in examined calcites ranges from +13.98 to +22.70 ‰ which greatly deviates from the standard (SMOW, $\delta^{18}O=0$). This points to the pronounced oxygen fractionation and change of the isotopic composition, or pronounced enrichment in heavy isotope. According to Taylor (1979) such enrichment is more characteristic of reduction environments and most probably other types of water, apart from juvenile, also took part in calcite deposition .

In terms of conditions of development of the deposit and the nature of hydrothermal changes of surrounding rocks it can be assumed that hydrothermal ore-bearing solutions consisted of waters which originated from several sources, mainly of meteoric. Nevertheless, this conclusions needs further investigations in the example of the Buchim deposit.

PHYSICO-MECHANICAL CHARACTERISTICS OF HYDROTHERMAL ORE SOLUTIONS

The characteristics of hydrothermal solutions at the moment of their development and the changes during their evolution can not be determined from direct observation because environments in which solutions developed moved to significant depths beneath earth's crust. This makes their definition possible only by assumptions or deductions. Thus, physoco-chemical conditions of development of deposits are mainly based of personal assumptions and conclusions.

There are many assumptions which relied on results of investigations of relationships between

Table 4. Temperatures of homogenization in different types of inclusions in quartz from the Buchim porphyry copper deposit.

Mineral association	Type of the inclusions	Number of measured inclusions	Range of the homogenization temperatures (in °C)
Quartz, K-feldspar	three-phases, 2, 3 or more solid phases	7	over 580
Quartz,magnetite, hematite, rutile	three-phases, solid phase-halite, hematite	25	550-500
Quartz,magnetite, hematite, rutile	three - phases, one "daugther"mineral	58	530-550
Quartz,pyrothite, chalcopyrite ±cubanite, valeriite	two-phases inclusions, very large dark buble, (1:g - 1:1 to 3:1)	22	490-430
Quartz,pyrite, chalcopyrite	two phases, (1:g - 4:1 to 6:1)	80	430-400
Quartz,pyrite, chalcopyrite ±bismuthinite,enargite	two - phases, relatively small buble	21	370-320
Quartz, pyrite	two-phases, small light buble, secondary origin	17	200-180

mineral parageneses and accompanying events surrounding rocks. Today, information about characteristics of hydrothermal solutions rely on studies of gas-liquid inclusions in minerals of ore paragenesis. Information about composition of ore-bearing solutions, the character of environment (pH), temperature range are obtained in this manner.

Investigations of gas-liquid inclusions (Blecic, 1974) in quartz of Buchim deposit indicate that ore-bearing Cu-solutions are predominantly of Na-Cl type, in which concentration of dessolved salts varies between 10 and 25 %, with specific weight from 0.6 to 0.8 cm^3.

There are a lot of open issues with respect to environment of hydrothermal fluids, but in general, and bearing in mind other parameters, it can be said that it is poorly alkaline. The small calcite content in the Buchin deposit indicates alkali nature of hydrothermal solutions (pH greater than 7).

Determination of temperature at the time of development of the Buchim deposit is based on investigation of individual typomorphous minerals within mineral paragenesis or associations which comprise the process of deveopment of the deposit as well as changes in the stage of gas-liquid inclusions in minerals (Table 4).

The teperature of hydrothermal solutions at the time of deposition of ore minerals ranges from 600° C up to 200-300° C down to 100° C for the youngest occurrences of sterile hydrothermal movements which formed pyrite microfils.

The Table shows that the studied temperatures of homogenization in quartz in major ore parageneses in the Buchim deposit indicate teperature of formation of basic ore minerals within the span of 490 - 200°C which coincides with large number of porpyry deposits related to small subvolcanic intrusions.

Transportation most probably was conducted by water solutions in the form of complex ions of chloride compounds, sodium, potassium, and very seldom sulphate and carbonate. Chlorine preence noticed during investigation of gas-liquid inclusions in minerals from the Buchim points out the manner of transportation of ore components by chloride solutions in the form of chloride complexes.

Ways of circulation of hydrothermal ore-bearing solutions were in close relationship to the areas of increased permeability. They are fractured, tectonized with intensively developed joint-crackled systems, initiated by penetration of primary intrusions (Hrkovic, 1985).

The following order of successions and deposition can be distinguished: first sphen and rutite separated followed by deposition of a series of minerals such as pyrrhotine, cubanite, valerite and older generation chalkopyrite. After deposition of these minerals, hydrothermal ore-bearing solutions became richer in sulphur which conditioned abundant pyrite deposition. At the end deposition of younger generation chalkpyrite

MINERALS	DEVELOPMENT STAGES			
	Metamorphic	Magmatic	Hydrothermal	Supergene
BIOTITE		▬		
AMPHIBOLE		▬		
ZIRCON		▬		
APATITE		▬		
SPHEN	▬	▬		
ILMENITE	▬	▬		
FELDSPARS		▬		
QUARTZ		▬	▬	
SERICITE			▬	
CHLORITE			▬	
EPIDOTE			▬	
ANATESE			▬	
RUTILE	▬		▬	
CALZEDONY			▬	
CALCITE			▬	
GYPSUM			▬	
KAOLINE			▬	
MAGNETITE	▬	▬	▬	
CHALCOPYRITE			▬	
BORNITE			▬	
PYRROHOTINE			▬	
CUBANITE			▬	
MARTITE			▬	
SPECULARITE			▬	
MUSCHETOVITE			▬	
PYRITE	▬		▬	
MOLIBDENITE			▬	
KRENNERITE			▬	
NATIVE AU			▬	
BRAVOITE			▬	
BISMITHINITE			▬	
RECBANIITE			▬	
LUZONITE			▬	
TETRAHEDRITE			▬	
GALENA			▬	
CHALCOSINE				▬
COVELINE				▬
MALACHITE				▬
AZURITE				▬
TENORITE				▬
LIMONITE				▬

Fig. 5. *Succession diagram of minerals in the Buchim deposit Based on characteristics mentioned and conditions of deposition it can be inferred that genetically it belongs to porphyry hydrothermal Cu-deposit.*

ok place.The process ended by separation of ratin galena concentrations from hydrothermal lutions.

Deposition of all ore minerals present in the chim deposit was mostly related to the oceses as follows:

- Precipitaion from saturated solutions in cant areas
- Replacement of minerals in surrounding eisses and andesites, when components of laced minerals can be partially or completely placed
- Change of existing minerals in the process recrystallization,
- Recrystallization of pre-existing minerals,
- Permeability of environment etc.

Order of succession of separation of ividual mineral types is shown in Fig.5.

The relationship of chalkopyrite deposition in form of veins and veilets filling vacant joint-ckled systems, with respect to chalkopyrite which deposited as impregnation is larger in favour of stockwork type of ore mineralization.

ACCOMPANYING OCCURRENCES

The process of formation of deposits does not end by deposition of ore metals in the form of mineral aggregates, but there are other events which can be a characteristic trait in development of ore deposits (change in chemical and mineral composition of surrounding rocks, helos of scattering of individual components, zoning in replacement of mineral associations etc.

The following can be distinguished as important accompanying events that took place due to development of the Buchim deposit:

- primary helos of scattering
- alteration of surrounding rocks
- manner of replacement of mineral parageneses.

•*Primary halos of scattering* which accompany the development of the Buchim

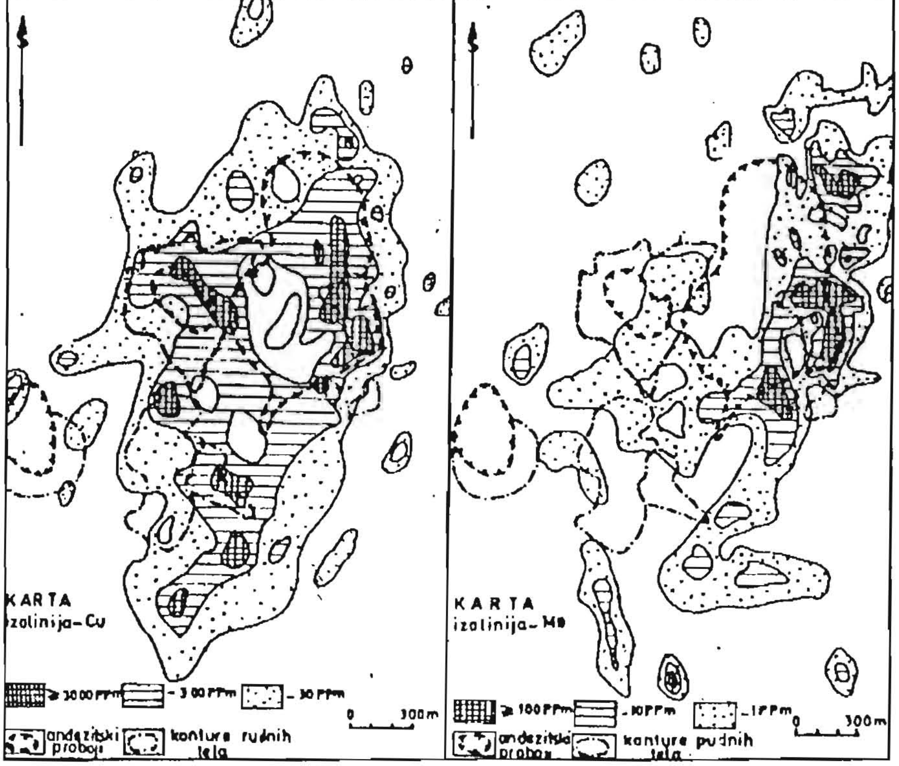

Fig. 6 *Halos of scattering of copper (Cu) and molybdenum (Mo) in the Buchim deposit (Petkovic and Mudrinic, 1974).*

deposit are characterized by replacement of low grade copper and/or ore minerals in surrounding rocks. It is very characteristic for this deposit because the relationship of ore metals concentration in primary halos of scattering and ore bodies is very pronounced.

The contrast of ore metals in primary halos of scattering varies from element to element (Fig. 6) and in different lithologic members.

Primary halos of copper scattering in the wider area identified by litho-geochemistry in the surface of the field can not be reliably related to identified ore bodies, but can represent occurrences of scattered ore mineralization. Such nature of copper distribution in rocks, most probably comes from the fact that in some cases mineralization occurs in deeper levels or in some cases (Cukar and Vrsnik) it is cementation zone.

•***Hydrothermal Alteration of Surrounding Rocks.*** Various kinds of hydrothermal alterations took place in the surrounding rocks by the influence of hydrothermal (ore- bearing) solutions. Based on investigations carried out so far, according to the time of formation as well as

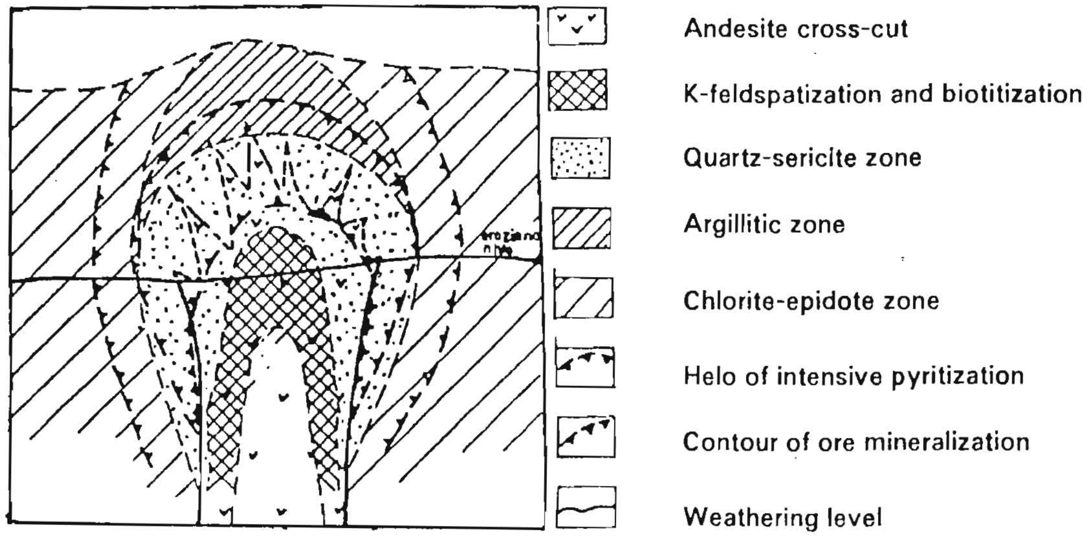

Fig.7. *Schematic presentation of zonal replacement of hydrothermal alterations in the Buchim copper deposit (Cifliganec, 1993)*

facies of alteration, the follwoing can be distinguished:

- Pre-ore alterations in the deposit took place prior to deposition of copper mineralization influenced by high temperature, acidic and gas-liquid solutions (most probably of subvolcanic orogon) on surrounding gneisses and seldom andesites. It is silicification, partially chloritization and epidotization and pyritization in some places.

Inter-ore alterations are closely related to mineralization. In Buchim they are hydro-biotization (products of potassium metasomatosis), sericitization, silification etc. The facies and their zoning od replacement are very pronounced in the Centralen Del and Cukar ore bodies (Fig. 7).

Post-ore alterations in the Buchim deposit can be distributed in two groups:

- ascending alteration developed after ore mineralization, such as silicification, calcitization etc.

- descending alteration, first of all kaolinization and limonitization.

In terms of spatial distribution of ore mineralization and their eventual zonality it can be said that:

- the copper ore mineralization is spatially located round the subvolcanic dikes, where going farther from the contact parts the metals contents (first of all Cu and Au) are lower. Ore mineraliztaion can be followed in the deep parts to over 300 m with varying metals contents. Based on experiences obtained so far as well as exploitation of the deposit it is not possible to give a precise scheme of zonal distribution of metals and minerals since it has not been found.

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