

A method for mineralogical predicting the mining and metallurgical centers of the Early Chalcolithic to the Bronze Age (Case study from the water-catchment basins of the rivers Struma and Mesta, SW Bulgaria)

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Метод за минераложко прогнозиране на площи за търсене на рудодобивни и металургични центрове от ранния халколит до бронзовата епоха (във водосборните райони на реките Струма и Места, ЮЗ България)

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РЕЗЮМЕ

Описана е методика за минераложко прогнозиране на площи за търсене на рудодобивни и металургични центрове от ранния халколит до бронзовата епоха. Извършена е апробация на методиката във водосборните райони на реките Струма и Места, ЮЗ България. Използвани са данни от шлихоминераложкото картиране на района с обем 34387 проби в които са установени: самородна мед (32); куприт (36); азурит (3); малахит (126); торбернит (1); халкопирит (37); самородно олово (706); пироморфит (527); каситерит (79). В скоби е броят проби с минерала. Като независима контрола на построенията са данни за веществен състав и координати на полезните изкопаеми в региона и данни за поселища и находки на медни клинове и брадви от халколита. Описани са пет възможни начина за получаване на самородна мед в природата, както и геохимичните особености на различните процеси. Установени са статистически връзки между минералите самородно олово, пироморфит и каситерит с минералите на медта, които връзки са обяснени с действие на горски пожари и пирометалургия. Изготвените прогнозни карти са с точни и еднозначни площи за търсене на металургични центрове от халколита и ранната бронзова епоха.

Key words: metallurgical centers, Chalcolithic, Bronze Age, South- Western Bulgaria

Current state of knowledge

I. Archaeological Evidence

Findings of copper artifacts along the Struma River (Cochadziev, 1998, Mihailov, 2008, Fig. 1) were dated by the accompanying pottery and bone material (organic carbon 14 method) to an age of 4,800 BC and were of high purity (see Table 1).

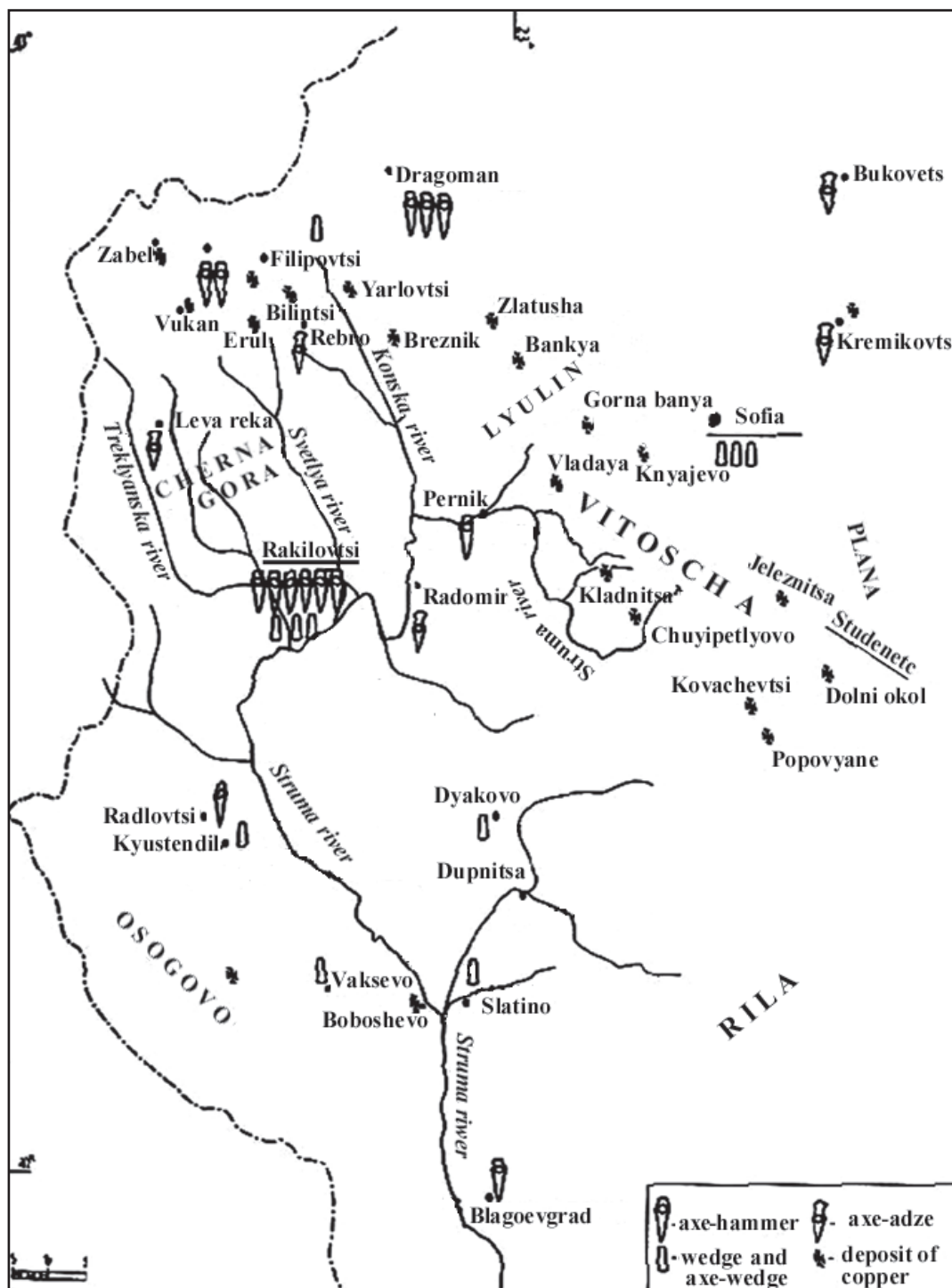


Fig. 1. A – localities of excavated copper artefacts.

The up to date studies of the chemical composition of copper artefacts from museums in Bulgaria (data from emission spectral analysis) demonstrate a logical progression of their chemical composition: the earliest artefacts contain more than 99.9% of copper, later ones have more impurities (95-97% copper), and then the arsenic content increases ("arsenical brass"). This process ends in time with objects with 20% tin ("tin bronze"). It is assumed that the first copper artefacts were forged pieces of native copper. Later, the extraction of copper and copper alloys in a thermal reduction en-

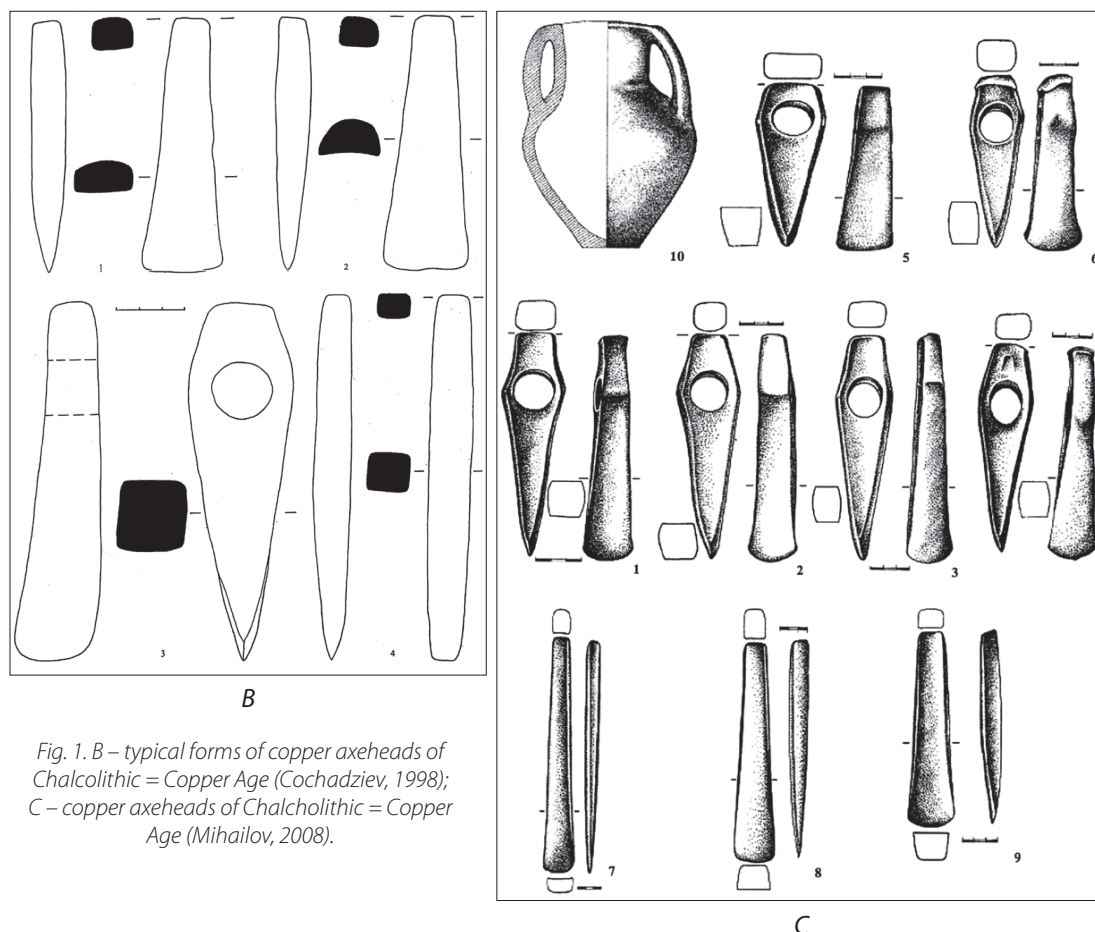


Fig. 1. B – typical forms of copper axeheads of Chalcolithic = Copper Age (Cochadziev, 1998); C – copper axeheads of Chalcolithic = Copper Age (Mihailov, 2008).

vironment with charcoal came into use. Unlike the mining work of the Thracians who left visible trenches on the surface, the miners that came before them buried ritually their pits and galleries after their mining works were complete. That is why no slag and scoria from their metallurgy are visible on the surface (Chernyh, 1978). The latter is confirmed by the geological studies in the ore exposure area at the Garbino occurrence in the Kyustendil District which revealed that canvas work (trenches) with a depth of 2 m near the protruding quartz veins with low-grade gold-polymetallic mineralization are sealed from above by the material of ancient mining with fragments of stone tools and pieces of pottery (Fig. 2; Parvanov, Vatshev, Kraevski, 1968; Zinoviev, 1974; National Geological Fund; Vitov, 2007). This is the answer of the question why ancient mines are very difficult to find, and why there are no visible traces of mining and metallurgy. Usually, nearby the mining areas there are scatters of pottery shards, but their identification requires the assistance of professional archaeologists.

The inadequate evidence of mining and metallurgy in our lands and their importance for the history of civilization motivates specialists to develop methods and tools that will enable them to identify new metallurgical centers from the Early Chalcolithic to the Bronze Age and to study and preserve them as historical monuments. Studies fulfilled so far are re-directed from focusing on archaeological finds to search for the source of the known metal deposits. However, systematic surveys have not been applied in the areas near the known deposits and manifestations of minerals.

The starting point in this study is the fact that mining and metallurgy can be realized only in the presence of mineralization. In the archives of the National Geological Fund of Bulgaria there are numerous geological reports with information about the geological structure of the country; traces of ancient mining; geochemical, mineralogical and geological maps. A summary on the distribution of ores in Bulgaria in a scale of 1: 100,000 is made in the unpublished catalog of Maznikov (1997, National Geological Fund). It refers to co-ordinates, detailed information on the ore composition and

№	Находище Site	Елемент (g/t) Element (g/t)								
		Zn	Ag	Ni	Pb	As	Co	Sn	Au	Σ = g/t
1	Слатино Slatino	12,80	306,00	51,80	5,31	3,34	0,45	0	28,90	408,60
2	Слатино Slatino	6,97	406,00	51,40	47,90	3,08	1,13	0	13,50	529,98
3	Дяково Dyakovo	6,97	1180,00	96,70	34,10	3,09	0,69	0	2,86	1324,41
4	Радловци Radlovtsi	7,98	22,00	68,40	218,00	2,27	0,37	0	0	319,02
5	Бобошево Boboshevo	35,60	31,20	21,20	112,00	41,90	23,30	30,00	2,11	297,31
6	Бобошево Boboshevo	15,00	44,30	29,10	2,30	23,00	3,70	0	8,32	125,72
7	Ваксево Vaksevo	12,30	634,00	57,80	130,00	1200,00	2,28	0	0,37	2036,75
8	Перник Pernik	336,00	12,40	132,00	97,70	74,90	66,00	0	0,28	719,28

Table 1. Chemical composition (ICP) of impurities in copper axes and wedges from the early Chalcolithic along the Struma River (Cochadziev, 1998).

to size, classifying the objects as deposit, manifestation and indication of useful minerals. Important and independent information in the search for archaeological sites is the heavy minerals map of Bulgaria (Vitov, 1995, 2001) – a virtual database of co-ordinates and mineral composition of samples taken from river sands during stream-sediment pan-concentrated surveys (“schlih” from German).

In this work a method for predicting the areas of mining and metallurgical centers from the Early Chalcolithic to the Bronze Age is focused on the water-catchment basins of the rivers Struma and Mesta in SW Bulgaria. It analyzes the available data from stream-sediment pan-concentrated surveys.

II. Mineralogical Notes

Native copper in nature (Fig. 3, Table 2) is a product of:

1. An endogenous process called “carbonate-zeoliticfacies” of mineral formation (Minerals, I, 1960). It is formed under the action of vapors, gases and hydrothermal solutions in mafic and ultramafic rocks. Native copper forms in fissures and cracks as cement between the minerals where it accumulates in association with analcime, laumontite, prenite, datolite, adularia, chlorite, epidote, pumpellyite, quartz and calcite. Pieces of native copper weighing more than 400 tons have been found near the Lake Superior, Michigan, USA. In Bulgaria pieces of native copper were found near Vitosha Mountain (Knyajevo village) as filling of tiny cavities in andesite (G. Bonchev, 1923; Kostov et al., 1964).

2. The reduction in oxidative crusts of sulfide copper and polymetallic ores (Fig. 4). Native copper that is a product of these conditions is found in “the surroundings of the village of Glušnik, Gorno Aleksandrovo and Trapoklovo, Sliven District, in pieces weighing up to several kilograms, accompanied by cuprite; the Izvor village, Bourgas District; the village of Belitsa, Harmanlij District; the Popovi Rupi locality; above the Gorna Banya and Knyazhevo, Sofia District; in Breznik District; on the hill of St. Ilya and around the village Krusha; in the area of oxidized copper and polymetallic mineralizations like Elshitsa, Radka and around Banya, Panagyurishte District; in the Chelopech deposit, Pirdop District; in Burgas mines named ‘Hidden Water’; locality of Čiplaka; Sarneshko Kladenche, Varli Briag; Bardtseto occurrence, MalkoTarnovo District; lead-zinc deposits of the Madan orefield; Ustrem, Topolovgrad area; Madzharovo deposit, Harmanli area; south of Bo-

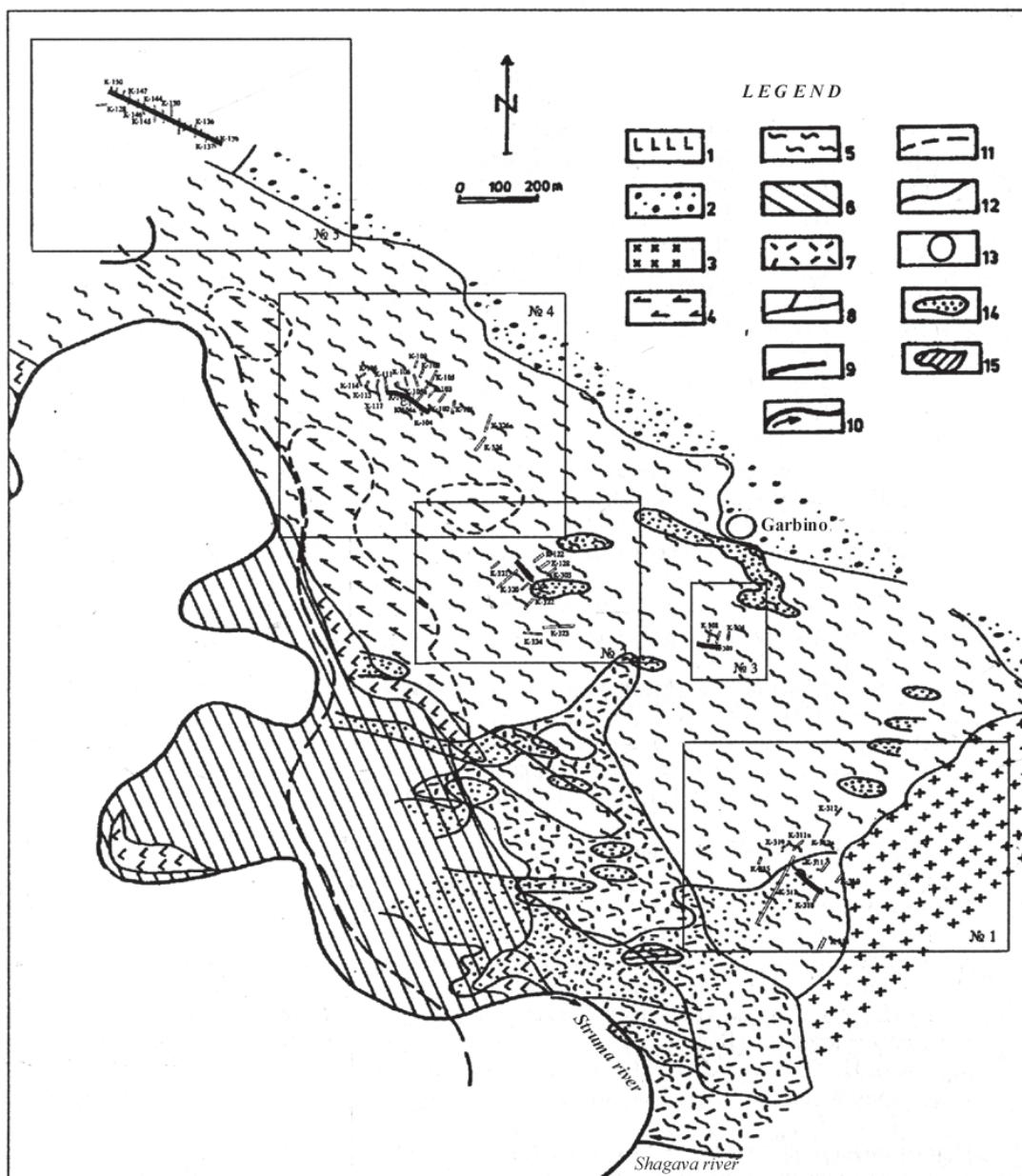


Fig. 2. Geological map of the Garbino occurrence (Parvanov, Vatsev, Kraevski, 1968; Zinoviev, 1974, National Geofund) and the areas of geological prospecting by trenches (rectangles) (Vitov, 2007): 1-peridotites, gabbros, gabbro-diorites; 2- red basal conglomerates; sandstones and schists (Lower Triassic); 3- gabbro-diorites, quartz-diorites, granodiorites; 4-amphibolites; 5-pegmatoidplagiogranites, schists and gneisses; 6- metamorphosed limestones, chlorite and sericiteschists, calcschists (Cambrian); 7- hydrothermally altered rocks (Shagava zone); 8- faults; 9- quartz veins with galena, sphalerite, chalcopryite, malachite, azurite, covellite, gold and pyrite; 10- river; 11- railway; 12-thirdclassroad (gravel); 13-village. Mercury halos: 14-<10 g/t; 15->10 g/t.

boshevo, Stanke Dimitrov District as well as in Triassic limestones along with cuprite, malachite and azurite” (Kostov et al., 1964).

Native copper as typomorphic mineral of the weathered zone of copper ores in Srednogorie metallogenic zone is noted by Tokmakchieva (1997).

2.1. The action of micro-organisms: biological methods for extraction of metals (Almagambetov, 2008; Gaitandziev, 1973) are based on direct bacterial leaching of metals like copper, zinc, lead, nickel, cobalt, gold, silver, arsenic and uranium. The attention of the researchers is focused on about

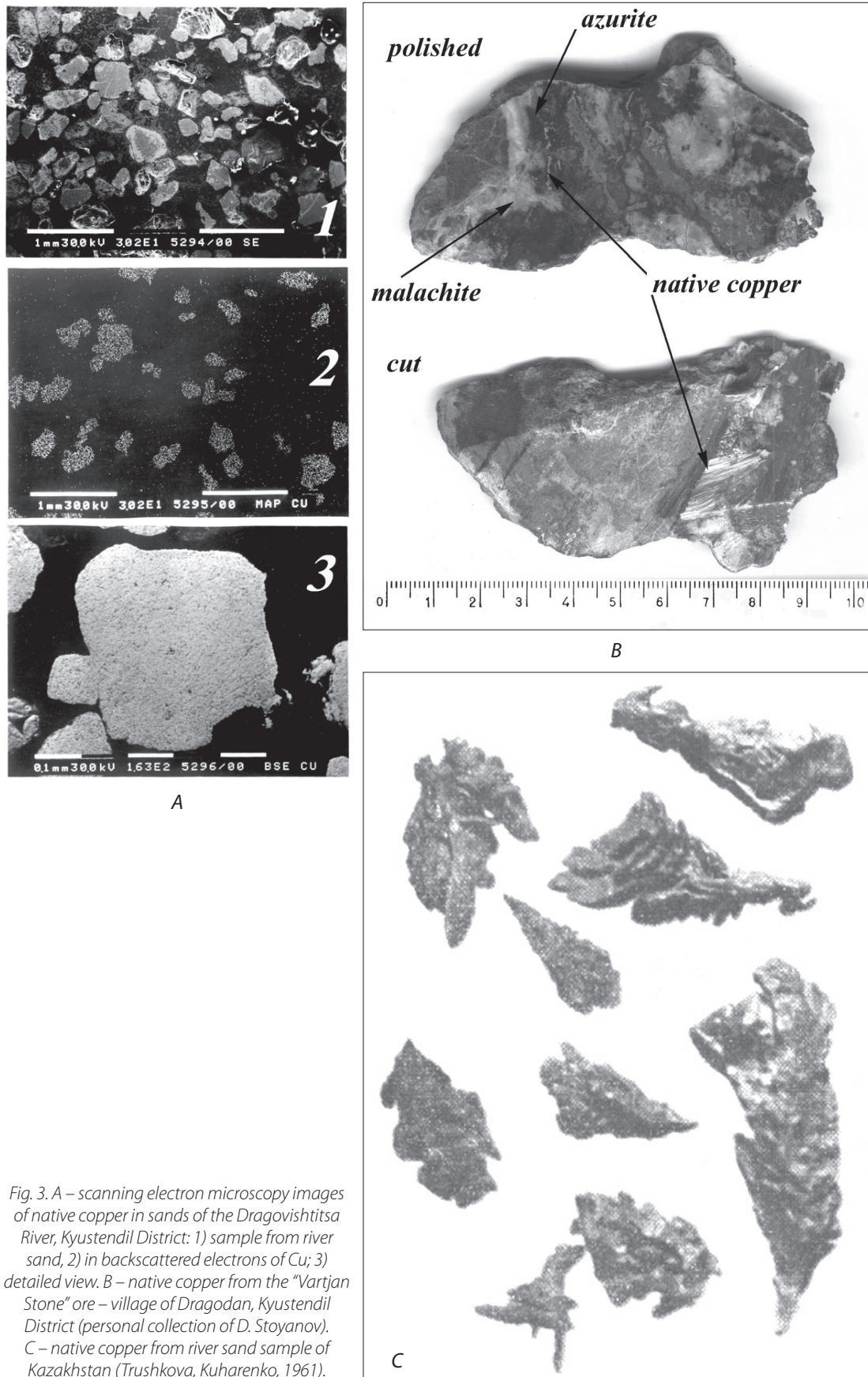


Fig. 3. A – scanning electron microscopy images of native copper in sands of the Dragovishtitsa River, Kyustendil District: 1) sample from river sand, 2) in backscattered electrons of Cu; 3) detailed view. B – native copper from the “Vartjan Stone” ore – village of Dragodan, Kyustendil District (personal collection of D. Stoyanov). C – native copper from river sand sample of Kazakhstan (Trushkova, Kuharenko, 1961).

Анализирана с лазерна аблация и ICP-MS в ГИ-БАН, в g/t (д-р Е. Стефанова).									
Analyzed by laser ablation ICP-MS in the GI-BAS, in ppm (Dr. E. Stefanova).									
Locality	⁶⁶ Zn	¹⁰⁷ Ag	⁶² Ni	²⁰⁸ Pb	¹⁰⁷ As	⁵⁹ Co	¹¹⁸ Sn	¹⁹⁷ Au	Σ = g/t
Драгодан Dragodan	4,51	827,30	0,12	0,37	35650,00	0,31	1,48	0,20	36484.29
Анализирана със микросондов анализ в ИМК-БАН (Л. Петров)									
Analyzed by electron microprobe analysis in IMC-BAS (L. Petrov)									
Драгодан Dragodan	-	-	-	-	26800,00	-	.	-	26800,00

Table 2: Chemical composition of native copper from Dragodan village, Kyustendil District (Fig. 3B).

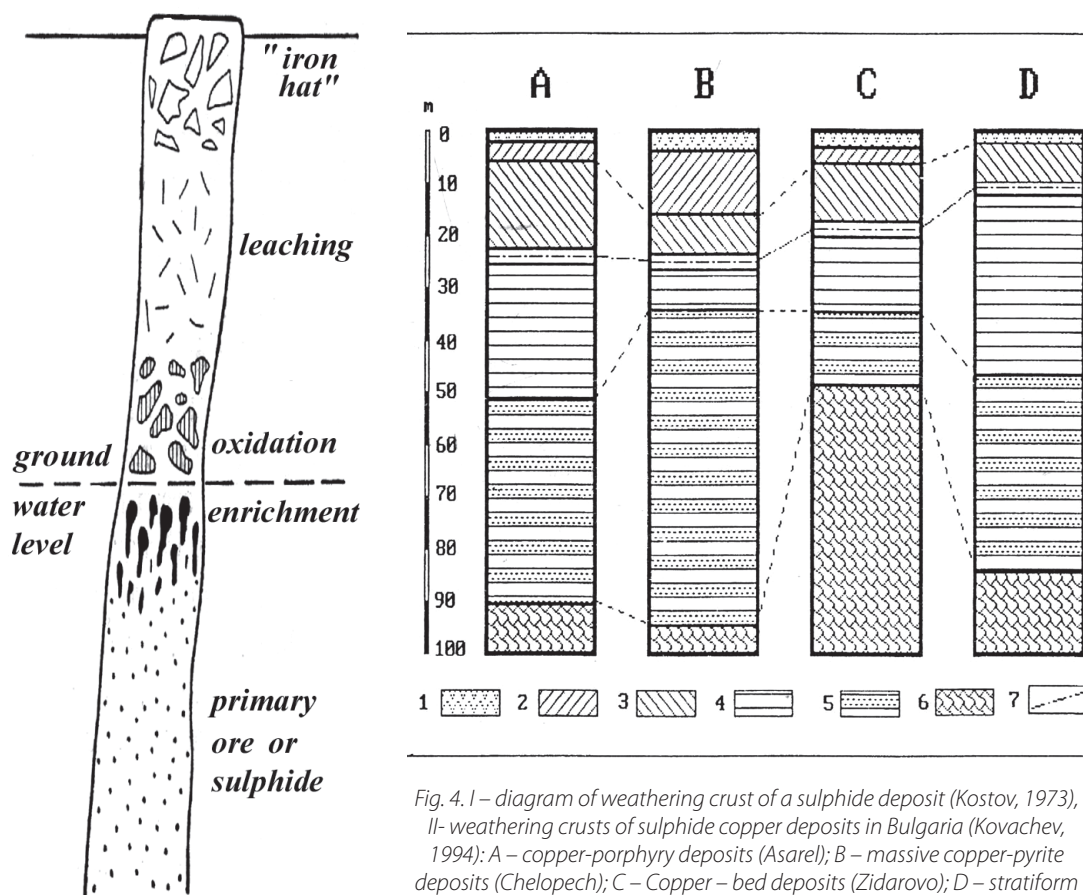


Fig. 4. I – diagram of weathering crust of a sulphide deposit (Kostov, 1973), II – weathering crusts of sulphide copper deposits in Bulgaria (Kovachev, 1994): A – copper-porphyry deposits (Asarel); B – massive copper-pyrite deposits (Chelopech); C – Copper – bed deposits (Zidarovo); D – stratiform deposits (Plakalnitza). 1 – soil; 2-5 weathering zones: 2 – subzone of leaching (goethite, lepidocrocite, hematite); 3 – oxidation subzone (upper part of the subzone – malachite, azurite, antlerite, chalcantite, brochantite; lower part of the subzone – native copper, cuprite, tenorite, native gold); 4 – subzone of secondary copper enrichment (vitreous copper, covellite, bornite); 5 – subzone of mixed copper ore (vitreous copper, covellite, bornite, pyrite, chalcopyrite); 6 – zone of primary copper ore (pyrite, chalcopyrite, copper sulfosalts, etc.); 7 – level of the underground waters.

1,500 species of bacteria among which *Acidithiobacillus ferrooxidans* is responsible for the sulphide micro-oxidation of minerals, mainly in poor chalcopyrite ores, (the industrial installation “Vlajkov peak”, Bulgaria) to metallic copper; *Leptospirillum ferrooxidans* has dominant role in the oxidation of the ores of uranium; *Bacillus circulans* attacks aluminosilicate minerals ($\text{AlSiO}_4 \rightarrow \text{AlSi}_2\text{O}_6 \rightarrow \text{AlSi}_3\text{O}_8$) with citric and oxalic acids; *Celibacterium arsenooxidans* is an arsenic-transforming bacteria. *Cupria-*

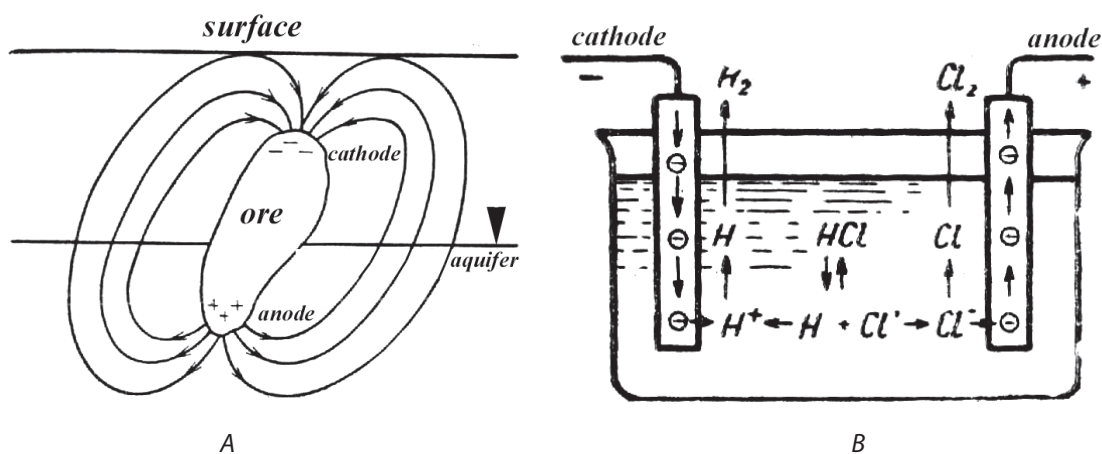
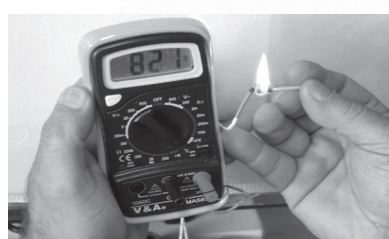
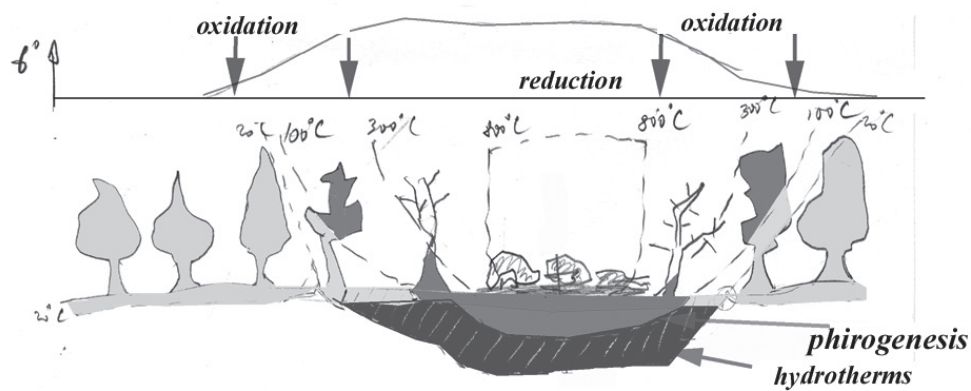
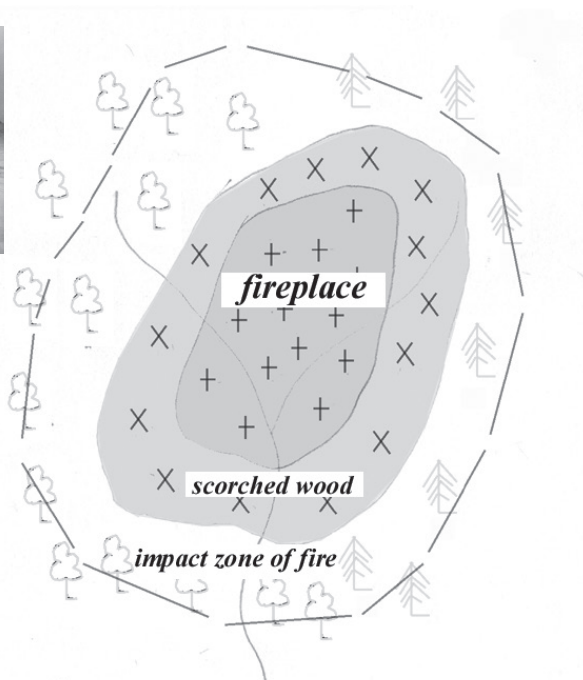


Fig. 5. A – Electric field around sulphide ore body (Paounov, 1961);
B – diagram of electrolysis (Nekrasov, 1965; Vassilev, 1980).



A



B

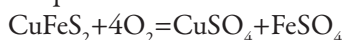
Fig. 6. A – determination of the temperature of the flame of wood; B – diagram of wildfire (Dimitrov, Vitov, 2007).

vidus metallidurans bacteria and *Delftia acidovorans* separate gold from aqueous solutions. Strains of different bacterial species are being extracted from the oxidation zones of deposits.

2.2. Electrochemical deposition under the influence of telluric currents. In the Earth there are telluric currents caused by different sources of electromotive force (solar wind, lightning, piezoelectricity, potential differences). Under special conditions (the presence of underground water courses) telluric currents are generated around sulfide ore bodies wherein the cathode is in the area of the weathering of the ore. According to the law of Michael Faraday (Nekrasov, 1965, Vassilev, 1980), with the flowing of current in electrolyte solutions native copper and hydrogen are deposited on the cathode. The voltage of these telluric currents is measured by geophysical instruments used in the prospecting for ore bodies and for studies of their size and morphology ("method of natural electric fields", Paounov, 1961).

2.3. Chemical reduction processes in aqueous medium ("Minerogenesis in the oxidation zone of copper deposit"; Stoynov, 1975):

Oxidation of copper ores (*chalcopyrite* CuFeS_2) in near-surface conditions produces copper and iron sulphate:



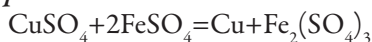
Copper sulfate reacts with the carbon dioxide and water (in the presence of carbonates) and forms *azurite* $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$:



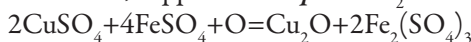
but when there is plenty of water it produces *malachite* $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$:



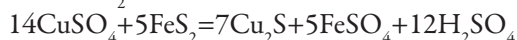
In the abundance of iron sulfate and with oxygen deficiency, copper sulfate is reduced to *native copper* Cu :



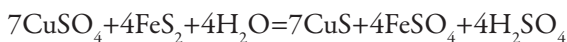
Otherwise, copperoxide *cuprite* Cu_2O is formed:



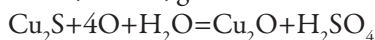
In the area of groundwater there is a secondary enrichment (cementation) with the formation of *chalcocite* Cu_2S :



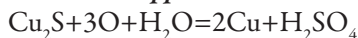
or *covellite* CuS :



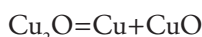
which, in turn, gives rise to oxidation and formation of *cuprite*:



and *native copper*:



Dry conditions (dry climate, desert) yield *chalcanthite* $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue stone), *melanterite* $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (green stone), *brochantite* $\text{CuSO}_4(\text{OH})_6$, *atacamite* $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ and others. According to Kovachev (1994) *native copper* is formed by the transition from oxidation of cuprite to *tenorite* CuO :



These minerals create a unique coloration of the oxidation zone – a deep blue azurite, green malachite, black tenorite, while cuprite is red, covellite is indigo blue, pirolusite (MnO_2) is black, hematite (Fe_2O_3) is red, etc. This rich coloration leads to the term "afleurment" (spring blooming) and creates numerous toponyms that designate various ore occurrences – "Green valley", "Red banks", "White Scree", "Black Peak", "Black stone" River, "Black village", "Sazhdanik – ashy." Acid and saline solutions from the zone of oxidation change the taste of the water in springs ("Hot Wells"), cause deforestation ("Bald", "Baldy") and salinization of soil ("Saline") or change vegetation ("Black grass" peak). Toponyms indicate the area of polymetallic deposits in the Ossogovo Mountain, Kyustendil District. Malachite (green) and azurite (blue) were used as paints for frescoes in churches. Over time and in the presence of moisture within the premises with paintings, the color of azurite turns from a "blue sky" to green. Research of Chernyh (1978) shows that malachite and azurite in the region of the Stara

Zagora mineral baths was used as pigment by the ancient artists. They did not use it as copper ore.

2.4. Pyrogenic processes of reduction of oxide copper ores under the influence of forest and steppe fires: experimentally it was found that the temperature of a flame of wood is 827°C which, coupled with the abundance of carbon and catalysts in the outbreak of forest fire (Fig. 4), generates a process of pyrolysis and causes a reduction of copper sulfides, carbonates and oxides to native copper. This process is known from the modern metallurgy, which includes the following steps: 1. Roasting the ore with air releases sulfur and forms a «matte» – a mixture of Cu_2S (chalcocite) and FeS (troilite- pyrrhotite); 2. Oxidic ore is blown with air, and the iron and sulfur are removed from the melt to give a “black copper” with a purity of 95% Cu without reheating; 3. Melting in a reverberatory furnace yields 99.7% Cu; 4. Refining through electrolysis (99.99% Cu). It is well known fact that Egyptians were able to produce large quantities of “black copper”. They used carbonate and oxide ores and produced copper through the process of copper melting in reducing charcoal furnaces 3,000 years BC (Nekrasov, 1965).

The forest and steppe fires combined with the respective mineralization in soil creates spontaneously drops of lead and tin (Kuharenko, 1961; Lunev, 1964; Vitov, 2008). Ash formed in this way has plenty of phosphorus (Table 3; Kyst, 1987) which binds to the lead thus forming pyromorphite (PbPO_4). This process is mirrored in the metallurgy of copper when one roasts complex ores which always contain impurities of lead, what in turn gives rise to the formation of pyromorphite.

From these remarks it is clear that the formation of native copper in the oxidation zone of a sulfide deposit requires the existence of a special regime of interaction between ground water, telluric currents, micro-organisms and chemical processes. The practice of the ritual burial of trenches carried out by the civilizations before the Thracians and identified by Chernyh (1978) can be classified as a functional activity that aims to restore the natural processes that produce native copper with high purity. In this way no pyrometallurgical processes were used in the production of copper and no slag and cinders can be found today. It is important to say that the copper produced by forest fires and thermal processes has many impurities that degrade the quality of the metal. The positive role of impurities such as arsenic and tin was established later, and with them began the Bronze Age.

III Geochemical Notes

Native copper is non-stable form of copper in the oxidation zone of sulfide deposits and the consequent changes of the acidity of the solutions and the content of oxygen and carbon dioxide leads to the transition of copper (Fig. 7) into carbonate, oxide or sulfide form (Garrels, Christ, 1968) what explains the corrosion of native copper and copper artefacts found in archaeological excavations.

In the near vicinity of ore outcrops (affleurements) and around metallurgical centers soluble compounds create geochemical halos of dispersion – contamination of the soil and water with heavy metals: lead, zinc, copper, antimony, bismuth, manganese and others. These geochemical anomalies (Bogdanov, 1980) can be found by examining the chemical composition of soil – the “method of the secondary dispersion halos” and by the analysis of water from springs and groundwater – the “hydrochemical method in the prospecting for minerals”. Stable minerals dissipate around the source and create mechanical surface halos. These methods consist of systematic tracking of soil or water in order to identify the sources of the revealed geochemical anomalies. To identify the source of ore mineral there are another methods like “chunks method” which requires field registration and documentation of the finds of pieces of ore, slag and altered rocks and the “shlihov method” – washing with fan-like pan of river sediments to separate the grains of ore minerals and their alteration products. Ore bodies, their zones of weathering, of surface dispersion, and metallurgical facilities (furnaces) create geophysical anomalies (natural electric fields, zones of conductivity, magnetic anomalies; the metal pieces are detectable by a metal detector) whose mapping makes it possible the direct search and differentiation of promising areas for study.

The sets of geological, geochemical, hydrochemical, geophysical and mineralogical maps compiled when one use the proposed further method, in combination with the available archaeological artifacts – slag, pottery and metal artefacts gives an opportunity for unambiguous pointing out the sources of ore bodies and associated with them prehistoric metallurgical centers. The small pieces of native

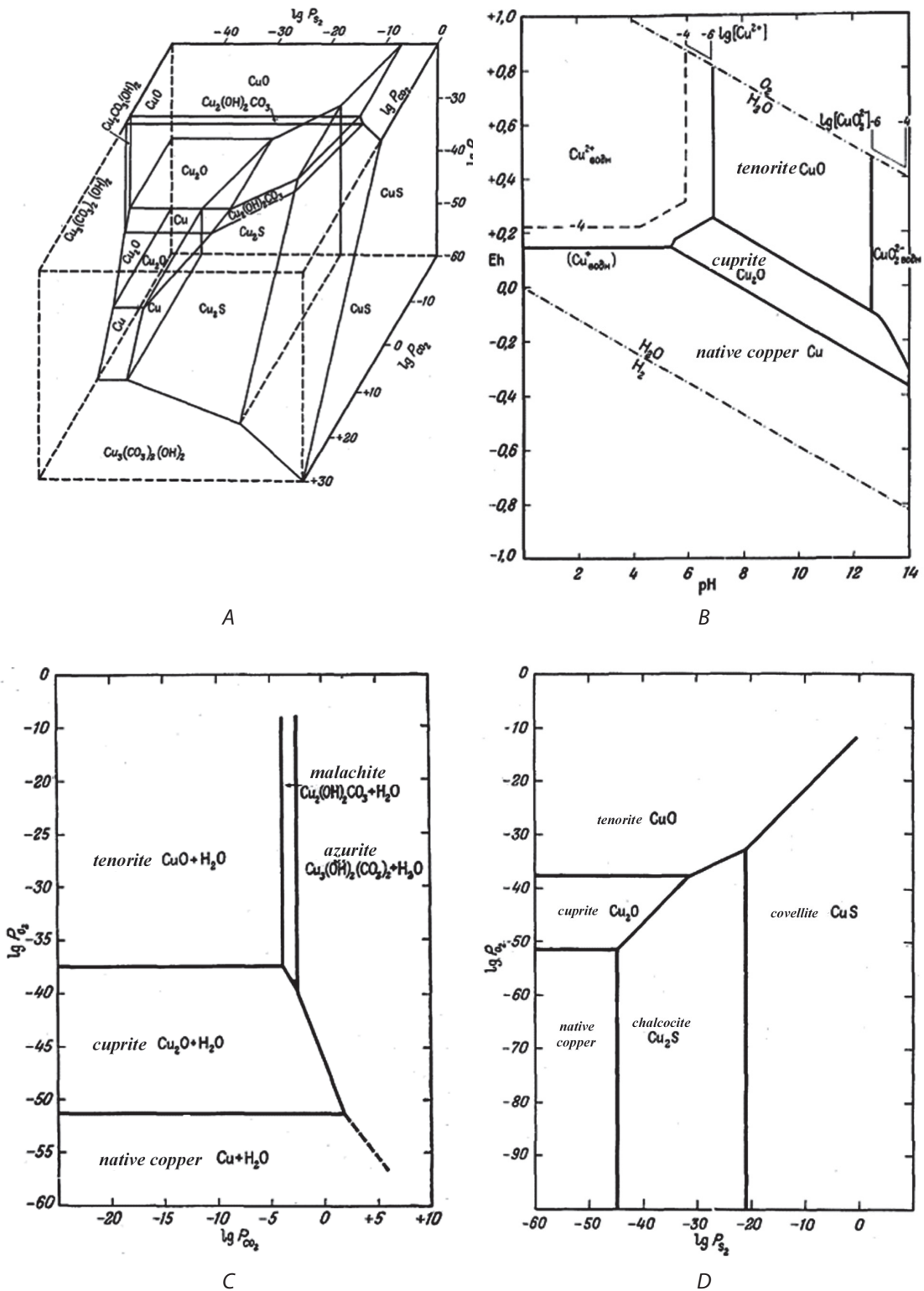


Fig. 7. Fields of resistance of native copper and copper minerals as a function of the redox potential of the medium and its parameters: A – combined diagram, B – acidity; C – active carbon dioxide gas; D – active sulfur (Garrels and Christ, 1968).

Table 3. Chemical composition of wood ash (Kyst, 1987).

element	C[kg/t]	element	C[g/t]	element	C[g/t]
Si	150	Zn	900	Sr	30
Mg	70	Cr	250	Mo	20
P	70	Cu	200	Co	15
S	50	Br	150	Li	11
Ca	30	Rb	100	Pb	10
Na	20	SRZE	100	F	10
K	20	Ba	100	It	10
Al	14	V	61	Sn	5
Cl	10	Ni	50	Be	2.1
Fe	10	B	50	Cs	2
Mn	7.5	Ga	50	Au	1
Ti	1	J	50	Ag	1

copper, copper minerals, native lead and pyromorphite are also indicative for the presence of ore outcrops and metallurgical centers.

Spontaneous production of tin bronze is only possible in areas of special geological conditions – a combination of copper ores with cassiterite. It is known from the geochemistry of copper and tin that these metals behave differently in the Earth crust – copper accumulates in relatively mafic rocks (gabbroa, diabases), while tin is specific to acidic rocks (granites, greisens). The presence of cassiterite and copper minerals in sand samples from rivers in Bulgaria as well as the described copper-tin mineralization near the town of Kazanlak (Bonchev, 1923; Ivanov 1998; Vitov, 2002) are evidence for the spontaneous formation of tin bronze in the metallurgy of copper practiced by ancient communities.

The method

Mapping of the results from stream-sediment pan-concentrated surveys is a method of studying the distribution of minerals in a given region (Kiryazova, Iliev, 1976; Zakharova, 1989; Yushkin, 1982). Minerals like native copper, cuprite, malachite, azurite, torbernite, native lead, pyromorphite and cassiterite are indicators of possible presence of metallurgical centers from the Chalcolithic and Early Bronze Age.

For applying the method indicative maps containing information about sampling points and the number of each mineral found in each sample are compiled. The study area is divided into 1,027 squares with equal sizes of 12 km² and for each square the probability of finding a given ore mineral is calculated by dividing the number of samples of the given ore mineral to the total number of samples for each square. By the method of triangulation a map of the probability of finding of ore minerals for the entire region is drawn. This map also presents the halos of mechanical dispersion of the minerals at a chosen level of statistical significance. By comparing the observed number of cases of the actual finding of ore minerals with the expected number the Bernoulli's (Poisson's) test was applied assuming independence of occurrence of minerals in critical area of less than 0.001. In result minerals which appear indirect indicators (or correlates) of chosen ore mineral in the samples have been determined. Further the relationships between the mineral-correlates are presented in the form of a network-graphic (graph) from which the expected connections can be visualized.

The final predicative map is obtained by the super positioning of dispersion halos of different ore minerals indicated by the stream-sediment pan-concentrated surveys what allows one to outline the perimeters of the complex halos.

Data

From the previously compiled database of stream-sediment pan-concentrated surveys of Bulgaria (Vitov, 2001) numbering 134,000 samples, a separate, regional database of samples was derived to encompass the territory of the water-catchment basins of Struma and Mesta rivers in SW Bulgaria, which falls in three administrative districts: of the towns of Pernik, Kyustendil and Blagoevgrad (Vitov, 2005, 2006, 2007, 2009). The derived database consists of 34,387 samples which contain the following minerals: native copper (32), cuprite (36), azurite (3), malachite (126), torbernite (1), chalcopyrite (37), native lead (706), pyromorphite (527), and cassiterite (79). Bracketed is the number of samples for each identified mineral. An independent control of this database appear the dataset presenting the mineral composition and co-ordinates of the known mineral deposits, occurrences and indications in the region – extracted from the catalog of Maznikov (1997, National Geological Fund). Lead and lead-containing deposits number 5; 58 are the lead manifestations and 92 are the lead indications. Copper and copper-containing deposits are 5, 48 are manifestations and 97 are indications. In this way parts of the designated sites overlap due to the complexity of the ores. Tin deposits, manifestations and indications are not known till now in the study area, but 79 stream-sediment pan-concentrated samples contain cassiterite (SnO_2). There is information that in Roman times (Denteletika province), in the Middle Ages and the Ottoman period tin was mined in Kyustendil District. On the topographic map K-34-71-B (Blagoevgrad sheet) a peak “Kalajjiiska (= tin) stone” (1447.6 m) is marked. This peak is omitted in the geological map (Sarov et al., 2011, Bulgarian National Geological Service, Project 425/20.07.2004). Instead, it is noted that in the area “migmatized biotite and two-mica gneisses with levels of mica schists occur”. In the “Slany Dol”, a tributary of the Jerman River, cassiterite was found in association with gold and barite (Bakalov, 1971, National Geological Fund). Paleogene conglomerates and sandstones interlayered with coal (Bobov Dol coal basin) are stratified beneath the river sediments in the area.

Results

1. Halos of copper minerals

The maps (Fig. 8) present the spatial distribution of the probability of finding of copper minerals – halos of mechanical dispersion, at a confidence level of 1% with a 10% step. Areas of copper and copper-containing deposits (red circle), manifestations (red rectangle) and indications (red triangle) are marked according to Maznikov (1997, National Geological Fund). According to the practice of the theory on the formation of halos of mechanical dispersion of minerals each deposit, manifestation or indication has to be plotted on the map. In reality, there are cases of halos without any source as well sources without halos. These cases may come from gaps in the sampling, sample analysis errors, and insufficient quality of the geological mapping and prospecting in the region (Vitov, 2009).

Native copper was found in the area of the “Zlata = Gold” mine (Tran District), in the vicinities of the town of Kyustendil (Banshtitsa River), north of Blagoevgrad (Dragodan village), the Predel locality, Banya, Yakorouda (water-catchment basin of the Cherna Mesta River and the southern slopes of Rila Mountain), and eastwards of the town of Sandanski. The contents are from 1-2 to 20-50 characters, rarely more. The most prominent anomaly is near Belitsa and Banya.

Cuprite is established near the “Zlata = Gold” mine, in direction of the village of Dren to the town of Radomir, upstream of the Mesta River and its tributary Cherna Mesta, near the villages of Belitsa and Banyja, and near Razlog.

There are established halos of dispersion of azurite near the “Zlata = Gold” mine (Tran District) and in the southern part of Pirin Mountain close to the village of Teshevo.

Malachite forms large surface halos of dispersion in a strip from Ruy Mountain through Lyuskan Mountain up to the town of Pernik. Small halos are established in and around Zlogosh village and in the Vlahina Mountain, Kyustendil District. The Osogovo ore region (in the Osogovo Mountain) has abundant malachite occurrences in the water-catchment basin of the Crna River (locali-

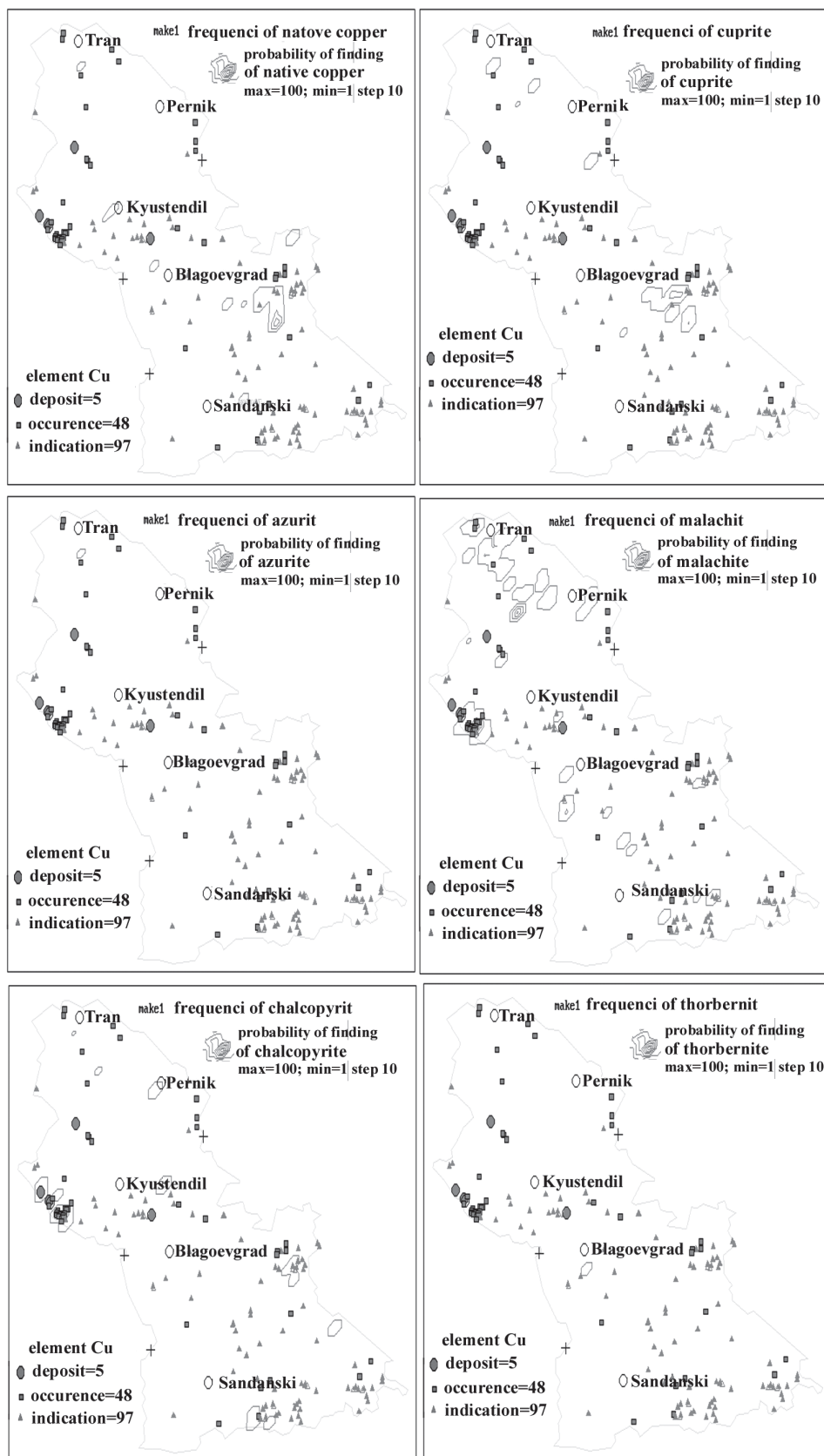


Fig. 8. Halos of dispersion of the copper minerals native copper, cuprite, malachite, azurite, chalcopyrite and torbernite in the water-catchment basins of the rivers Struma and Mesta, SW Bulgaria.

ties: Lisichidupki=Fox holes, Green valley, Venina darjava, etc.) and in the area of the springs of the Lebnitsa River (Gueshevo town). South and southwest of the town of Blagoevgrad there is a chain of small halos of dispersion of malachite most likely coming from known manifestations and indications (Green valley). Similar halos occur in the southern parts of the Pirin Mountain along the border with Slavianka Mountain (the village of Teshevo).

Dispersion halos of chalcopryite are outlined in the Lyuskan Mountain around the town of Pernik, in Konyavska Mountain (east of Kyustendil), Osogovo ore region, Buntsevo and Southern Pirin (Slavianka deposit).

Torbernite is found only to the south of Blagoevgrad (possibly coming from the Oranovo uranium mine).

The stream-sediment pan-concentrated surveys outline complex anomalies of copper minerals (Fig. 9A) that occur along the Rui – Lyuskan – Pernik – Dren strip (malachite, azurite, native copper). A large complex anomaly is established in the Osogovo ore region (malachite, chalcopryite). Most likely it was created by ancient ore mining activities near the town of Gueshevo and in the Crna River valley (Lisichidupki=Fox holes). The largest and most pronounced anomaly appears in the region of the Cherna Mesta River (the stripe Yakorouda – Banya – Belitsa – Razlog). It consists of halos of native copper, cuprite and malachite. The comparison between the known settlements from the Early Chalcolithic (Chohadzhiev, 2007) and the predicative maps shows good convergence (Fig. 9B) and these facts appears a good prognosis for finding of new Copper Age settlements in the region.

2. Correlation between minerals of copper, lead and tin

All of the cases of finding of minerals of copper, of native lead, of pyromorphite and of cassiterite as well as the cases of their co-location in samples (N_{avb}) are calculated. We estimated the probability of finding and the expected number of co-location (λ) if the minerals are independent. The sum of the probabilities of finding from zero to the observed number (N_{avb}) as well as the calculation of the expected correlates between the found minerals is given in Table 4.

The diagram of expected relationships between the minerals of copper, native lead, pyromorphite, and cassiterite (Fig. 10) shows that these minerals form a logical sequence – the primary sulfide mineral chalcopryite has a connection with malachite, azurite (to torbernite) and cuprite, which in turn is associated with native copper. This is a statistical presentation of the chemical processes and transformations of copper minerals in the zone of oxidation of copper sulfide deposits. Native lead and pyromorphite associate statistically with malachite, cuprite and native copper, which is an indication of the relationship established in the process of pyrogenesis (metallurgy and forest fires). Cassiterite is probably correlated with native copper and cuprite in connection with metallurgy of tin-bronze, but it is possible to come as a result of natural co-occurrence of copper and cassiterite in copper-tin mineralization.

3. Occurrences and halos of dispersion of lead, pyromorphite and cassiterite, and their contents

The attached maps (Fig. 11) show the locations of stream-sediment pan-concentrated samples (black dots) and the presence of native lead or pyromorphite or cassiterite in them with a colored circle. The content of these ore minerals is represented by color as follows: yellow (1-10 grains), violet (11-20 grains), cyan (21-50 grains), green (51-100 grains), blue (101-200 grains), black (201-500 grains), gray (0.001 to 0.01%) and dark yellow (more than 0.01%). A separate map shows the surface halos and the deposits, occurrences and indications after Maznikov (1997, National Geological Fund).

The halos of dispersion of cassiterite in the valley of the Cherna Mesta River are with high contrast and the samples have relatively high concentrations (up to 20 characters in sample). Their source is not established till now.

In the valley of Strumica and in the southern area of the Pirin Mountain an area of small, non-contrasted halos of dispersion of cassiterite with low contents of 1 to 10 characters was outlined. It can be assumed that this halos is related to the cassiterite-fluorite-quartz vein mineralization in the valley of Strumica established by N. Zidarov (unpublished, National Geological Fund). It is expected that similar manifestations will be found along a line from Sandanski to Teshevo.

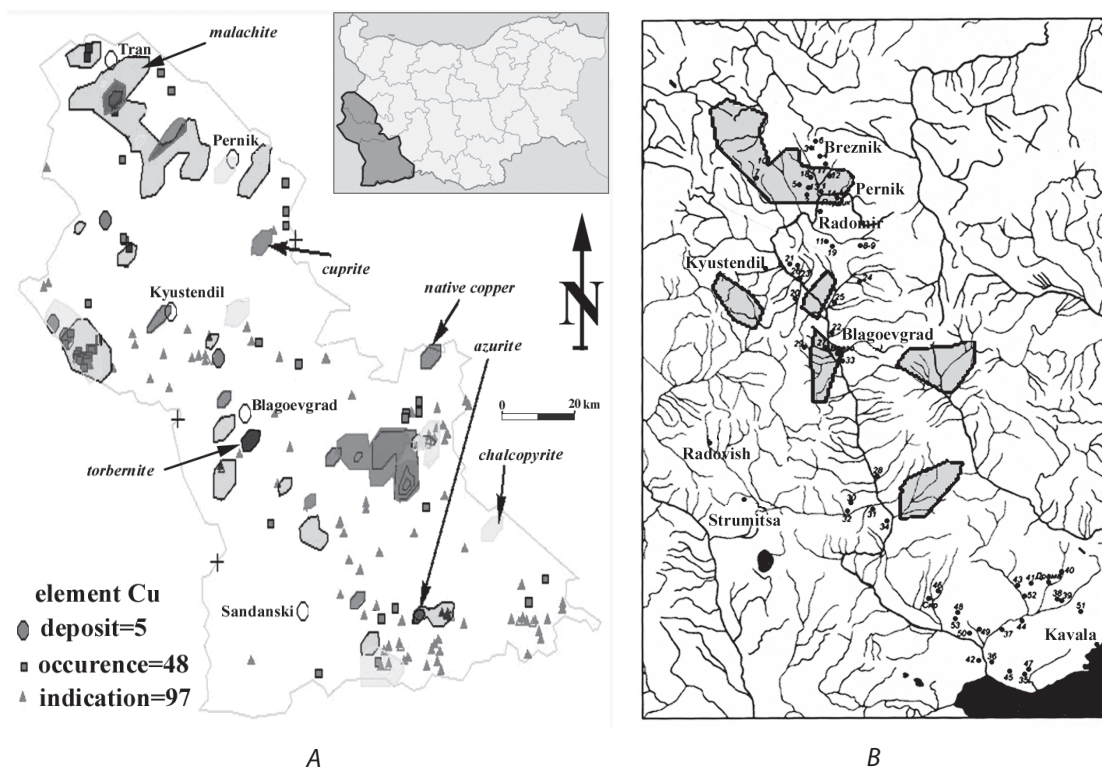


Fig. 9. A-Complex anomalies of copper minerals revealed by stream-sediment pan-concentrated sampling, B- Settlements from the early Chalcolithic (Copper Age) (Čohadžiev, 2007) and pronounced complex anomalies of copper minerals along the rivers Struma and Mesta.

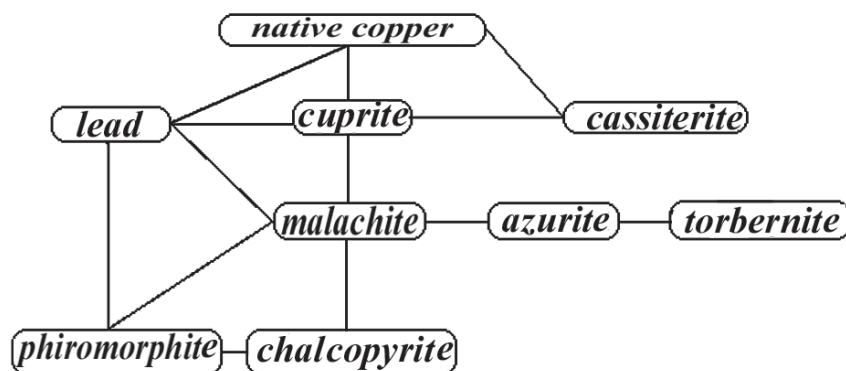


Fig. 10. Graph of expected links between copper minerals, native lead, pyromorphite and cassiterite in river sands of the water-catchment basins of Struma and Mesta rivers, SW Bulgaria.

Native lead is commonly found in a strip from the Trun ore region to the town of Pernik. It forms a large contrasted anomaly but there is no evidence of lead mineralization in the area. A similar strip connects the village of Dren and the town of Kyustendil through the Konyavska Mountain with no lead mineralization. In the Osogovo ore region no samples with native lead were found. Southwards of this line near the town of Blagoevgrad, in the Mesta River valley and in the Cherna Mesta River valley there are many halos of lead dispersion. The southern parts of the Pirin Mountain have an anomaly with a pronounced contrast which is also localized on the northern slopes of the Slavanka Mountain. Samples from this region have high concentrations of native lead (0.01 %).

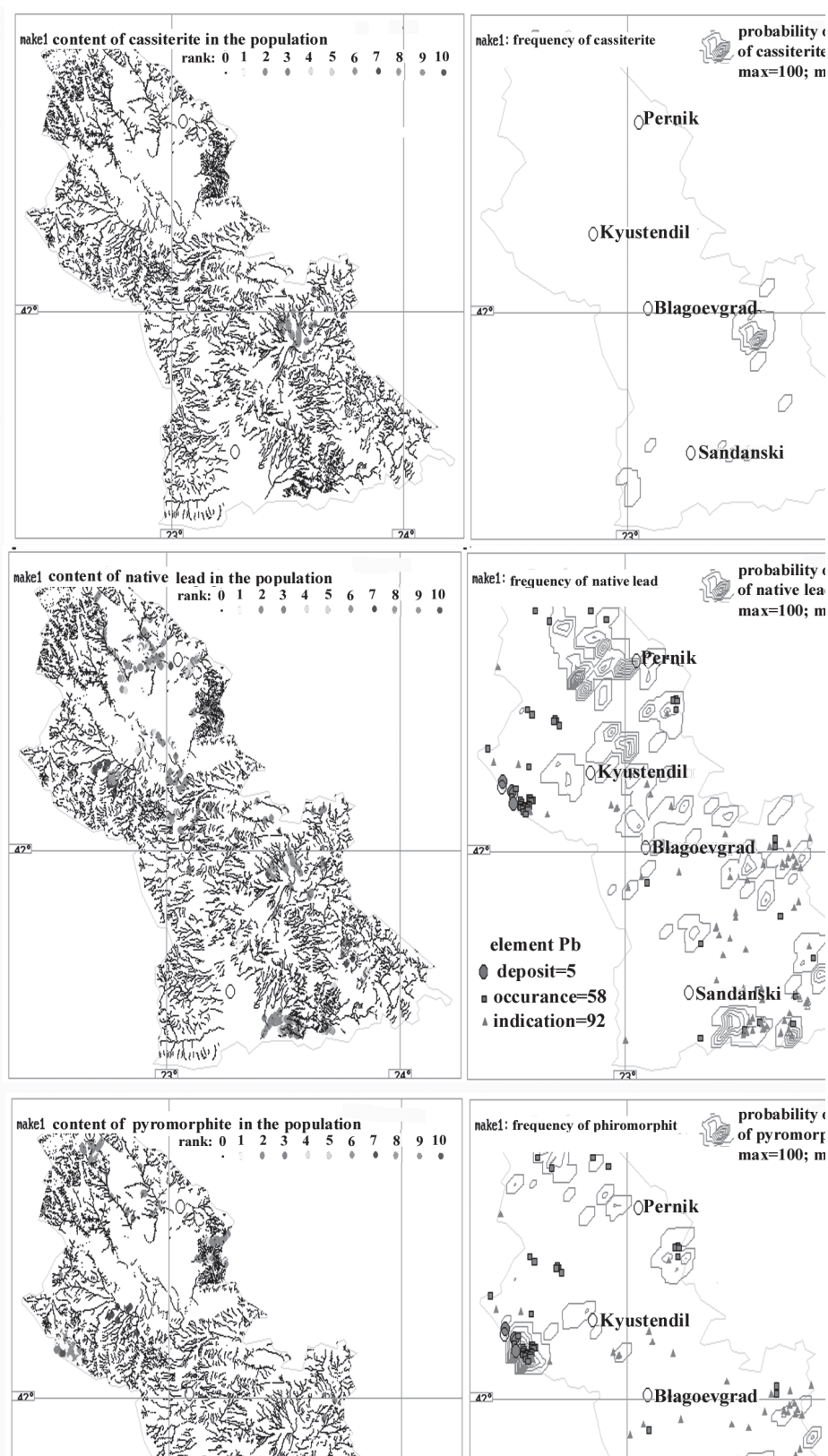


Fig. 11. Site of finding, concentration and halos of dispersion of cassiterite, native lead and pyromorphite in the water-catchment basins of Struma and Mesta rivers, SW Bulgaria. The location of copper and copper-containing deposits is designated with circle, of respective occurrences – with square and of respective indications – with triangle.

Минерал “а” Mineral “a”	N _a	Минерал “в” Mineral “b”	N _b	N _{avb}	$\lambda = \frac{N_a N_b}{N}$	$\sum_{k=0}^{k=N_{avb}} \frac{\lambda^k}{k!} e^{-\lambda}$
Самородна мед Native Copper	32	Куприт Cuprite	36	6	0,03	1,000
		Олово Lead	706	9	0,66	1,000
		Каситерит Cassiterite	75	2	0,07	0,999
Куприт Cuprite	36	Каситерит Cassiterite	75	6	0,08	1,000
		Олово Lead	706	6	0,74	0,999
		Малахит Malachite	126	2	0,13	0,999
Малахит Malachite	126	Олово Lead	706	17	2,59	1,000
		Пироморфит pyromorphite	523	20	1,92	1,000
		Азурит Azurite	3	2	0,01	1,000
		Халкопирит Chalcopyrite	37	5	0,13	1,000
Азурит Azurite	3	Торбернит Torbernit	1	1	8.10-5	0,999
Халкопирит Chalcopyrite	37	Пироморфит pyromorphite	523	6	0,56	0,999

Table 4. Correlations between copper minerals, cassiterite, native lead and pyromorphite revealed by 34387 stream-sediment pan-concentrated samples from the water-catchment basins of the rivers Struma and Mesta, SW Bulgaria.

Pyromorphite is abundant in the Osogovo ore region, the northern slopes of the Slavianka Mountain, in the valley of the Mesta River near the border with Greece, near the Dren-Radomir area, and to the northeast from the town of Pernik in the Trun ore region.

Discussion

An important element of the cultural heritage of Bulgaria is its history of mining and metallurgy (First Symposium..., 1975). The periods of intensive mining and metallurgy mark the high points of cultural progress and prosperity of our country. Studies conducted by G. K. Georgiev (1987) with reference to 154 titles of papers providing information about mining and metallurgy at Thracian time and before show the unsatisfactory state of our knowledge about the ancient mining. On the other hand, foreign authors and researchers (Chernyh, 1978; Ivanov, 1983; Ryndina, 1998) insist on claiming that the earliest metal objects of Europe were created on the territory of modern Bulgaria and date before the Thracian civilization. These ancient communities had amazing skills in mining and processing of metals like gold and copper. There appears an impression that the territory of modern Bulgaria played the role of a cradle of the metallurgical technology for mankind (Chernyh, 1978). Already in the Neolithic in Bulgaria (Todorova and Vaysov, 1993) there is a marked appearance of metal tools (Chohadzhiev, 1989, 2007), the first findings of processed (faceted) mineral grains (Kostov, 2009) and the technology for extraction of metals (Boyadzhiev 2009; Roussev and others., 2010). Studies on the distribution of

minerals in the available stream-sediment pan-concentrated samples (Vitov, 2002) show that in our country there are plenty of native copper and copper minerals, gold (Vitov, 2002), mercury and mercury minerals (Vitov, 2002; Vitov, Marinova, 2005), and native lead and lead minerals (Vitov, 2003, 2008). New data has been obtained about the presence of tin ore (cassiterite) in river sands (Vitov, 2002). This is a result from the relationship between the geological structure, availability of natural resources and the arising and development of mining and metallurgy in Southeastern Europe.

The facts show that on the territory of modern Bulgaria, in the valley of the Struma River, technologies of mining and metallurgy have been known from 4 or 5000 BC. Minerals are a natural phenomena, which when combined with forest fires spontaneously create metals. The people of that remote time observed these processes and reproduced them in the technology of metallurgy and manufacturing of metal objects – jewelry, tools, weapons and ritual objects – the regalia of power and ritual plates for religious activities (rituals, mysteries). During the Chalcolithic, hunters, farmers and pastoralists systematically occupied the valleys of the rivers Struma and Mesta. After the last glaciation the terrain was close to the present relief but the traces of glaciations were more preserved. The Slatina site (Kyustendil District), a prehistoric settlement, known with its copper wedges and axes, is located on authentic glacial moraines. The region has abundant deposits, occurrences and indications of minerals that are visible on the surface. The natural weathering destroys minerals and they fall into the rivers. The native metals like gold, copper and lead can be seen with naked eye and their great weight, malleability, color and luster attract man's attention. After an evaluation of their usefulness, the metals became desirable and wanted, and later – mined. Bearing in mind that mining and metallurgy are labor-intensive and time-consuming activities it may be assumed that the settlements of the people associated with these activities will be in close proximity to the mineral deposits. Thus the data about the distribution of mineralization in the region and the mineralogical anomalies of native copper and copper minerals become an important element in localizing prehistoric metallurgical and mining settlements.

Of particular interest is the connection between the Copper and Bronze Ages what appear to be the “arsenic bronze” artifacts (Vaksevo village, Chohadzhiev, 1998, Table 1). Arsenic is a highly volatile and its incorporation in the molten copper is problematic. At the same time, research has shown that there is a natural native copper with high contents of arsenic (Dragodan village, Table 1). It can be assumed that the “arsenic bronze” is hammered out (or casted) from naturally enriched arsenic pieces of native copper. Distance between the villages of Vaksevo and Dragodan is only of a few kilometers.

The discussion of these issues (Vitov, 2012) demonstrated the interest, competence and empathy of the Bulgarian geological community in supporting archaeological research related to mining and metallurgy during the Chalcolithic and Bronze Age.

Conclusions

This paper presents a methodology for compiling predictive maps of promising areas for further archaeological studies for identifying the provenance of metals of known artifacts from the Chalcolithic and Early Bronze based on data about known ore deposits, occurrences and indications, and about the mineral composition of river sands.

The approved already methodology showed that in the water-catchment basins of the rivers Struma and Mesta in SW Bulgaria there are predictive areas of archaeological prospecting for archaeological excavations of Copper and Bronze Age settlements. The most promising areas are: the Cherna Mesta River valley (Yakorouda – Belitza – Banya strip), near the town of Boboshevo, Osogovo ore region (Zelendol), Garbino village, the Tran ore region (Lyuskan and Rui mountains), near the village of Dren (Radomir District), Strumica River valley and the area near Teshevo village in the southern part of the Pirin Mountain.

It is shown that the designation on a map of the mineral composition of stream-sediment pan-concentrated samples and the outlining of halos of dispersion of copper minerals, cassiterite, native

lead and pyromorphite is an effective method of reasonable search for metallurgical centers from the Chalcolithic to the Early Bronze Age. Combining mineralogical methods (stream-sediment pan-concentrated sampling and mapping) with soil geochemistry, hydrochemistry and geophysical methods (the method of natural electric fields) increases the efficiency of finding particular ore bodies and associated ancient mining and metallurgical centers.

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