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Editor's Foreword

The 'western borderland' of the Tripolye culture, appearing in the title of this volume of the 'Baltic-Pontic Studies', refers to the cyrcle of neighbouring cultural systems of the Upper Tisza and Vistula drainages. As neighbours of the Tripolye culture such groups are discussed as Lengyel-Polgár, Funnel Beaker and, albeit to a much narrower extent, the Globular Amphora (cf. B-PS vol. 8) and the Corded Ware cultures. The papers discuss the reception of 'western' traditions by Tripolye communities as well as the 'western borderland' mentioned in the title.

Defined in this way, these questions have been only cursorily treated in the literature. The consequences of accumulated omissions in the study of the cultural surroundings of 'Tripolye' have been felt by us when we worked on this issue. Thus, we submit a greatly limited work as far as its subject matter is concerned hoping that it will open a sequence of necessary studies. Such studies should, in the first place, focus on the co-ordination of the 'languages' of taxonomy and then they should investigate different aspects of the mechanisms of the outlined processes of the 'cultural contact'.

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ISSUES CONCERNING TRIPOLYE METALLURGY AND THE VIRGIN COPPER OF VOLHYNIA

The metal artifacts of the Tripolye culture (TC) — the most ancient artifacts on the territory of the right bank of the Dnieper river of Ukraine and Moldova — have been attracting the attention of researchers for a long time. Significant success has been achieved in the study of their morphology, with their connection to the related Balkan and Southern Carpathian cultural centres having already been determined. Large scale studies on spectra-analytical and metal-graphical examinations were summarised in the exhaustive monographic review of N.V. Ryndina [1998].

These studies did not, however, resolve the question of the raw material sources of the ancient metallurgy. This question is crucial to an understanding of the character and orientation of the ancient population of Ukraine in relation to neighbouring territories, as well to the reconstruction of the structures and systems of the organisation of metal production in the different chronological and local variants of the TC.

In recent years, archaeologists and geo-chemists have co-operated in the examination of archaeological finds of copper and bronze, and the determination of the sources of raw materials for the production of metal artifacts. Previous studies of the element composition of metal focussed generally on the chemical composition of the artifacts, whereas our present aims are more extensive and include the determination of the mutual relations between: artifact — metal — virgin copper; artifact — metal — dross — ore.

The results of the geological-chemical analyses of the copper ore expositions on the territory of Ukraine testify to the presence in ores of certain geo-chemical specificities, i.e. the sets of chemical elements (para-genetic combinations) characteristic for each ore exposition, as well as their analogies observed in dross and in finished metal artifacts. Such geo-chemical analogies have been discovered during examinations of finds made of metal, metal ore and its dross in a range of ancient centres of non-ferrous metal industry in Ukraine.

The examination of the virgin copper of Volhynia and the specimens of metal artifacts from the archaeological sites of the central and western regions of Ukraine is a characteristic example of the first stages of research into possible comparisons between the chemical composition of metal and copper ore raw materials. Selected for this testing were sixteen specimens of archaeological finds, attributed according to their composition to copper and bronze artifacts, from the excavations in the villages of (a) Glubochok and (b) Bilche Zolote in the Borshchiv District of Ternopil Region, and also from (c) Sofievka in the Kiev Region.

a. The settlement in Glubochok was excavated by the expedition of the Borshchiv Museum under the management of M. P. Sokhatskiy. The settlement is multileveled: the upper layer is attributed to the Noua culture, and the lower layer to the B I stage of the TC (according to the period division of T.S. Passek). In the vicinity of TC dwelling no.1, at a depth of 0.5 m, four copper artifacts were discovered among fragments of TC pieces: a ring 35 mm in diameter, fashioned from a plate 5 mm wide and 2 mm thick (Fig. 1:2); a 25 mm diameter ring made from a rod round in cross-section and 2 mm in diameter (Fig. 1:4); a sickle-shaped 'eye-hook' (fishing hook?) — 45 mm long, up to 35 mm wide, 1.5 mm thick near the eye, and 1 mm thick in the lower part (Fig. 1:5).

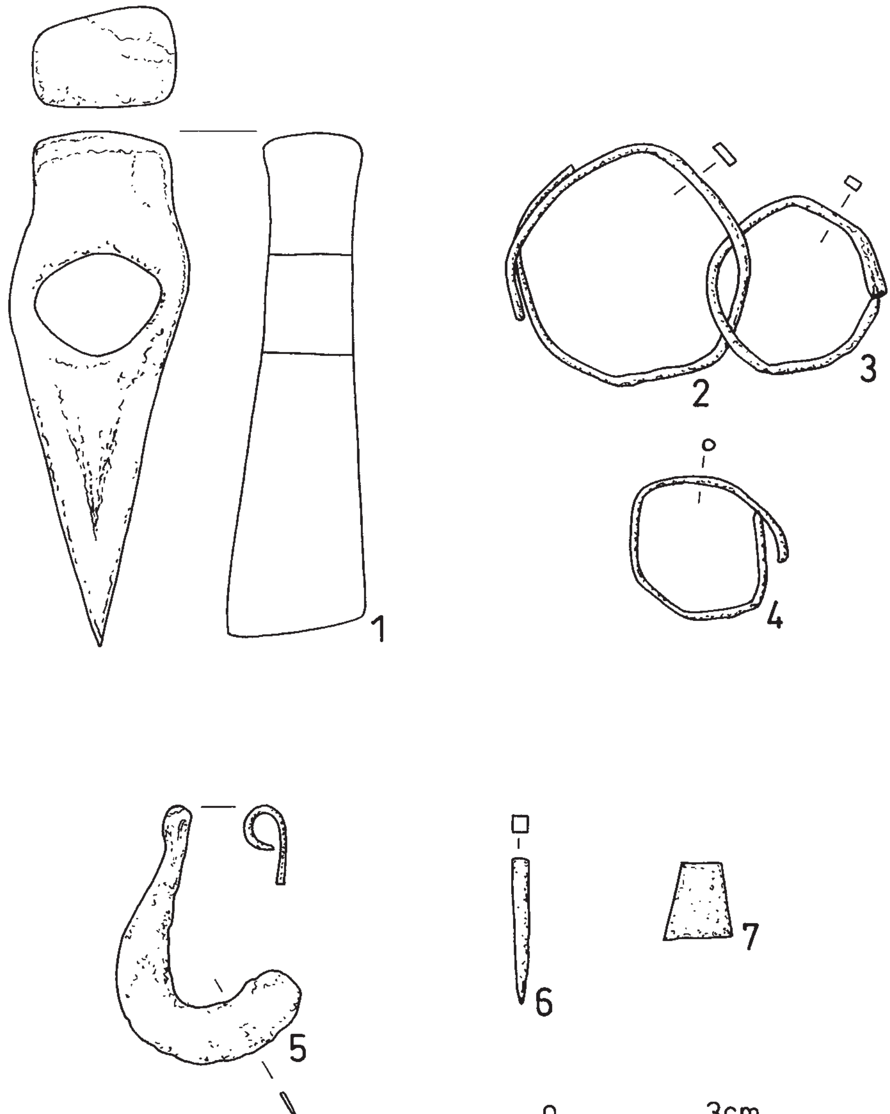
A 30 mm long fragment of a four-sided awl (Fig. 1:6) was found in TC dwelling no. 2 near the remains of an oven. A thin trapezoid plate with mirror-polished surface was found in dwelling no.3 on the surface of the clay ground. The length of the plate is 13 mm, the width 1.5 mm (Fig. 1:7). Additionally, two fragments of pins from the Noua culture of the Late Bronze Age have been submitted for examination (bronze artifacts).

b. The TC settlement in the village of Bilche was excavated at the end of the XIX century. The Polish archaeologist G. Ossowski [1892] distinguished two cultural layers there, which are presently attributed to the stages B II and C I according to the period division of T.S. Passek. A hammer-axe was found in the settlement. This artifact has numerous analogies among the Neolithic axes of the Carpathian region, although damage caused by the finders makes its accurate typological determination impossible.

c. Also selected for the research work were fragments of spiral beads from the materials of the Sofievka cemetery excavated in the suburbs of Kiev in 1947-1948, which was attributed to the C II stage [Klochko 1995].

The geo-chemical basis for the proposed work was formed by an examination of the element composition of specimens made of Volhynian virgin copper originally discovered in a quarry near Rafalivka village, and obtained from the geological museum of the Institute of Geochemistry, Mineralogy and Ore Generation of the National Academy of Sciences of Ukraine. The specimens had been found in the area of oxidisation adjacent to the basalt strata and represented virgin metal in the form of extended plates 4-6 mm wide (Fig. 2:2). The surface is covered with an oxidised film, occasionally with pale green coloration attributed to the development of malachite.

The copper from the boring well in the area of Rafalivka village was also examined in order to provide a comparison with the chemical composition of the virgin copper selected in the quarry. It allowed possible variations to be determined in the distribution of chemical elements of the virgin copper and their influence on the chemical composition of the adjacent basalt strata (Fig. 2:1).



F i g . 1. Copper artefacts of the Tripolye culture: 1 - hammer-axe (Bilche Zolote); 2 - bracelet; 3 - wide ring; 4 - thin ring; 5- ear-ring; 6 - awl; 7 - plate (Glubochok).

Table 1.

The results of the spectral analysis of admixtures in the specimens of the virgin copper from different fields (weight %)

Elemnts	Ukraine, Rafalivka Volhynia Region	Ukraine Donetsk Region	Russia, the Urals, Sverdlov Region
Ag	0.6-0.8	0.001	>0.1
Au	0.003	—	n/o
Pd	0,002	—	n/o
Pt	0,002-0,003	—	n/o
Al.	0,03	1,5	n/o
Si	0,1-0,5	30	n/o
Ti	n/o	0,2	0,008-0,05
Cr	n/o	0,005	0,2-0,8
Fe	0,1	0,4	1,0
Co	—	—	n/o
Ni	0,001	0,003	0,03
Zn	0,05-0,1	0,006	0,003-0,03
As	—	0,005	—
Sn	0,01-0,03	0,0015	0,004
Sb	0,01-0,03	0,1	—
Pb	0,002-0,01	0,2	0,03
Bi	—	0,003	0,002

The virgin copper from the copper sandstone of the Donets basin and Volhynia has been examined as a specimen of the geological-chemical specificity of the virgin copper of the diverse genesis strata (Table 1). The varying fluctuations of a range of chemical elements in the virgin copper of Volhynia, determined in the process of analytical research, have been considered in the analysis of the metals of artifacts, including the possibility of losses in their composition during the process of fusion.

A comparative analysis of element composition, which included the determination of chemical elements and their combinations, was carried out on the available specimens of virgin copper (Table 1), copper and bronze articles (Table 2-3). The artifacts have been classified into two metal types, according to their chemical composition: comparatively pure copper and bronze (the analytical research was carried out by the Laboratory of Physical Methods of Studies of the Institute of Geo-chemistry, Mineralogy and Ore Generation of the National Academy of Sciences of Ukraine). The archaeological finds from the excavations in Sofievka marked as nos. 16a, 23, 86, 254, 285, 380, from Bilche Zolote no. 1 and from Glubochok nos. 3, 4, 5 can be classified as copper artifacts.

Table 2.

The results of the spectral analysis of the copper artefacts from Sofievka, Kiev Region (weight %)

Elements	Numbers of specimens					
	16a	23	86	254	285	380
Ag	0,1	<0,1	>0,1	>0,1	0,001	0,1
V	0,001	—	—	—	—	—
Ti	0,005	0,006	0,06	0,05	0,001	0,02
Cr	0,4	0,04	1,0	0,9	0,006	0,7
Fe	1,0	1,0	1,0	1,0	0,01	1,0
Ni	0,001	—	<0,001	0,001	—	0,001
Zn	—	0,03	0,01	0,008	—	0,01
As	—	—	—	—	—	—
Sn	0,003	0,004	0,005	0,006	0,001	0,003
Sb	—	—	—	—	—	—
Pb	0,003	0,004	0,005	0,006	0,003	0,003
Bi	0,003	0,003	0,002	0,003	—	0,003

Taking into consideration the correlation features, the artifacts made of pure copper can be divided into three groups:

1. The specimens nos. 3, 4 (Table 3) and 285 (Table 2) are the closest to the virgin copper from Rafalivka in terms of chemical parameters. The absence of cobalt, arsenic and bismuth are conclusive factors, whilst their iron content, directly correlated with chrome, is a certain degree lower.

2. The specimens nos. 16a, 23, 86, 254, 380 (Table 2) illustrate the metal worked from the virgin copper. It is worth noting that their chemical composition is close to that of the Rafalivka artifacts. The distinction between these metals and the metal from the first group is that the iron content in them is a degree higher, whilst the tin, lead and antimony content is lower. The high content of iron in these artifacts may be linked to its accumulation in the virgin copper, whilst the lesser content of tin, lead and antimony may be caused by losses during the metal fusion process in the original raw materials. Consequently, the above-mentioned peculiarities of the chemical composition of this set of artifacts permits us to assume that both the virgin copper of Volhynia and the virgin copper connected with the crystalline strata of the Ukrainian Continental Shield, the finds of which are verified by certain data published in specialist literature, could have served as the raw material for their production.

3. The specimens nos. 1, 2, 35 (Table 3) can be isolated into one group due to their specific geo-chemical similarities with the metal from the Donets basin, obtained from the copper ores of copper argillites, sandstone and aleurolites, in which the tin, lead

and antimony content is almost two degrees higher than that in the copper of Volhynia [Tatarinov 1993]. At the same time, one cannot eliminate the possibility that the metal could have been obtained from the virgin copper which is encountered in the form of small grains imbedded in the sedimentary strata of oxidised ores (the ore mines of the Bakhmut and the Kalmius-Torets fields).

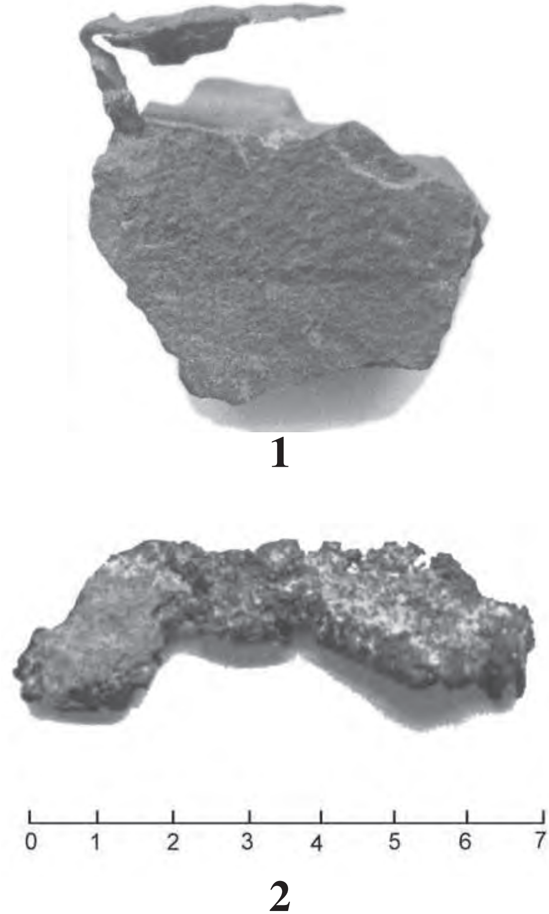
The virgin copper is encountered in the ore deposits and lodes in the sedimentary crystalline strata, but its chemical composition still has certain peculiarities, which can serve as a significant correlative feature for its identification both with copper exposition and with ready-to-use tools made of it. For instance, a significant admixture of antimony and lead is frequently observed in the virgin copper from sedimentary copper ores of the Bakhmut field of the Donets basin. This feature considerably distinguishes it from the virgin copper of Volhynia, in which the zinc content is greater and the content of arsenic, cobalt and bismuth is either less or completely absent. In the virgin copper of the Urals, arsenic and antimony are absent, but the content of nickel and lead is comparatively high.

The frequency of virgin copper encountered in the different copper deposits varies significantly. In the ore strata of sedimentary genesis it is represented by small individual nuggets (up to 159 g). The copper is more frequently represented in the form of small--scale dissemination or grains in the most oxidised parts of strata and, particularly, in the organic substance, concentrated in the argillaceous-aleurithic strata.

A special interest deserve ore deposits of Volhynia, located in the basalt strata which, in comaprosion to other depostits on the territory of Western Ukraine, are characterised by the significant scale of copper mineralising. The first data concerning the discovery of virgin copper appeared in Polish geological literature at the end of the 1920s. However, some publications indicate that the finds of Volhynian virgin copper had already been described in 1887.

Virgin copper was found on the outskirts of the village of Velykiy Mydsk in 1927, and reported by the Polish geologist S. Malkowski in 1929 [Malkowski 1931]. Then, in 1935, the Polish geologist R. Krajewski [1935] discovered virgin copper in the basalt strata of Yanova Dolyna (Janowa Dolina). The next important discovery of virgin copper by a Polish geologist was made in 1939 by I. Wojciechowski in the volcanic glass of both basalt and tufa strata of Volhynia [Wojciechowski 1939]. Since that time, virgin copper has been found in many areas of Volhynia, such as Dovge Pole, Gutvin, Berestovets, Oleksandria and Goryngorod. Some historical data show that virgin copper had already been known to the ancient Slavs. There is evidence for this in the names of settlements (Mydsk, Medysche etc.), actually deriving from the ancient Slavic word m'd'-med'. It is known, moreover, from published sources that ancient ore fields have been revealed in these places. This can be testified to by the virgin metal exposure close to the surface of the ground. The significant weight of individual nuggets of copper, which reached 1 kg and more, meant that it was economically profitable to excavate.

Presently, the mineralising of Volhynian virgin copper is fixed in an area 6 km wide and 120 km long [Gurskiy *et al.* 1997]. This covers a part of the southern slope of



F i g . 2. Virgin copper of the Volhynia area, the Rafalivka quarry: 1 - virgin copper in the basalt stratum; 2 - plate of virgin copper.

the Brest field and the northern part of the Volhynian Palaeozoic platform [Gurskiy *et al.* 1995]. Well-known ore exposures, such as Rafalivka, Dovge Pole, Velykiy Mydsk, Gutvin, Berestovets, Oleksandria, Goryngorod, Vapnytsa, Rudavtsy, Stydni and Yanova Dolyna are located on the territory of this belt (Fig. 3). According to their parameters, many of these ore expositions may be large ore carriers. General reserves of Volhynian ore are estimated at 28 million tons of metal. Besides ore, the concentrations contain silver (up to 0.03%), gold (up to 1 g/ton), platinum (up to 0.8g/ton) and palladium (up to 0.4 g/ton).

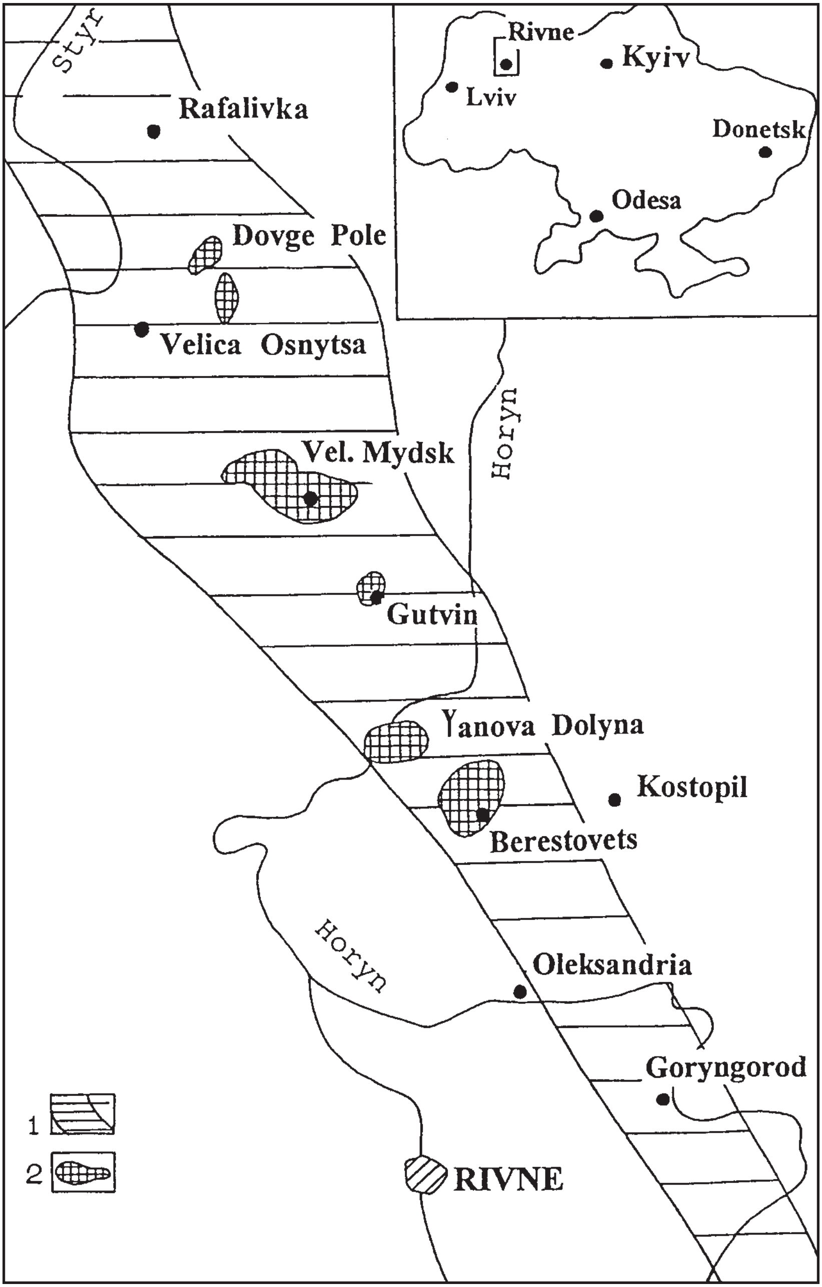


Fig. 3. Territory of Volhynia copper mineralization development (1) and large basalt rocks outcroppings with virgin copper manifestation (2).

The morphological diversity of the virgin copper of Volhynia can be illustrated by the example of its apportionment in the hydrothermal changes in the massive and almond stone basalt in the Rafalivka quarry [Gurskiy *et al.* 1997; Kvasnitsa *et al.* 1995]. The processes of massive basalt processing (chlorinating, zeolitisation, quartzination, ferrugination, potassium metasomatisation) are most intensively represented in the areas of the tectonic origin and primary cracked structure of strata. Small grains of almond stone basalt located among their massive analogies are subjected to similar changes, but to a greater degree.

In the hydrothermally-processed basalt, virgin copper is found in the form of small grain dissemination, thin crusts, small vein-shaped and large dendrite-shaped isolations, plates and small growths, most frequently in association with quartz. The weight of some plates reaches up to 1 kg. Calcite impressions are frequently observed on such specimens. Copper rhombus-dodecahedrons and their accretions appear in the areas of free growth.

Almonds and cavities are filled with minerals of a hydrothermal origin (quartz, chalcedony, calcite, chlorite, barite, ceolites etc.) which are frequently associated with the virgin copper. Cases of the adjacent radial-radiant growth of virgin copper and chlorite are comparatively frequent. Copper accumulations along the clefts around the circumferences of almonds are distinctive.

The chemical composition of the Volhynian copper is very pure (up to 99%), with admixtures of iron, silver and other elements. The colour of its non-oxidised expositions is copper-red or copper-yellowish. The generation of a small, thin bordering of cuprite, malachite and azurite is attributed to the oxidisation of the grains. The significant content of zinc — up to 1000 mg/kg — and silver — 800 mg/kg; the lesser quantities of antimony and tin — 300 mg/kg — and lead — up to 100 mg/kg; and the complete absence of arsenic, cobalt and bismuth are significant characteristics of the chemical composition of the Volhynian virgin copper from the Rafalivka copper deposit.

On the territory of the development of the Volhynian copper ore field, other surface copper expositions are also known. Although the chemical composition of this copper has not yet been investigated, we may suppose that it possesses certain distinctions from the copper from the Rafalivka ore mine.

The territory of the Bakhmut field of the Donets basin is an example of the diversity of chemical composition in the different ore mines, where combinations of copper + lead, copper + zinc, copper + zinc + lead, copper + lead + arsenic are observed in the copper-bearing strata. A greater content of antimony in combination with these is less frequent. This kind of specificity of ore mines is determined by the mineral strata composition, by the type and intensity of the secondary processes in the oxidisation area, and by the hypogene tectonics. Therefore, in order to obtain a complete and objective type division of the virgin copper of Volhynia, it is necessary to investigate its analogies on the whole territory of the copper expositions.

The next set of artifact specimens (nos. 6, 8, 9) can be attributed to bronze: arsenic — tin and arsenic — tin — antimony bronze, in which the content of major admixtures exceeds 1%. With regard to cobalt and antimony admixtures, their content is negligible.

In terms of its chemical composition, the metal of specimen no. 7 can be attributed to bronze or yellow metal. Its zinc content exceeds 1%. The higher content of arsenic, lead and zinc most probably testifies to the diverse elementary composition of the original ore raw material in relation to Volhynian virgin copper. According to the classification of E.N. Chernykh, these bronze artifacts could be attributed to the Carpathian-Transylvanian chemical group or, to a lesser degree, to that of the basin of the right bank of the Dnieper, which are linked by the source of ore raw material located in the Carpathian region [Chernykh 1976].

In the process of the examination of the bronze artifacts, certain problems arise concerning the metal fusion technology, as bronze is considered to be an alloy based on copper with different alloy admixtures, except for zinc. The final product can be obtained by the addition of tin alloy (the most widespread admixture) to the pure copper liquid, by the mixing of copper and tin ores before fusion or by the processing of copper ores characterised by such a quantity of natural admixture that enable the transition into metal and transform it into an alloy. In such cases, we can speak about bronze of both an artificial and a natural origin. The accurate determination of the metal origin — natural or technical — is the most difficult problem in this context.

In the process of solving this problem, it is very important to examine the elementary composition of the possible raw sources for alloy production. The examination of the chemical composition of copper ores, genetically connected both with the crystalline strata and with the sedimentary strata deserves special attention. As a rule, the distinctive feature of the copper ores of sedimentary genesis is a rich variety of admixtures, including lead, zinc, tin, antimony, arsenic, bismuth and silver, which is attributed to the polymineral composition of ores themselves (content of galena, sphalerite, arsenopyrite and other minerals).

The examination of the ancient metallurgical centres and of the metal samples from the archaeological monuments in Ukraine reveals that the sedimentary type copper was used more frequently in non-ferrous metallurgy, while the pure copper (possibly virgin copper) was used only in about 4-11% of the total quantity of articles [Bartseva 1981]. On the territory of Ukraine, geologists have investigated sedimentary type copper expositions in two western regions — the Dniester river basin and the cis-Carpathian area (Fig. 4), as well as the Donets basin in the east of the country.

Within the confines of the Dniester river basin, two large copper expositions located on the left bank of the Dniester river (Ternopil Region) are known.

1. Ivano-Zolote copper exposition located on the south-eastern side of the village of the same name. Broadly speaking, this is characterised by deposits of aleurolites and argillites in which copper is frequently represented by thin lentils of malachite. Copper content is up to 9%.
2. Ustechnykov copper exposition, mainly characterised by the inter-bedding of sandstone,

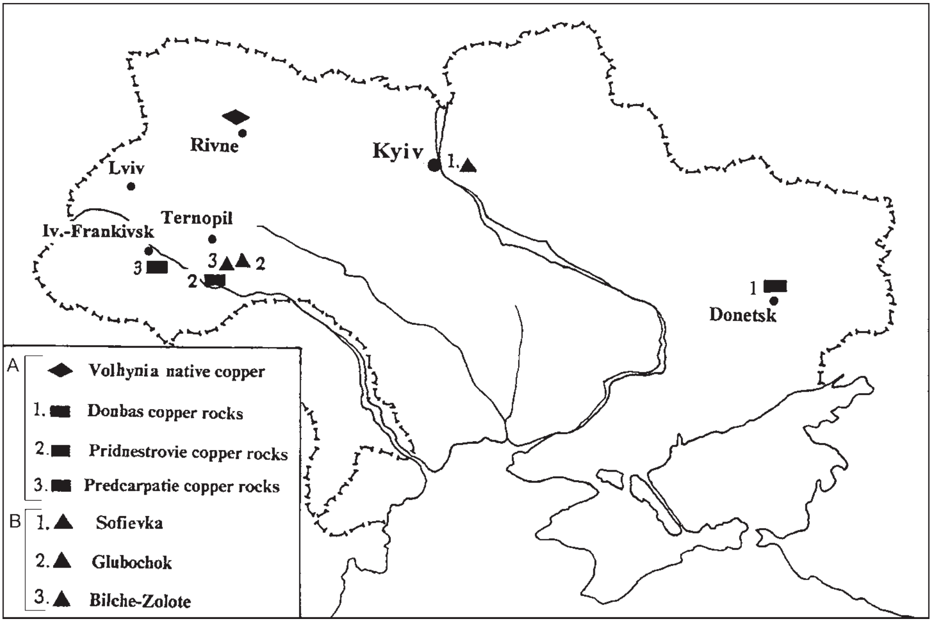


Fig. 4. Map of copper deposits locations on the territory of Ukraine (A) and archaeological sites - sources of the geological-chemical analyses (B).

aleurolites and argillites. The maximum content of copper in these strata comprises 2.5%. The presence of chalcopyrite, chalcocite and bornite, and occasionally pyrite, galena and silver (up to 50 mg/kg) is recorded in the mineral composition. The ore extends up to the daylight surface and could have been extracted by the open method.

On the territory of the Regions of Lvov and Ivano-Frankivsk, in the south-eastern and central areas of flexure before the Carpathian mountains, one can observe copper mineralising of the sedimentary strata of Neogene with exposures on the daylight surface (Nadvirne, Loivskiy, Yablonevske, Kaluzhskiy and Delyatynskyy sites). Ore grains are attributed to the sandstone strata and clays. The major copper minerals are malachite, chalcopyrite, covellite, azurite, chalcocite, bornite and occasionally virgin copper. Lead minerals (galena) and zinc minerals (sphalerite) are also frequently encountered. Copper content varies from decimal points to 16%. Lenses and layers of clays with a high quantity of herbal remains are the most copper-enriched.

The question of the possibility of producing bronze of an industrial genesis, using virgin copper and tin fused from Volhynian ore, demands special detailed studies, in which particular importance should be given to specialised examination. Tin ores of the Suschano-Perzhan zone have been recorded in Volhynia. These could certainly have been used particularly in metal, as well as in bronze fusion.

The Volhynian ore exposition is one of the most significant in Ukraine. It is represented by cassiterite ore in which tin content reaches 1% and more. The spectral composition of the ore shows an almost complete absence of arsenic and a high quantity of lead, tungsten, niobium, beryllium and lithium in its composition. Regarding the range of the other chemical elements in the tin ore, they are either completely absent or present only in insignificant quantities, with the exception of lead [Nekhayev *et al.* 1986].

In addition to the commonly-accepted elementary composition analysis, also applied in the process of examination was the author's method of spectral analysis, which permits the element composition of multi-component heterogeneous objects of natural and industrial origin to be examined. The advantage of this method lies in the additional option of registering of the structural connections between chemical elements which cause the appearance and existence of solids. With the help of this method, the form of admixture is established — differentiated as structural (idiomorphic) or mechanical.

A further result of the application of the above-mentioned method is that the typical features of virgin copper and copper polymineral ore have been determined (such as the presence of the basic component across several generations, formed under peculiar thermal conditions), which correspondingly are characterised by certain set and content of admixtures according to their thermal physical characteristics.

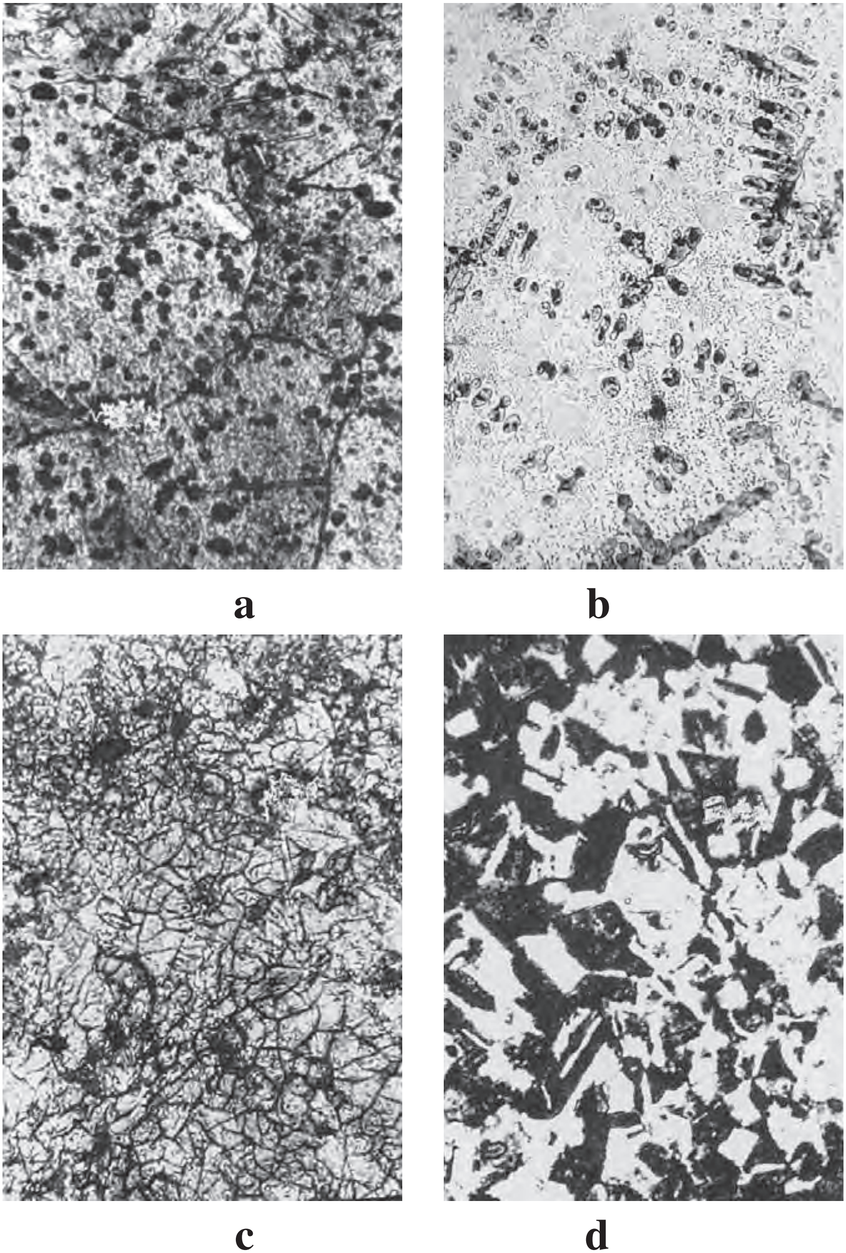
In addition, it is possible to determine the presence of those chalcophile elements which are able to generate their own minerals in association with copper, such as Sn, Pb, Zn, As, Sb and Bi. The varying quantity of these elements differentiates one copper generation from another and determines its origin.

Finally, spectral analysis also enables us to determine the presence of the small number of stratum-forming elements — Si, Mg, Al and Ca — which are not connected in pairs and are not mechanical admixtures, but rather 'element-prisoners', being in various states at different stages.

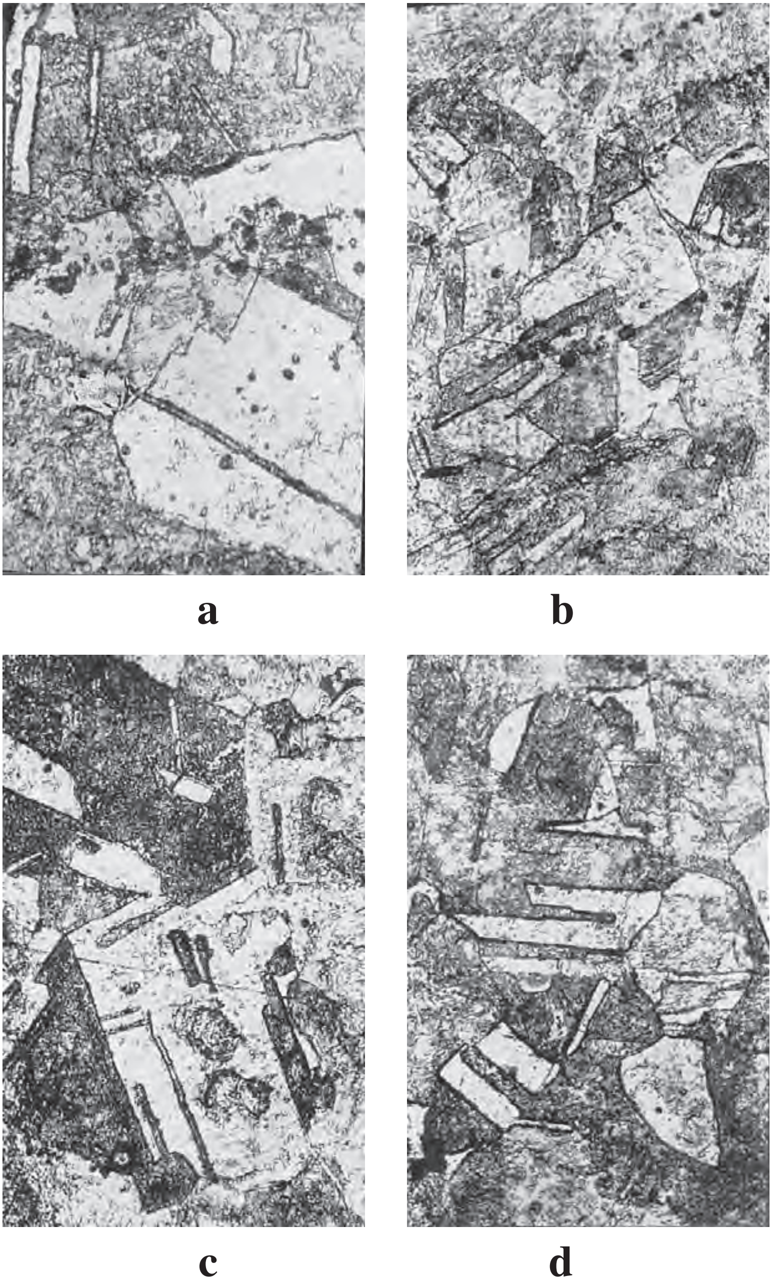
The virtues of this method as an instrument for the identification of the material composition of archaeological objects seem to be unquestionable, since, in a number of cases, the presence or absence of a particular chemical element in a certain generation and the significant or insignificant changes of its quantity from one object to another testify not to the 'deficiencies' in metallurgical production, but rather to the natural heterogeneity of the basic raw mineral.

Spectral analysis appeared to be the most efficient method in the examination of bronze articles, since the data obtained demonstrates that the polymineral ore raw material could have been used in the manufacture of these articles. On this basis, the copper alloys correspond to a greater extent to bronze of natural origin. In other words, they represent the metal produced as a result of natural ore processing, rather than by means of a special alloying of pure copper.

The above-mentioned research work also studied the options for the application of this metallographic method of examining ancient metal structure, reflecting the mechanical-technical conditions of its appearance. In contrast to the problems of modern



F i g . 5. Microstructure of virgin copper and alloys (x 480) from: a - Volhynian virgin copper; b - Donbas virgin copper; c - structure of bronze (Glubochok site - awl, alloy); d - structure of brass (Glubochok site - plate, alloy + MTO).



F i g . 6. Specifics of deformational structure of the metal artefacts made of poor copper (Glubochok site): a - x 480; b - x 360, bracelet; c - x 480; d - x 360 - wide ring.

metallography, where the distinct conditions of metal production and processing, creating the structural composition of the metal and determining its solidity, rust resistance, plasticity and other properties, are assigned in advance, this method works in reverse, and is correspondingly more complex.

The virgin copper of Volhynia is a natural metal, whose creation is linked to high temperature copper-bearing solutions, and which is characterised by a structure distinct from that of the metal of copper articles. The virgin copper generated in the low temperature conditions of the oxidisation of sulphide ores possesses a significantly different structure.

Since virgin copper of a distinct genetic type has been previously revealed in finds together with dross wastes, one can assume that raw material of a different origin had been used in the ancient foundry industry. The micro-structural idiosyncrasies of the virgin copper specimens under investigation allow us to determine not only the geography of raw material sources, but even to reconstruct the type of field which can be clearly associated with the mineral composition.

The development of the structural criteria for the determination of virgin copper, in this case the Volhynian copper, provides a high degree of certainty in the attribution of the copper ingots found in the ancient centres of metal industry to a given technological process or to the initial raw material.

However, research shows that the spectral composition and morphology of these finds do not always represent convincing evidence of their belonging to a given technological type.

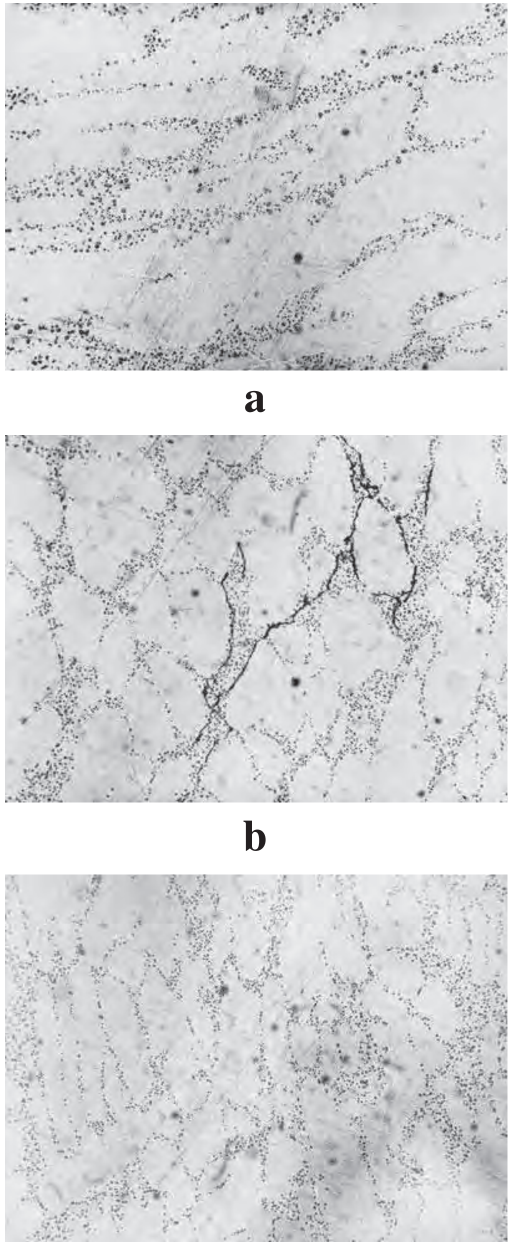
Hence the comparative analysis of the microstructures of two genetic types of virgin copper - the Donets basin type and the Volhynian type — with precisely this purpose in mind. The crystalline structure of these types is given in Fig. 5. The analysis of graphs of optical microscopy shows that the virgin copper of the Donets basin (Fig. 5a) differs from the Volhynian copper (Fig. 5b) in the degree of oxidisation. The etching pits on the metal surface are a common feature, appearing because of the heterogeneity and defects of structure, in this case caused by the grains of cuprite (Cu_2O). In the low temperature Donets copper, the dissemination of cuprite grains is of a dendrite form, and the structure of grain boundaries is almost indistinguishable, in contrast to the high temperature Volhynian copper. With regard to the possibility of using the comparative structures of the copper artifacts and the virgin copper as a key indicator of its application in the foundry industry, the authors consider that this problem requires a somewhat different approach than that previously used by the Russian specialists, which has failed to provide any positive results [Ryndina 1993]. An examination of the thin structure of metals by means of electronic microscopy, with the help of which the difference in the structure of the natural virgin copper and the fused virgin copper can be determined, would certainly solve the problem. In order to determine the difference in the structure of the virgin copper from the different origin sources with the help of metallography and electronic microscopy, a data base needs to be created, based on a significant quantity of specimens of archaeological copper ore raw material from both the archaeological sites and the contemporary ore fields.

Metallographic studies of the structure of metal articles made from pure copper (Glubochok, Ternopil Region) (Fig. 6) showed that they had been manufactured by means of mechanical-thermal metal processing. The specimens of the typical deformational structures most likely formed in the process of high temperature forging, such as the grains and doubles sizes (shown in the picture) are relatively large. It is practically impossible to trace any connection between the raw material source and the ready-to-use product manufactured by the deformational processing. Such a connection can be traced between the specimens of virgin copper and ingot specimens direct from cast forms or cast articles. Even in these cases there exist certain equivocations, but the distorting caused by deformations is eliminated.

The results of the examination of the structure of copper-based alloys used for the production of the archaeological articles from the village of Glubochok are shown in figure 5. In 5a, one can see the small-grained structure of the cast, non-deformed metal. This is obtained by means of rapid heat removal, determined by the comparatively small cast dimensions of the article, in contrast to the slower cooling technique applied in the case of large-scale pieces. The alloy consists of bronze CuSnAs on the base of the solid alloy solution.

Also found in this feature was a brass plate, the structure of which is represented in figure 5d. It has a clearly fine-grained structure, with a deformed composition, which means that the article was possibly cast and then forged at low temperatures. The metallographic examination of the metal structure used for the production of the hammer-axe in Bilche Zolote showed that it had been worked by the cast method out of pure copper (Table 3). The typical structure from the different points and plains of the article's cross section is given in Fig. 7. The specific structural nature of this specimen consists in its decoration with copper monoxide, generated directly in the places of heterogeneous structure. The polycrystalline structure and boundaries of crystallites are formed from liquid in the course of the crystallisation of the alloy. They possess different coefficients of admixtures retaining and represent areas of heterogeneity where, under certain conditions, the first processes to occur are those of oxidisation. The absence of features of the deformational structure of grains indicate that the surface of the hammer had not undergone any strengthening treatment. The development of fractures in some areas of grain boundaries, especially in the working part of the implement, most probably resulted from its utilisation.

The metallographic method used in the structural examination of copper and bronze articles, in combination with x-ray and spectral methods, enables the determination of the peculiarities of the ancient technologies of metal production and processing. These technologies may vary according to regional features, since the structural characteristics are dependant on the thermal deformational processes which occur in the course of the production of functional pieces by the schools of different masters. A comprehensive



a

b

c

F i g . 7. Microstructure of the alloyed copper hammer-axe from Bilche Zolote: a - x 70 - blade, sheer cross-section; b - x 70, surface layer of the sheer cross-section; c - x 70, central part of the sheer cross-section.

Table 3.

The results of the spectral analysis of the artifacts from the burial place in Glubochok and in Bilche Zolote of Borshchiv District, Ternopil Region

Number of specimen	Elements										
	Al	Si	Fe	Co	Ni	Zn	As	Sn	Sb	Pb	Bi
1	0,05	1,0	—	—	0,1-0,2	0,1	0,01	—	0,01	0,02	0,001
2	0,05-0,1	0,6-1,0	0,1	—	0,005-0,006	—	0,01	0,03-0,05	0,3	0,02-0,04	0,02-0,03
3	0,05-0,2	>1,0	0,1	—	0,003-0,05	—	—	0,03	0,01	0,02-0,03	0,002
4	0,05-0,1	>1,0	0,1	—	0,005	0,02-0,05	—	0,01	—	0,01-0,02	—
5	0,04-0,05	10,	0,06	—	0,005-0,01	—	0,007-0,01	0,005-0,01	0,005	0,005-0,007	0,002
6	0,1	0,2-0,5	0,05-0,1	—	0,1	—	>1	>1	0,2	0,1-0,2	0,03-0,06
7	0,02-0,03	0,04-0,2	0,1	0,03	0,01-0,02	>1,0	0,01-0,5	0,02-0,03	0,04-0,1	0,1-0,3	0,06-0,1
8	0,02	0,5	0,2	0,03	0,1	0,05	>1,0	>1,0	>1,0	>1,0	0,1
9	0,1	0,5	0,1	0,02	0,1	—	>1,0	>1,0	>1,0	0,8	0,1

1 - hammer-axe (Glubochok); 2- large bracelet; 3 - wide ring; 4 - thin ring; 5- ear-ring; 6 - awl; 7 - plate; 8 - pin; 9 - ingot.

set of standard article metal structures and raw material sources would be necessary for such studies to be undertaken.

CONCLUSIONS

1. From a comparison of the standard values of the chemical composition of Volhynian virgin copper (based on the specimens from the Rafalivka open-cast mine), and of copper and bronze work-pieces from the archaeological monuments in the villages of Sofievka, Glubochok and Bilche Zolote, three groups of copper artifacts can be distinguished:

- the TC artifacts nos. 3, 4 (Glubochok) and 285 (Sofievka), according to the main geological-chemical indices, correspond to the virgin copper of Volhynia;
- the copper artifacts nos. 16a, 23, 86, 254 and 380 (Sofievka) are close in terms of their chemical composition, although they possess significant distinctions from one another;
- there is a geo-chemical similarity in the metal of artifacts no.1 from Bilche Zolote and nos. 2 and 5 from Glubochok, and also between these and the work-pieces, which could have been produced from copper raw material of the sedimentary type (possibly from the Dniester river basin). The location of these villages, 20-25 km from the copper strata exposures, gives significant grounds for this hypothesis.

2. The bronze artifacts from the monument in Glubochok are attributed to the later layer of the Noa culture. This could possibly confirm that copper ore raw material was taken from the same source. The geo-chemical peculiarities of the alloys of these artifacts indicate the sedimentary copper ores of the oxidisation zone, close to those of Donets in their composition.
3. A solution to the questions related to the further development of the geological--chemical criteria for the identification of the virgin copper of Volhynia and the metal artifacts from the different archaeological monuments requires, first and foremost, the creation of a base of analytical data of the chemical composition of the virgin copper specimens selected from throughout the territory of the Volhynian ore field. This kind of material can be found in industrial geological institutions and in the collections of geological museums in both Ukraine and Poland, as Polish scientists were the initiators of studies of Volhynian virgin copper. The examination of the virgin copper in the copper fields of the cis-Carpathians, the Dniester river basin and the Middle Dnieper river basin (within the boundaries of the Ukrainian Continental Shield) could present substantial supplementary information for these studies.
4. The development of the geo-chemical indices of the virgin copper of Volhynia will allow the resolution of important issues connected with the determination of the initial ore raw material type used for the production of the artifacts. At the same time, similar geo--chemical characteristics of the copper ores from the Regions of Lvov, Ivano-Frankivsk and Ternopil may provide additional information concerning their application in the non-ferrous metallurgy on the territory of western Ukraine.
5. The most efficient approach to the examination of the virgin copper of Volhynia and its possible connections with the non-ferrous metals of the archaeological artifacts seems to be the complex approach, with the application of modern methods of examination, including studies of the structural idiosyncrasies of metals and the determination of the absolute age of the virgin copper and the copper work-pieces by means of the radio--isotope examination of levels of lead, not previously used in the Ukrainian studies.
6. The metallographic examination of copper and bronze artifacts allows us to determine the features of the ancient technologies of metal processing, as the structural characteristics of both pure metals and their alloys greatly depend on the thermal deformational processes occurring in the course of the production of functional work-pieces. A comprehensive set of standard metal structures of the artifacts and raw sources is undoubtedly necessary for this to be undertaken.
7. One of the components of the examination of the microstructure of virgin copper metal work-pieces is analysis connected with the forging of the virgin copper under a range of different thermal conditions. This is necessary in order to specify the typical structures that could be used as standards for the comparison of ancient metal structures.

Translated by Maria Ogiyenko

ABBREVIATIONS

AP	–	Archeologia Polski, Warszawa
APS	–	Archeologia Polski Środkowowschodniej, Lublin
BPS	–	Baltic-Pontic Studies, Poznań
KSIA	–	Kratkiye soobscheniya Instituta Arkheologii, Moskva
KSIA AN USSR	–	Kratkiye soobscheniya Instituta Arkheologii Akademii Nauk Ukrainskoy SSR, Kiev
KSIIMK	–	Kratkie soobshcheniya Instituta Istorii Materyalnoy Kultury Akademii Nauk SSSR, Moskva.
MIA	–	Materialy i issledovaniya po arkheologii SSSR, Moskva
NA IA NANU	–	Naukovy Arkhiv Instituta Arkheologii Natsionalnoi Akademii Nauk Ukrainy, Kiev
SA	–	Sprawozdania Archeologiczne, Kraków
SCIVA	–	Studii şi Cercetări de Istorie Veche si Arheologie, Bucarest
WA	–	Wiadomości Archeologiczne, Warszawa
Zapiski NTS	–	Zapiski Naukovogo Tovarystva imeni T. Shevchenka, Kiev

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