

# The Study of Prehistoric Metallurgy

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The puzzle we have to solve is: How did prehistoric man live? Archeologists and scientists, chemists and prehistorians have now joined forces in applying much imagination and painstaking effort to the search for a solution. Some of the fruits of their cooperation are presented in this progress report.

## 1. Scientific Methods

Archeology is now able to provide us with an—admittedly still rather sketchy—picture of prehistoric man, his way of life, customs, and environment. The more we see and learn of his utensils, jewellery, and tools, the more pressing becomes the question of how all these objects were made, *i. e.* the question of the technical knowledge, aptitude, and scope of prehistoric man. This field is to some extent the precinct of the archeologist himself. However, as far as the study of prehistoric metallurgy goes, *i. e.* the working of metals and their extraction from ores in prehistoric times, it is clear that close cooperation between archeologists and scientists is very necessary. The aim of such studies should be, on the one hand; a metallographic investigation of the structure of prehistoric metal finds, and, on the other, a chemical investigation of such finds to ascertain their quantitative composition. It is primarily the second aim that has been pursued during the last twenty years by the “Study Group for Ancient Metallurgy of the Central Roman-Germanic Museum” with whose work the present article is largely concerned. With the support of the Deutsche Forschungsgemeinschaft such studies have been carried out at the Württemberg State Museum in Stuttgart, this work now having become the main research activity of the physical chemistry laboratory.

At Stuttgart attention was first directed to the analytical study of a large number of prehistoric copper and gold specimens rather than metallographic texture investigations, since:

1. Analytical studies require only a small sample of material; the object itself can remain in the museum. This aspect becomes particularly important when considering specimens in the possession of foreign museums. Textural studies, on the other hand, require that the object of investigation be transported to the laboratory.

2. Analytical studies also promised to reveal trading routes and connections between prehistoric cultures whenever it is possible to detect differing degrees of skill in alloying metals or to distinguish between metallic materials of different origin according to the various constituents pre-

sent and to recognize historical and geographical boundaries. The eventual goal is to elucidate the direction and rate of spreading of ancient methods of metal extraction and working.

In contrast, textural studies mainly yield information about the technical details of the way in which the metal was worked to give the finished product, *e. g.* whether it was beaten, cast, annealed, or quenched. It would certainly be most interesting to be able to follow the dissemination of this technical knowledge too; however, chemical analysis appeared more promising and more practicable.

For the reasons mentioned in point 1 above, it was not so much a matter of finding a completely non-destructive method of analysis—as might initially be thought—but of choosing a method capable of providing a complete quantitative analysis with a small sample of material, in which the possible concentrations of minor components may range over several powers of ten. Bearing in mind that an examination of several thousand objects, and not just random samples, was intended (over 20 000 prehistoric copper finds and about 3300 gold ones have so far been analyzed), it becomes clear that time-consuming micro or semimicro wet analyses had to be ruled out immediately. Emission spectroscopy offered a working compromise between the time and effort invested, size of sample, and costs incurred on the one hand and accuracy and sensitivity of analysis on the other.

An additional factor influencing our choice was the existence of earlier spectral analyses of prehistoric copper objects by Winkler<sup>[1]</sup>, Otto and Witter<sup>[2]</sup>, and van Doorselaer<sup>[3]</sup>. Scheufele<sup>[4]</sup> utilized the available experience to develop a method requiring 40 mg of substance that was suitable for routine analyses. However, the technique requires calibration alloys containing all likely minor components Sn, As, Sb, Ni, Bi, Ag, Pb, *etc.*, which are not always easy to prepare.

It was only after several years' experience in the analysis of about 10 000 Early Bronze Age copper objects producing some encouraging results that the question arose of extending such studies to prehistoric gold finds.

The particular value of the objects involved makes it all the more important to work with samples that are as small as possible. A method was successfully developed<sup>[5]</sup> that permits spectral determination of minor components down to 0.01% or less in a 2-mg sample of gold. Above all it proved possible to avoid use of calibration alloys of gold/silver/copper containing possible minor components by

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applying drops of the dissolved sample to graphite electrodes. Calibration then only requires gold solutions containing the same minor components in known concentrations.

In this way it was possible to include even highly valuable collections from German and foreign museums in our studies and to dispel any original misgivings.

## 2. Interpretation of Copper Analyses<sup>[6]</sup>

As mentioned above, spectral analyses of prehistoric copper objects can be interpreted in two ways. Firstly, the kinds of alloys can be determined and technical advances traced; secondly, it appears possible, on the basis of characteristic impurities, to establish the ore used and thereby the deposits from which prehistoric man obtained the raw materials for certain utensils. The distribution of the utensils and their distance from the source of raw materials should then permit further conclusions to be drawn regarding trading in the period concerned and thus also regarding the direction and rate of propagation of techniques for extraction and working of metals.

However, whereas the determination of the kinds of alloys gave rise to no significant difficulties, ascertainment of the ore deposits proved less simple than originally envisaged since the deviations between the deposits are hardly sufficient to provide more than rough indications. Moreover, comparison of presently accessible ore samples with analyses of prehistoric finished articles is beset with problems. The ore samples come largely from modern underground mines and their composition may differ widely from those surface outcrops accessible to prehistoric man. In addition, we have no knowledge of the smelting processes used at the dawn of history to extract metals from their ores; the technical details—*e.g.* temperature control alone—of the process would certainly affect the composition of the final product.

The direct question of ore deposits was therefore dropped by the Stuttgart group and some indication of origin sought instead by comparison of analyses of prehistoric objects. Such comparisons require a method capable of sifting through large amounts of analytical data for material whose uniform composition can be attributed to the same raw material and corresponding technical processes. The method of choice was a statistical model previously described by Klein<sup>[4]</sup>. Its use permitted classification of materials having the same combinations of elements to a first approximation as so-called "material groups". The material groups can be localized geographically and chronologically, as will be seen from the maps in Figures 1—4.

The distribution of a material group A indicates the area in which this material has been most frequently used and those in which it remained unknown, it can also be seen in which prehistoric periods it first featured in trading, when it dominated the market, and when it disappeared again. Although the exact origin of the raw material is not established, a definite contribution is made to the history of

commerce. And if it also proves possible to demonstrate that the material in question is endowed with characteristic qualities that render it suitable or unsuitable for one purpose or another, then reasons can also be given for its popularity or decline.

Copper and its alloys and gold were chosen for our studies. A factor in their choice was that these two materials are the first metals to have been used by man. This is not altogether surprising since they both occur as the native metal. Prehistoric man will have been more readily confronted with them than with, *e.g.* iron, which occurs native only in meteorites.

It is important to realize the full meaning of the sentence: "Man was confronted with these materials." In the course of prehistory we see man constantly searching for materials—this searching is therefore by no means limited to the industrial age—and subjecting all new substances to familiar technical procedures. For instance, we know that during the Neolithic age, in which the first copper and gold was found, man had mastered the following techniques: hewing, chipping, grinding, perforation of soft stones and bones; hewing and grinding of flint; all kinds of woodworking with stone tools; firing of clay (ceramics). On application of these techniques to native gold or copper he will have seen how to shape these materials by beating and thus discover "cold forging". After overcoming his initial disappointment about the lack of any hardening effect akin to that clay when the metals were heated in an open fire or in a simple potter's kiln, he will have found that they are more readily shaped while hot ("hot forging"). He must also have seen the melting of these metals although unable to utilize it because of the inadequate temperatures reached in his simple pottery kiln. Such temperatures only became accessible in the kilns available in the Mesopotamian cultures of the 4th millennium BC. Although there was no copper in Mesopotamia itself such a state of culture had been reached in the 4th millennium that raw materials could be transported from deposits in the surrounding mountainous country. The demand arose when the Mesopotamian cultures began to fashion precious materials into amulets, statuettes, jewellery, *etc.* Polished malachite was one such material used for adornment. It is conceivable that fire testing in a pottery kiln gave the first smelted copper, although we shall never be able to prove it. We can be sure, however, that the first copper artifacts come from the 4th millennium in Mesopotamia, as do the oldest gold objects known. The exploitation of the malleability as a characteristic metal property marks the beginning of metallurgy.

Our reasons for not studying objects from hither Asia are of a purely practical nature. It would simply have been too costly to obtain sufficient analytical samples from relevant finds, for we were fully aware that only extensive series of samples could provide conclusive results in view of the statistical method of evaluation necessary. We therefore began our investigations on prehistoric finds from Europe although we knew that we were dealing with a kind of "developing area" where the first techniques of metalworking were introduced as established procedures. However, we may assume that then, as now, nobody would freely

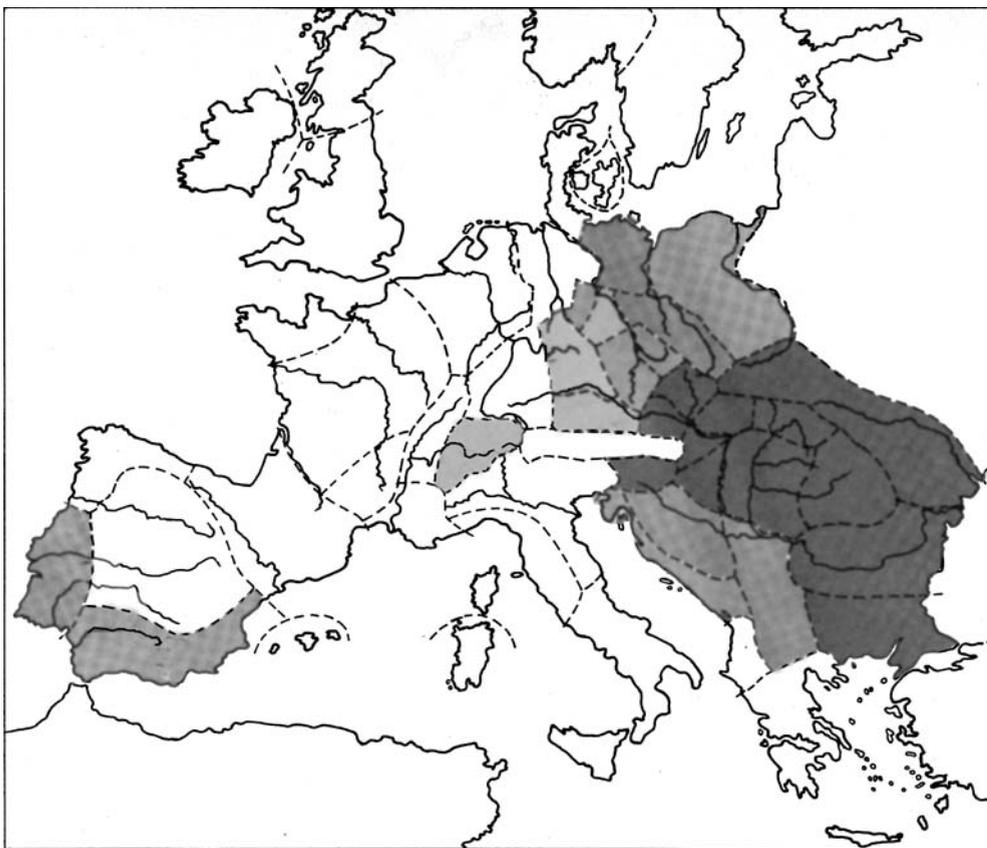


Fig. 1. Distribution of material group copper E 00 during the Copper Age at the end of the 3rd and beginning of the 2nd millennium BC. The material is free from impurities except for small quantities of silver. The map shows the first regions of copper-working in Europe and the directions in which it spread. It is assumed that the requisite knowledge was transmitted from the Near East. The areas of densest distribution are most heavily shaded and those of less dense distribution correspondingly lightly.

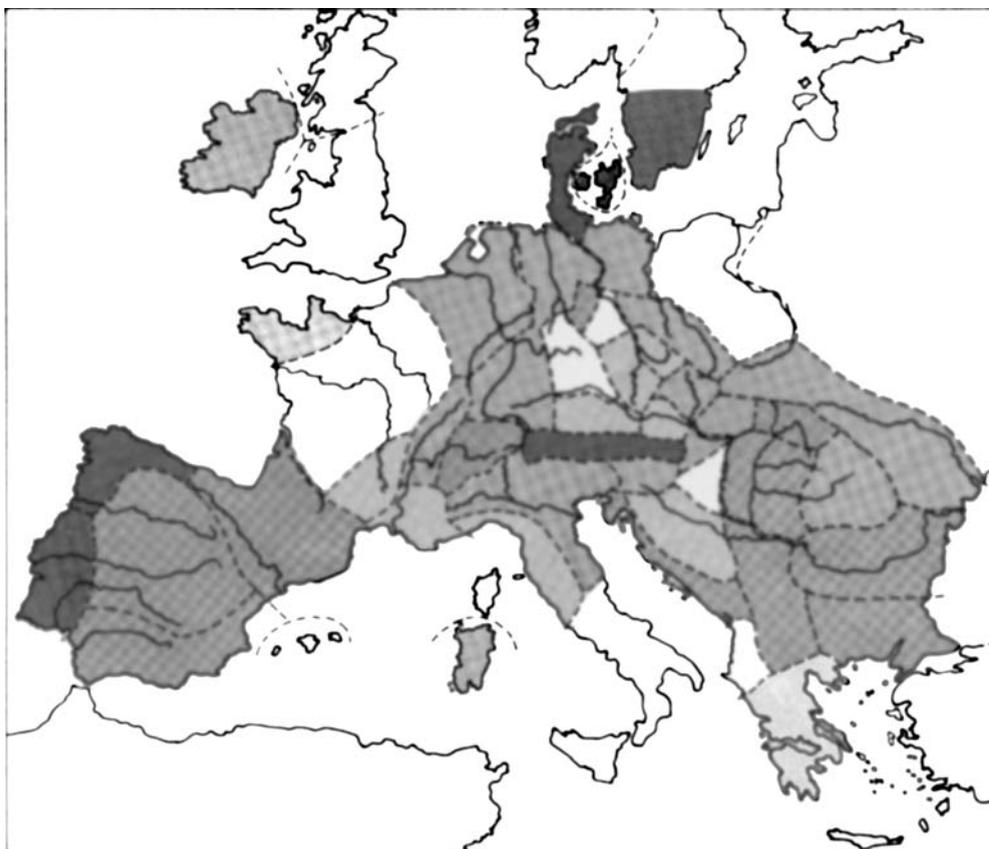
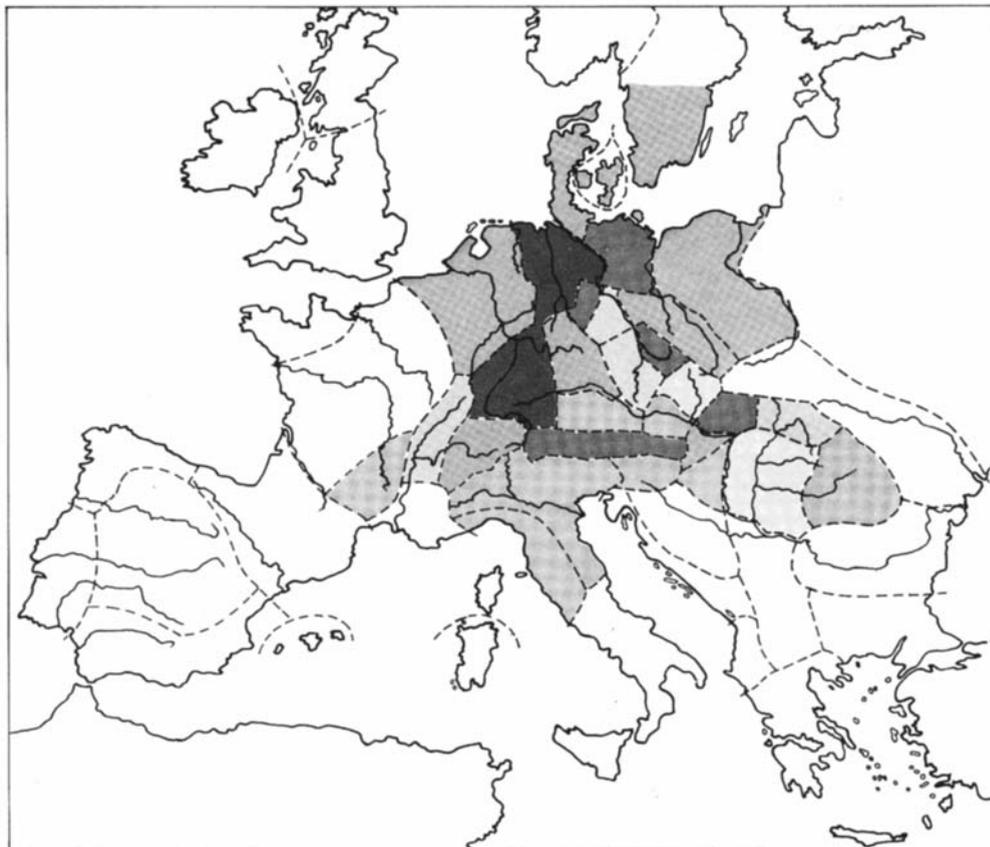
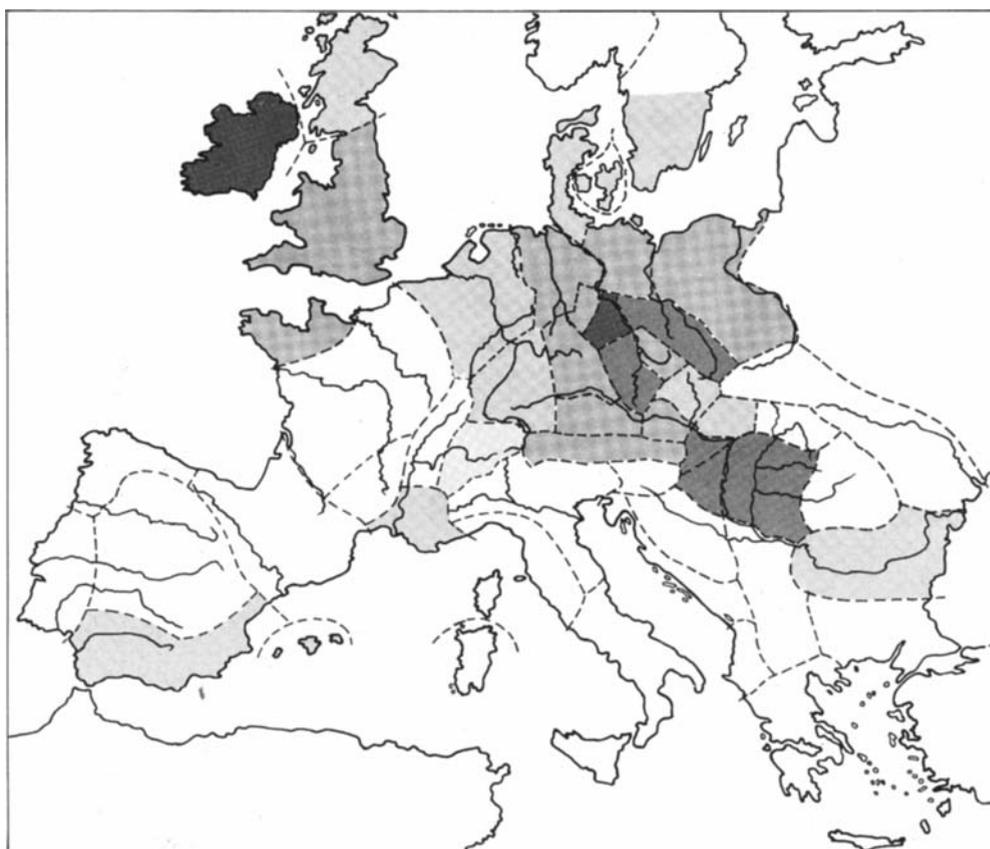


Fig. 2. Centers and distribution of the first arsenic bronze (material group copper E 01 A). Arsenic bronze seems to have been discovered in the Aegean and then produced in areas possessing the raw material. From these areas it was traded over large distances during the later Copper Age at the beginning of the 2nd millennium BC. The material shown contained no impurities other than arsenic (up to about 7%) and small amounts of silver. For meaning of shading see Fig. 1.



ABBL 3

Fig. 3. Distribution of material group copper A during the Early Bronze Age, 18/17th century BC. The material is characterized by high contents of arsenic, antimony, silver, and nickel and by the complete absence of bismuth. Antimony and nickel often reach several per cent. For meaning of shading see Fig. 1.



ABBL 4

Fig. 4. Distribution of material group copper E 11 B, characterized by contamination with arsenic, antimony, and silver, by the absence of nickel, and by the presence of less than 0.02% of bismuth. The material was used exclusively during the Early Bronze Age, 18/17 century BC, although apparently discovered later than A. For meaning of shading see Fig. 1.

broadcast the secrets of working a new material. Rather, attempts will have been made to satisfy home demand from foreign deposits without revealing too much secret knowledge.

### 3. Results of Copper Studies<sup>[6]</sup>

After preliminary evaluation of about 20000 analyses of prehistoric copper and bronze objects we can now provide the following picture regarding Europe.

In the middle of the 3rd millennium BC certain communities having a farming economy and living in permanent settlements in present-day Bulgaria, Romania, and southern Yugoslavia came to know copper. They used it to produce simple utensils and jewellery such as awls, needles, and wire and sheet rings. The copper is almost completely free from impurities and probably partly native copper and partly won from surface outcrops of ore. Possible sources are deposits in the neighborhood of Niš in Yugoslavia and in the Carpathians. This copper is very different from that used during the same period in the eastern Mediterranean and Anatolia, in so far as suitable analytical samples were at our disposal. This seems to confirm the assumption that copper-seekers from the Near East traveling to the Carpathians and the region of Niš passed on a knowledge of rudimentary metallurgical processes to the local inhabitants.

The picture changes about 100 years before the beginning of the 2nd millennium. It appears that large scale exploitation then began of the copper deposits throughout the whole Carpathian basin, the material being worked for local requirements and for export. The utensils, axes, axe-adzes, hammer axes, *etc.*, are characterized by their large size, thickness, and corresponding weight. They were possibly also used as a source of raw material in the same way as the later ring ingots. They are frequently found, like the latter, in large numbers where they had apparently been hoarded. This would also suggest that a special closed guild of metalworkers provided the farming settlers with an established supply of utensils. Utensils produced in these parts traveled as far as the Baltic in the north and Bavaria in the west. The copper of this period is practically free from impurities and was therefore probably still obtained largely from oxide ores. The large amounts worked preclude any large contribution by native copper.

An analogous process probably took place in west Europe during the same period. Originating from the Cyclades or from Syria, the copper seekers seem to have established a series of fortified factories along the coast of Spain and Portugal. They probably again initially used oxide ores from surface outcrops, as is apparent from the complete lack of impurities in the oldest artifacts. A little later, evidence is found for all stages of copper extraction and working; crude ore was in places transported more than 40 km from the deposits to the factories where it was smelted on a small scale and made into ingots, utensils, and jewellery, and prepared for transport and stored. Some of the objects resemble those from the eastern Mediterranean, as does the composition of the material in a number of cases, thus

suggesting a certain degree of mutual trading. The metal concerned is characterized by the, presumably natural, presence of antimony, arsenic, and bismuth.

Thanks to its arsenic content the eastern Mediterranean copper produced during this period—at the dawn of the 2nd millennium BC—could readily be cast in one- or two-piece molds, as have also been found. It would also seem probable from the suggested trading that searches were instigated for copper ore having a similar arsenic content and the same good casting properties on the Iberian peninsula. Such deposits were found in abundance and formed the basis for the production of “arsenic bronze” in which copper-arsenic alloys having 5–8% As were manufactured by raising the proportion of arsenic, possibly even by addition of the native element.

Arsenic bronze, equally familiar in the western and the eastern Mediterranean, then spread throughout the whole of Europe. Interestingly, the first metal-saving utensils, *e.g.* small sharp-edged axes, appear simultaneously with arsenic bronze. The material clearly competed with other kinds of copper produced at the same time in southeast Europe. However, the latter were technically inferior to arsenic bronze because the impurities they contain—antimony, silver, in some cases bismuth too—do not enhance its properties, at least in the proportions present.

A further metallurgical improvement occurred in the 18th century BC when new ores were worked and production began using central European ores from the eastern Carpathians to the Harz Mountains, and possibly even those from the Harzt region in southwest Germany. These ores are characterized by a varying high content of arsenic, antimony, nickel, silver, and bismuth. They yield at least five readily distinguishable kinds of copper and explain the abundance of metal objects in particular groups of societies, an abundance that led archeologists to speak of “Bronze-Age” cultures. It is only since the advent of chemical analysis that we know the frequently light-colored products to be neither arsenic- nor tin bronzes but that their light color is often attributable to their content of silver and nickel, the impurities amounting to 5 to 10% in many cases.

The production of these kinds of copper is associated with a whole new range of utensils and jewellery. It appears that the ring ingots were then first used as currency. They are open neck rings with recoiled ends which, after surface finish, were worn as adornment, and also represented the trading form of the metal. Hoards of several hundred such ring ingots have been discovered. They usually still carry direct evidence of the casting process.

Each variety of copper in this period has its own area of distribution from which the production and marketing regions can be deduced as exemplified by the distribution maps in Figures 3 and 4. Thus Figure 3 depicts the rather narrow distribution of the variety of copper denoted as material group A, while Figure 4 shows the much larger export distribution of another variety of copper (E 11 B) from central Europe. Such exports traveled to areas that had hardly been reached before, for instance Ireland and England, and areas, such as northern Germany, where they were in direct competition with the established

southern European suppliers (cf. Fig. 1). This trade also extended to the south, namely to Italy, where it counteracted local trade not discussed here. It even penetrated the old exporting regions of southeast Europe, without going much farther to the east or south, however, than the Carpathians. Southwest Europe was hardly affected by these exports, for production of the extremely useful arsenic bronze was continued there (Fig 2).

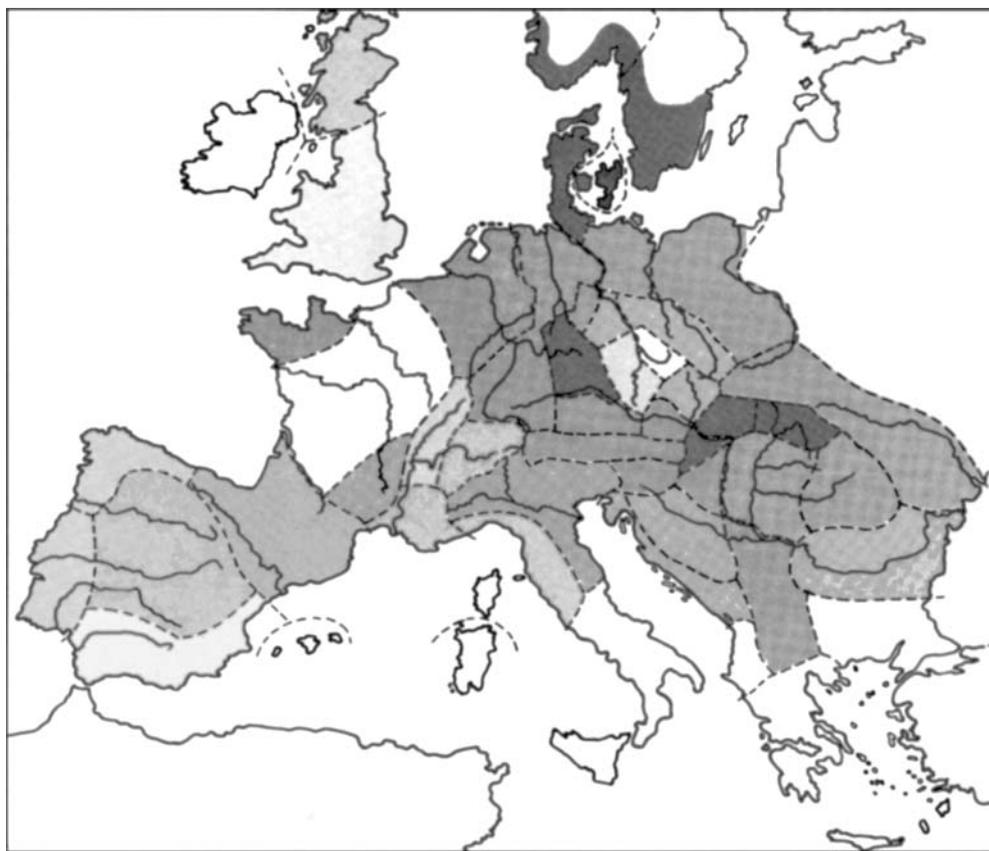
One of the export routes mentioned above assumed particular importance because it initiated the next step in metallurgy, for this period of central European copper manufacture witnessed the crucial step of alloying with tin, to produce the genuine tin bronze which played a dominating role for many centuries until finally ousted by iron.

Even today we still cannot say where and when alloying with tin was discovered. It appears that tin bronze was known in the orient during the 3rd millennium BC although it is still mysterious from which deposits the tin came. We do know that the tin bronze that suddenly appeared in central Europe in the 17th century BC was manufactured from typically central European varieties of copper. It therefore appears reasonable to think of a rediscovery of bronze in these regions, particularly since one of the few accessible tin deposits was located in the frontier mountains between Saxony and Czechoslovakia. Copper seekers and -workers could have come across a mixture of copper and tin ores

and thus become acquainted with the tin alloy which was even superior in its casting and hardening properties to arsenic bronze. Possessing such experience, concentrated searches for tin ores could now be made.

Alloying with tin opened up further technical possibilities. Reuse of older material, which could be rendered suitable for producing all kinds of castings by admixture of tin, became more important. As a result new varieties of copper dating from about 1600 BC and thereafter can be legitimately suspected to have been manufactured from previously worked material. Hoarded older material—belonging to scrap collectors—features far more often in archeological finds from this time than deposits of bars (Fig. 5).

Understandably, it becomes difficult in these circumstances to find really informative material groups on analysis of prehistoric objects. We have to content ourselves with distinguishing between groups obtained from raw materials and those produced from salvaged material or from a mixture of scrap and ore. It already appears possible to make a preliminary statement on this topic: In the Mediterranean regions, from the Greek Archipelago *via* Italy to southern France, and also in Switzerland, recourse was apparently again made to ore deposits affording uncontaminated copper; or perhaps the first success at refining can be placed in this period. In southeast, central, and north Europe, however, it must remain an open question to what



ABBL 5

Fig. 5. Distribution of material group copper FB 1. The material appears to have dominated the central and north European market from the 16th century BC onwards. Arsenic and antimony are present in small to average quantities ( $\approx 0.05\%$ ), and the nickel concentration is invariably  $>0.1\%$ . It is possible that different kinds of older material were melted down together. For meaning of shading see Fig. 1.

extent local ore was worked together with scrap material from the whole region. We do know, though, that underground mining of copper had already begun by this time (as found in the Austrian Alps). The metal produced probably contained nickel as the sole impurity.

It may be of interest in conclusion to dwell for a moment on the effect of the smelting and working of copper on the social structure of European regions. Whereas copper-working played a subordinate role in the cultures of the Near East and Crete at the end of the 3rd and beginning of the 2nd millennium BC, it seems at least to have contributed to a change in social structure in Europe before the middle of the 2nd millennium. At this time, a socially superior class can be detected in many parts of Europe whose graves were richly provided with noble metal objects and other valuables. It is certainly significant that they are found in the Aegean commercial and cultural center, in the shaft graves of Mycenae, and in the copper production region of, *e.g.* Transylvania, the western Carpathians, the Harz Mountains, and in west Switzerland. They likewise occur in the tin producing areas of Brittany and the south of England. Applying all caution it is probably valid to assume a mutual connection between the appearance of this socially privileged class and a prosperity due to production of and trading in metal.

#### 4. Interpretation of Gold Analyses

Many parts of Europe have no natural gold deposits at all. As examples we can consider the whole north German plain, the Netherlands, Belgium, and Denmark. Nevertheless, these regions abound in archeological gold specimens dating from prehistoric times; indeed, Denmark can be regarded as particularly rich in such finds. The material used to produce the gold bracelets, dishes, beakers, *etc.* must therefore have originated from other parts, it remaining an open question whether the gold was transported and traded as the raw material or as finished jewellery. Analysis of the material can clearly provide no answer; each case must be treated individually on the basis of archeological considerations of style and similar characteristics.

Location of natural gold deposits, which were worked in prehistoric times and which produced such high yields as to supply regions devoid of gold, should prove easier than the search for corresponding copper deposits, since the number of gold deposits is far smaller. Only sources of elemental gold—primary or secondary deposits—need be considered. No prehistoric smelting process involving modification of impurities and accompanying elements took place; moreover, the deposits themselves—at least as regards those of a secondary nature—are much more uniform in their composition.

An attempt to characterize significant natural gold deposits on the basis of accompanying elements, and thus to retrace the routes by which the gold was transmitted to regions far and near in prehistoric times, could therefore be undertaken with considerable hope of success. It has so far proved possible to distinguish, with a fair degree of certainty, two of the European gold sources according to

their minor components and to recognize this gold in prehistoric finds.

Even if it proves impossible to ascribe the gold in prehistoric objects to particular natural deposits according to analyses of accompanying elements, *i.e.* the question of the origin of the gold must remain unanswered, it will still be possible to correlate gold finds on the basis of characteristic contaminants and to class them as so-called material groups, as in the case of copper. A material group comprises all those objects made of material whose content of accompanying elements is the same with regard to quality and quantity (within certain limits of variation). It is assumed that the gold occurring in all finds belonging to the same material group come from the same natural deposit, even if it has yet to be located.

Nevertheless, it will have to be borne in mind when considering such material groups that two distant natural deposits may well yield gold whose composition varies so little that the resulting objects are assigned to the same material group. The greatest caution must be exercised when a material group embraces widely differing periods and cultures and particularly when the nature and amounts of accompanying elements are not very characteristic.

#### 5. Results of Gold Studies

We shall first consider a number of observations made with natural gold. Copper and silver are regularly found in natural gold, although in very different concentrations. The silver content is at least about 2% and can reach values of 40%. In contrast, only 0.01% of copper is often present and is reported never to exceed 1.5%<sup>[7]</sup>. Apart from these two elements we found that more than 30 samples of native gold from the Rhine and its tributaries, Transylvania, Bohemia, Ireland, Wales, and Scotland all contain mercury, sometimes only in traces of less than 0.01% but usually in the order of 0.1%, irrespective of whether the samples come from primary or secondary deposits.

Platinum and tin, however, two elements frequently encountered in prehistoric gold finds, are completely absent in gold from primary deposits. Our studies on alluvial gold concentrates revealed them to regularly contain tin and in some cases platinum too. However, these two elements are not incorporated in the grains of gold present in the concentrate but are enriched owing to their density—tin in the form of cassiterite<sup>[8, 9]</sup> and platinum as the native metal<sup>[9]</sup>. Both elements will readily have gone into the gold regulus during prehistoric recovery operations and now witness to the production of the gold from placer deposits. Results of studies on about 3300 European gold finds dating from the Bronze Age to the beginning of our era indicate that placer gold was the only gold available, for, with very few exceptions, all these finds contain some tin<sup>[\*]</sup>.

[\*] Exceptions can arise owing to the presence of large nuggets in alluvial gold; such nuggets will readily be separable from accompanying minerals and are thus no longer associated with tinstone. Nevertheless, with regard to the other compounds, this gold exhibits the same composition as the stanniferous, finely divided material from alluvial deposits and is treated as such in our studies.

Mining for gold was apparently unknown in prehistoric Europe and seems to have been gradually introduced in Roman times.

Strikingly, it is precisely the earliest prehistoric European gold finds that are made from tin-free material which may well have been mined, although this naturally cannot be proved since alluvial deposits free from tinstone are perfectly conceivable. However, when it is remembered that this tin-free gold (which, moreover, generally has a silver content of less than 10% and rarely as much as 15%) is limited specifically to the earliest Metal Age—and disappears in the Middle Bronze Age—some justification may be seen for assuming that this material was imported from the eastern Mediterranean region where the cultures of Asia Minor are known to have engaged in the mining of ores as long ago as the 3rd millennium BC. When local extraction from alluvial deposits got under way in Europe there was no longer any need for these imports. This would provide a ready explanation for the disappearance of the tin-free material in the Middle Bronze Age.

Further support for this conception comes from the distribution of the tin-free gold we have designated "B", as shown in Figure 6. Each prehistoric gold object having this composition is indicated by a point at its place of discovery. It is clearly seen that such finds have been registered particularly frequently in coastal regions, again suggesting that they were imported, especially since the south coast of Spain and Portugal is known beyond doubt from the fortified factories established by copper seekers (Section 3) to have been exposed to the influence of the eastern Mediterranean. Non-coastal locations of such finds lie almost

exclusively in the region of the lower Danube and possibly mark an inland import route. Of course, a distribution map of this kind should not be consulted without remembering the respective gaps in research, applying in this case to the regions covered by present-day Greece, Italy, Bulgaria, and Romania. Closing of these gaps by future investigations will undoubtedly do much to clarify the situation.

Utilization of the tin-free material B coincides in the Early Bronze Age with that of the slightly later material "A<sub>3</sub>" having a considerably higher silver content (on average 26% Ag) whose distribution is shown in Figure 7. The map clearly shows the high frequency of finds in the middle reaches of the Danube. This would possibly suggest some connection with the well-known gold deposits near Brád in Transylvania. Unfortunately, we had no comparison samples of alluvial gold from this region at our disposal, but samples of gold from recent mining operations in the neighborhood of Brád also exhibit an average silver content of about 25% Ag<sup>[10]</sup>. It may therefore be assumed that during the Early Bronze Age material A<sub>3</sub> was obtained from alluvial deposits in a wide area surrounding the primary deposits of Transylvania (shown as hatched trapezium). This local gold displaced the imports of material B and was doubtless also exported since it is encountered in individual Bronze Age gold finds in Scandinavia, the Netherlands, and Germany, and even a flat gold ring found in Brittany appears to have been made of Transylvanian material. So far we are completely ignorant of the extent to which Transylvanian gold found its way to Mycenaean Greece, to the Hittite Kingdom in Asia Minor, and to

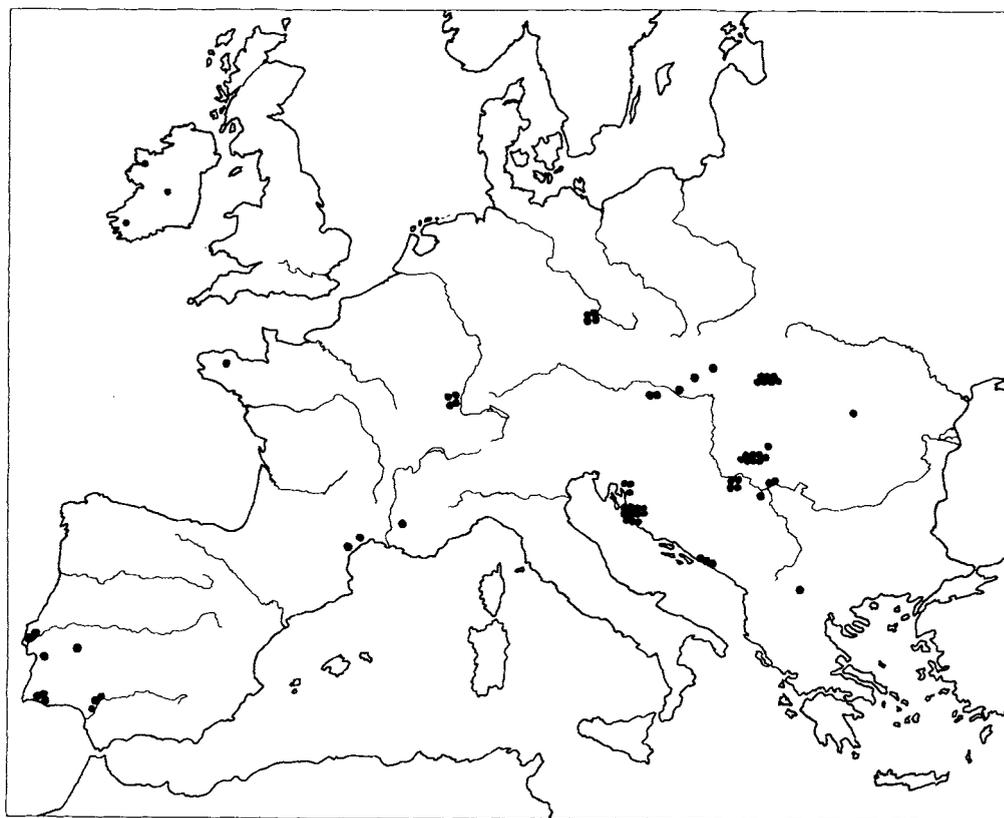


ABB 6

Fig. 6. Distribution of material group gold B.



ABB. 7

Fig. 7. Distribution of material group gold A<sub>3</sub>. Natural gold deposits in Transylvania shown as hatched area.

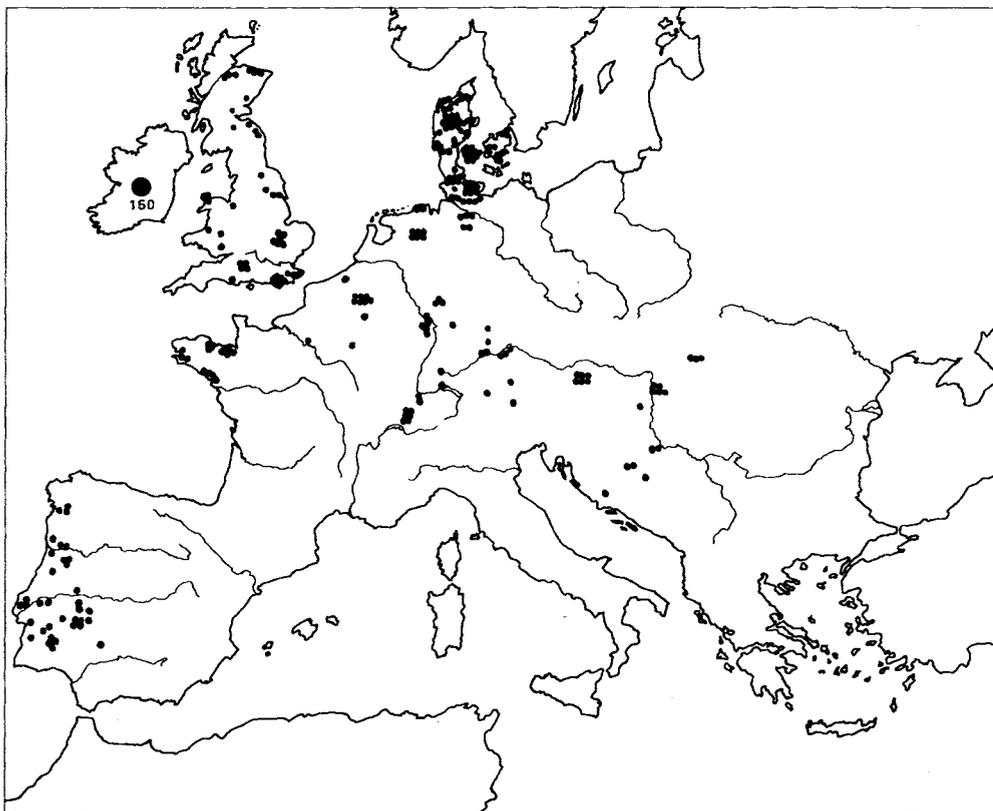


ABB. 8

Fig. 8. Distribution of material group gold N. More than about 150 objects found in Ireland belong to this group. Little work has so far been done on specimens from England (British Museum, London) and Denmark.

Troy. However, it is our hope that future research will shed some light upon these questions.

Towards the close of the Bronze Age in Central Europe—around the turn of the 2nd to the 1st millennium BC—a particularly widely distributed variety of gold appears whose tin content clearly points to its alluvial origin. Figure 8 shows how this material, hitherto unencountered in the geographical area studied, was in use from the Balkans to Spain and Ireland. The centroid of the distribution of this gold, which we have designated “N” and which is characterized by its relatively high tin content ( $>0.1\%$ ) and high copper content ( $\approx 2\%$ )\*], appears to lie in present-day Schleswig-Holstein/Denmark, the British Isles and the areas of Brittany accessible therefrom, and the western part of the Iberian peninsula. There is a temptation to regard the finds in the extreme west of Europe as comprising local gold of fortuitously identical composition; however, archeological excavations provide unequivocal evidence for extensive trading and cultural ties, particularly between Portugal/west Spain, Brittany, and the British Isles, going back far earlier than the period discussed in this report. It is therefore justifiable to relate this unexpectedly widely distributed variety of gold with a single source whose location we cannot yet define. However, the extent of this source seems so considerable that we can hardly expect to find it in west or central Europe. Furthermore, the appearance of N-type gold in central Europe coincides with that of the Urnfield culture in a period marked by significant folk migrations, and the time graduation of these folk movements from east to west is also reflected in the occurrence of N-type gold. Further conclusions will hardly be possible until the research gaps in the GDR, Poland, and Romania have been remedied. We would therefore like to do no more than cautiously express the tentative conjecture that this gold stems from somewhere in east Europe and was traded—as adequately shown by Figure 8—by a maritime route *via* the Baltic, the North Sea, and the Atlantic. Maritime trading routes must therefore have played a very important role at this time, as in the Mediterranean 1000 years previously (Fig. 6), a fact that is still not sufficiently appreciated. However, there remains some uncertainty as to what goods and valuables can have figured as objects of exchange in such a widely distributed gold trade.

This period, *i.e.* the dawn of the last millennium BC, also witnessed the first large-scale adulteration of gold with copper, particularly in the case of N-type gold. The amounts of copper found generally fluctuate in the order of up to 10% and only occasionally exceed this value. The gold assumes a particularly warm, golden-yellow color and its hardness also increases. Indeed, it is really rather surprising that this device was discovered so late: it soon became common practice in the British Isles but found somewhat less following on the European mainland. Considering that the art of alloying copper with tin had been known for half a millennium, one is forced to the conclusion that cer-

[\*] Although this copper content exceeds the upper limit given by Gmelin [7], we still consider it unlikely that the copper content was intentionally raised but rather that the natural copper content of this variety of gold was enhanced by the copper minerals in the secondary deposits.

tain mythical-religious concepts had hitherto prevented abasement of the pure native gold with copper.

Finally, this is a fitting place to take a stand on a question that has long occupied archeologists. The alluvial gold deposits along the Upper Rhine were actively worked until modern times, and the assumption that gold was obtained from this source in prehistoric times, and at least those prehistoric finds excavated in the neighborhood of the Upper Rhine Valley were made from Rhine gold, appeared not entirely without foundation. Since concentrates from gold-bearing Rhine sands are still accessible today we had no difficulty in following up this proposition and were able to confirm the composition of Rhine gold—low Ag content below 10% and, in the lower reaches of the Upper Rhine, mainly accompanying platinum—as found in early analyses. However, comparison with prehistoric gold finds, primarily from southwest Germany, showed that Rhine gold was not worked until the La Tène period, *i.e.* in the last centuries BC, and that gold extraction from the deposits of the Rhine was not practiced at all, or only to an insignificant extent, before this time. The low number of La Tène objects that are made of Rhine gold also emphasizes that the production of Rhine gold can never be compared with that from the Transylvanian deposits or possibly with that of material N discussed above.

The final problem dealt with stresses once again how indispensable the application of scientific methods is for investigations of prehistoric metallurgy when any serious attempt is made to engage in successful studies of this topic, which is so important for the history of technology as a whole. That the methods employed in the natural sciences are merely aids open to continuous improvement hardly needs demonstrating to the readership of this journal.

Received: July 8, 1971 [A 884 IE]

German version: *Angew. Chem.* 84, 668 (1972)

- [1] J. Winkler: Quantitative spektralanalytische Untersuchungen an Kupferlegierungen zur Analyse vorgeschichtlicher Bronzen. Veröffentl. Landesanstalt Volkheitskunde Halle, No. 7 (1935); *Z. Anorg. Allg. Chem.* 218, 149 (1934).
- [2] H. Otto and W. Witter: *Handbuch der ältesten vorgeschichtlichen Metallurgie in Mitteleuropa*. J. A. Barth, Leipzig 1952; H. Otto, *Spectrochim. Acta* 1, 381 (1940).
- [3] M. van Doorselaer, *Verhandel. Koninkl. Vlaam. Acad. Wetenschap. Belg. Kl. Wetenschap.* 12, No. 35 (1950).
- [4] S. Junghans, H. Klein, and E. Scheufele: *Untersuchungen zur Kupfer- und Frühbronzezeit Süddeutschlands*. 34. Bericht der Römisch-Germanischen Kommission 1951–53, pp. 77 ff.
- [5] A. Hartmann: *Prähistorische Goldfunde aus Europa. Studien zu den Anfängen der Metallurgie*, Vol. 3. Gebr. Mann Verlag, Berlin 1970.
- [6] S. Junghans, E. Sangmeister, and M. Schröder: *Metallanalysen kupferzeitlicher und frühbronzezeitlicher Bodenfunde aus Europa. Studien zu den Anfängen der Metallurgie*, Vol. 1. Gebr. Mann Verlag, Berlin 1960; *Kupfer und Bronze in der frühen Metallzeit Europas. Studien zu den Anfängen der Metallurgie*, Vol. 2. Gebr. Mann Verlag, Berlin 1968.
- [7] Gmelin *Handbuch der anorganischen Chemie: System No. 62*, 8th Edit., p. 43. Verlag Chemie, Weinheim 1954.
- [8] F. Kirchheimer: *Über das Rheingold*. *Jh. geol. Landesamt Bad.-Württ.* 7, 77 (1965).
- [9] P. Ramdohr: *Rheingold als Seifenmineral*. *Jh. geol. Landesamt Bad.-Württ.* 7, 92 (1965).
- [10] F. Schumacher: *Die Golderzlagernstätten und der Goldbergbau der Rudaer Zwölf-Apostel-Gewerkschaft zu Brád in Siebenbürgen*. Verlag M. Krahmann, Berlin 1912, p. 56.