TRACE ELEMENT ANALYSIS OF METALLIC ARTIFACTS FROM GEDİKLİ HOARD BY ATOMIC ABSORPTION SPECTROSCOPY

by

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ABSTRACT

The object of this study was to determine the trace and alloying elements of the metal artifacts recovered from Gedikli during excavation between 1964-1967. Most of the artifacts were from a cremation burial sight dated to Early Bronze Age, which includes pins, awls, rings, bracelets etc.

About 20-25 mg. samples, obtained from over 100 artifacts by drilling, are analysed using atomic absorption spectroscopy. The results showed that most of the samples were copper and copper alloys. Both tin and arsenic were present as an alloying element in some samples at about 7% and 5% respectively. Nearly half of the objects had both tin and arsenic together but at about 1% or less. Silver and iron were the other two elements that were present in almost all samples at trace levels. Zinc and lead concentrations were quite variable from trace levels to up to 27.4% and 15.5% respectively.

Artifacts are classified according to type, shape and to presence or absence of certain elements. Histograms, correlations and cluster analysis were carried out on the trace element distribution of these groups to determine particular trends, manufacturing techniques and common ore sources. The results showed that, there was no general trend in the trace element distribution in general for all artifacts. However, certain trends could be observed when artifacts are arranged into subgroups. Umbrella headed pins were all tin bronzes with similar trace metal distribution. Two clusters were also observed between artifacts having tin, arsenic, lead and nickel elements which may indicate two different ore sources.

Even though the artifacts recovered, cover a relatively short time span, the heterogeneity of the trace element distribution could be an indication of different ore sources, manufacturing techniques and trade routes,

A complete examination of the sight will show if the objects are locally manufactured or not. Chronological arrangement of the artifacts would yield information on the technological development as well as on trade relationships. This preliminary study shows that complete excavation of Gedikli could bring light to the metallurgy of the Bronze Age in the area.

ÖZET

Bu çalışmanın amacı, 1964-1967 Gedikli kazılarında elde edilen metal bulguların içerdikleri alaşım ve eser elementlerin tesbitidir. İncelenen iğne, bız, küpe ve bilezik gibi örneklerin büyük bir çoğunluğu, Erken Bronz Çağına rastlayan kremasyon mezarlığında bulunmuştur.

100 kadar madeni bulgudan matkap ile talaş halinde alınan 20-25 mg. miktarındaki örnekler atomik absorpsiyon yöntemi ile analiz edildi. Sonuçlar, örneklerin çoğunun, bakır veya bakır alaşımı olduğunu gösterdi. Bazı örneklerde kalayın (%7 dolayında) bazılarında da arseniğin (%5 dolayında) alaşım elementi olarak kullanıldığı gözlendi. Örneklerin hemen hemen yarısında hem arsenik hem de kalay %1 miktarında eser element olarak bulundu. Demir ve gümüş hemen hemen tüm örneklerde eser miktarlarda gözlenen diğer iki element oldu. Kurşun ve çinkoda önemli değişkenlik gözlendi. Bunlardan kurşun en fazla %27,4 civarında, çinko ise en fazla %15,5 olarak bulundu.

Örnekler türlerine, şekillerine ve belirli eser element içeriklerine göre gruplandırıldı. Eser element sonuçlarında histogramlar, korolasyonlar ve küme analizleri uygulanarak, belirgin değişimlerin saptanmasına çalışıldı. Sonuçlarda, tüm örnekleri kapsayan belirgin bir eser element dağılımının mevcut olmadığı gözlendi. Ancak, bazı kümelerde bir takım ayrıcalıklar izlendi. Özellikle şemsiye başlı iğnelerin tümünün kalaylı bronz oldukları görüldü. Bu örneklerdeki diğer eser elementlerin dağılımında da benzerlik mevcuttu. Ayrıca, kalay, arsenik, kurşun ve nikel elementleri içeren örnekler arasında iki belirgin küme gözlendi. Bu kümeler farklı iki maden kaynağını yansıtabilir.

Örneklerin bulunduğu zaman aralığı fazla olmamakla beraber gözlenen heterojenlik, örneklerin değişik maden kaynaklarından geldiklerini, farklı imalat yöntemlerinin uygulandığını veya değişik ticaret merkezlerinden elde edildiğini gösterebilir.

Gedikli'de yapılacak ayrıntılı bir kazı çalışması, bu örneklerin yerel olarak imal edilip edilmediğini ortaya çıkaracaktır. Örneklerin ayrıca kronolojik olarak sıralanabilmesi teknolojik gelişmeyi veya ticari ilişkileri ortaya çıkarabilecektir. Bir ön çalışma niteliğinde olan sonuçlar, Gedikli'de yapılacak ayrıntılı kazılar bölgenin maden teknolojisinin açıklanabilmesinde önemli olacaktır.

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CHAPTER I

INTRODUCTION

I. INTRODUCTION

The metals which have given their names to various Periods in human history have been analysed by physical (optical microscope, x-ray fluorescence, neutron activation etc.) and chemical (trace element analysis) methods. These analyses unfold the structure of the artifact such that where, how, from which metal it was made or even the ore source used in it. (1) As a result, the technological and cultural stage of that ancient society which manufactured the artifact could be discovered.

In recent years (2) beside the chemical and physical methods, new techniques including isotopic analysis, age determination and others are applied in archaeology, in order to accurately date antiquities and locate ancient raw materials. The term "Archaeometry" has been coined for this new discipline. The physical and chemical study of a metallic artifact inform us about the following questions: (3)

1. From which metal it was made?
2. Where was it made?
3. How was it made
4. Which ore sources were used?
5. Was it artificial or not?

Indeed archaeology provides us a history of prehistoric man, his way of life, customs and environment. The more one sees and learns of his utensils, jewellery and weapons, the more pressing becomes the question of how all these objects were made (4). In other words, the technology, manufacture and the metallurgical skill of prehistoric men are the main focus of attention. For this purpose there must be a close cooperation between archaeologists and scientists. When metals are reduced from their ores, the trace elements present in the ore are also reduced. The trace element distribution in the metal and the slag is very useful for the determination of the ore source. That's why a chemical (trace element) analysis is necessary in order to find the composition of ancient finds and to trace the sources of the objects. Such analyses also lead to information about the determination of metallurgy, technique of manufacture, culture, the commercial relationships between societies, trading routes and connections between prehistoric cultures. It is easy to distinguish between metallic materials of different origin, according to the various constituents present and to recognize historical and geographical boundaries. Such chemical analyses are practical and promising. (5)

In this paper 106 samples from Gedikli, situated in the South-eastern Anatolia, are analysed by the Atomic Absorption Spectrography (AAS) method. These samples are taken from different objects, which are: Pins, awls, bracelets, rings and various iron samples.These objects are obtained from an excavation made in 1964 in Gedikli by Prof. U.B. Alkım. They belong to the end of the Early Bronze Age (EBA) and to the beginning of the Middle Bronze Age. (MBA)

CHAPTER II

HISTORICAL BACKGROUND

II. HISTORICAL BACKGROUND

2.1. Methods of Determining the Composition of Metal Objects

The properties and manufacturing technology of metals vary considerably depending upon which metal or alloy it is made out of. Therefore it is extremely important to know its constituents. There are many techniques for the qualitative determination of the metals. (2) Chemical methods can be applied on a micro-scale to small samples and constituent elements can be identified by their characteristic chemical reactions. Spectrographic methods, however, are more accurate, fast and reliable and the following techniques are applied in this field (6) (Table 2.1.)

2.1.1. Optical Emission Spectroscopy

In the first stage of this method, the metal atoms must be activated by flame, electricity or arc. The activated metal atoms emit rays, characteristic of their electronic structure. It is very easy to determine the intensity and wavelength of these rays. This method is sensitive and accurate. One can analyse as much as 30 metals simultaneously. Five to 100 mg. sample is needed for the analyses. (7)

2.1.2. X-ray Fluorescence Technique

In this method, a specimen is irradiated first with a beam of sufficiently short wavelength x-radiation, which causes the elements present to emit their characteristic fluorescence lines. The fluorescence emission is dispersed and characteristic lines of the elements present are detected. (8) It is a non destructive method, because there is no need to take any sample from the artifact, however, one can analyse only the surface characteristics

TABLE 2.1. Spectrographic Methods Employed in Archaeological Chemistry

Analytical Method	Sample	Limits of Analysis	Elements Analysed	Best Application	Comments
Optical Emission	5 - 100 mg.	100 ppm - 10%	30-40 elements	pottery, metal glass	Versatile, cheap. Good for elements
X-ray Fluorescence	100 mg. - 2 gr.	5 ppm - 10%	Elements with Atom. No. higher than 22	Metal, glass, pigments	Nondestructive, best used for surface analysis
Neutron Activation	50 - 100 mg.	1 ppm - 10%	40-60 elements	Pottery, obsidian metals, stone, bone	Requires nuclear reactor
X-ray Diffraction	5-10 mg.	1 ppm - 10%			
Atomic Absorption	10-100 mg.	1 ppm - 10%	About 50 metals	Glass, metals, bone, obsidian	Simple, accurate but slow

of that artifact (7)

2.1.3. Neutron Activation Analysis

The sample is exposed to neutron for a long time, during which the nucleus of the atoms becomes radioactivated. Then the radioactive desintegration of these samples is measured. The spectrum obtained shows the characteristics of elements present in the sample.(8)

2.1.4. X-ray Diffraction Method

It is useful to study the sample at atomic level. The crystal structure of the atoms diffract the x-rays. As a result the crystalline structure of the sample can be determined by examining these diffractions.

2.1.5. Atomic Absorption Method

AAS is one of the most common techniques applied for the analysis of metal objects in archaeology. It is used in wide variety of scientific fields. (Table 2.2.) This method depends upon the absorption by atoms (present in a sample of a metal object) of light emitted from a hollow cathode lamp of the element being analysed. By this method, the qualitative and quantitative analysis of most elements can be determined with great ease. First, the sample is dissolved in an appropriate solvent. The solution is then sprayed into a flame to atomize the elements present. The interaction of these atoms with the characteristic lights emitted from the source (hollow cathode lamp) is measured for quantitative and/or qualitative analysis. (9) In atomic absorption, the wavelengths and energy levels of different elements should be calculated in order to make the analysis reliable, because due to electron spin effect, lots of variations in the energy levels are observed. In fact,

TABLE 2.2. Application of AAS

I. Biological samples
   - a. in the fields of bio and medical chemistry
   - b. in the field of agriculture
   - c. in the field of food technology.

II. Industrial samples
   - a. in metallurgy
   - b. for the petrolium product analysis
   - c. in glass and ceramic industry
   - d. in geological researches
   - e. in metal industry
   - f. in every type of water analysis
   - g. in geochemical mineral analysis
   - h. for controlling the purity of chemical substances

complex line transitions may be obtained during atomic absorption, and the best transitions are the ones which terminate in the ground state. Light is emitted and sharp lines are observed during these transitions. (9)

Absorption is dependent on the intensity of light. Meanwile, intensity is linearly dependent upon the atomic concentration of the solution:

$$I = KN^{x}$$

Where I = intensity
K = constant
N = atomic concentration
x = a constant approximately equal to one.

In practice it is difficult to find K and x during the analysis, therefore, the same concentration is calculated using the linear dependence of the intensity of light which belongs to the solution.

The Beer-Lambert equation (Beer's law) which is used in the molecular absorption spectroscopy can be written as,

$$A = \log \frac{I^{o}}{I} = \log_{10}\left(\frac{I}{I_{o}}\right) = -ELC$$

or

$$I = I_{o}\, 10^{-ELC}$$

Where, E = molar absorptivity
L = path length of the cell
C = concentration of the solution which absorbs the light.

It is observed that there is a direct propertionality between absorbance and concentrations, and the absorbance is given:

$$A = -ELC$$

Atomic Absorption spectrometer has five major components as is illustrated in Fig. 2.1. These are:light source, optical part, detector and amplifier, recorder and flame systems. Different hollow cathode lamps are used as light source for different atoms (Fig. 2.2.). These lamps are filled with Neon or Argon gases, electrodes are sealed in one end, a window of glass or silica is sealed on the other hand.

The cathode is a hollow cylinder with an internal diameter of less than ten mm. If sufficient voltage is applied between the two electrodes (400 volts), electrons start leaving the cathode, collide with atoms of neon or argon and cause them to ionize. The positively charged ions gain kinetic energy from the potential difference, strike the cathode surface (ground state) and eject atoms from its crystal lattice to the quartz window (9). The optical part of the spectrometer is made up of monochromator, chopper, mirrors and prisms.

During Atomic absorption analysis, a fine spray of the sample solution is introduced into a flame where it is desolvated, vaporized and atomized. Such solution spray permits a uniform distrubution of sample throughout the body of the flame and the introduction of a representative portion of each sample into the flame. (8) In atomic absorbtion spectrometry external light source emits the spectral lines. That correspond to the energy required for an electronic transition from the ground state to excited states of the element analyzed. The flame gases contain free, unexcited atoms capable of absorbing radiation from an external source, when the radiation corresponds exactly to the energy required for a transition of an electron. Unabsorbed radiation passes through a monochromator that isolates the exciting spectral line of the light source and into a detector. The absorption of radiation from the light source depends on the population of

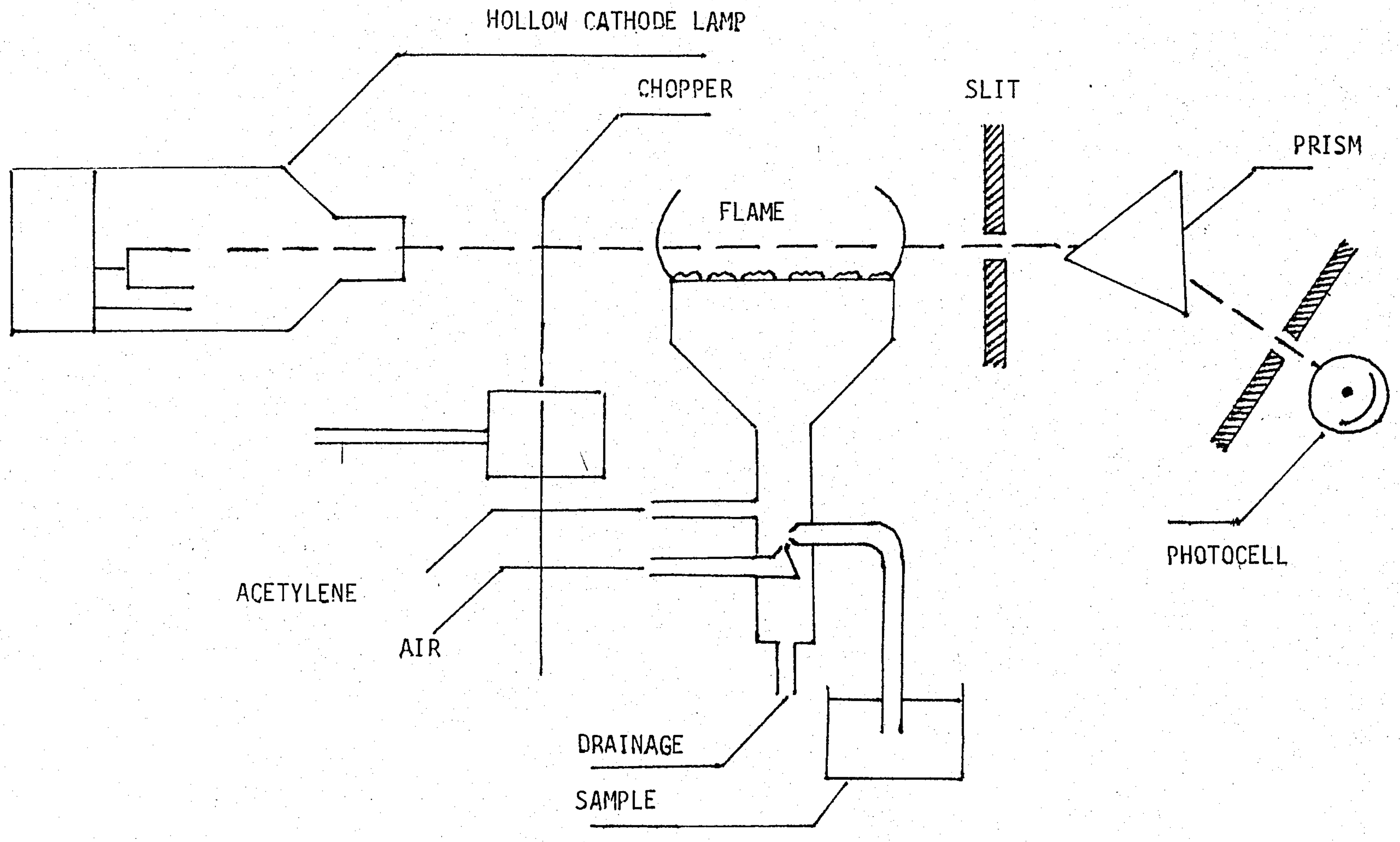


Fig. 2.1. Basic components of an atomic absorption spectrometer

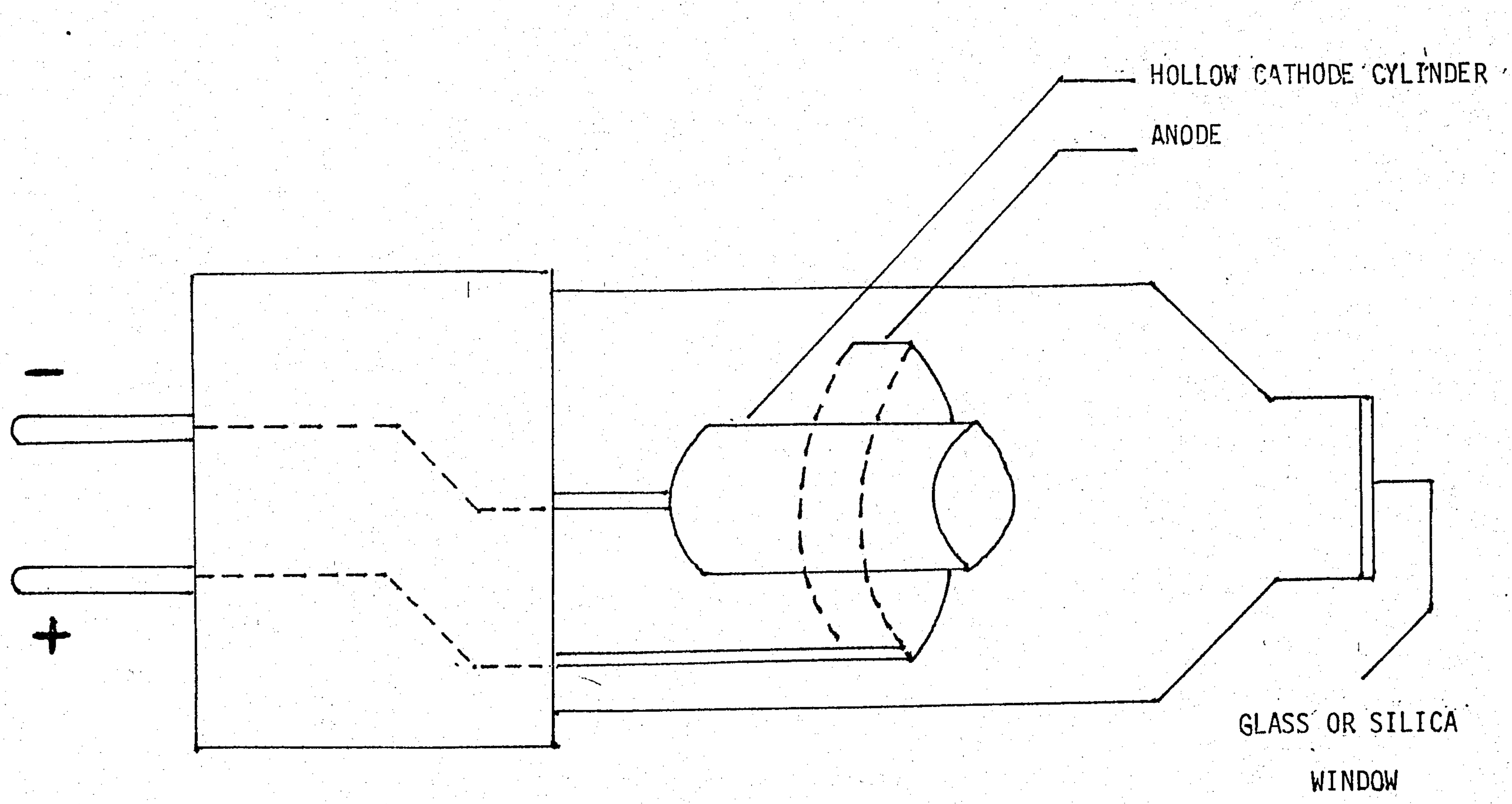


Fig. 2.2 Hollow Cathode Discharge Tube

the ground state, which is proportional to the solution concentration sprayed into the flame. Absorption is measured by the difference in transmitted signal in the presence and absence of the element to be analysed. The resonance spectral lines should be narrow as compared with the width of the absorption line to be measured.

During flame spectrometer, gas pressures and gas flows must be held constant to maintain a constant thermal environment. For this reason double beam instruments are used. The most important component of atomic absorption spectrometer is the nebulizer-burner system. This system converts the test ions in the sample solution to atomic vapor. However, such system wastes sample, since the residence time of metal atoms in the light part of a conventional flame is very short (on the order of milliseconds) (8). For these reasons non flame atomization devices are also useful when the sample is limited or is in the solid state. The heated graphite (Massmann) furnace consists of a hollow graphite cylinder 50 mm long and 10 mm in diameter placed so that the sample beam passes through it. In the middle of the cylinder top there is a hole about 2 mm in diameter through which the sample is pipetted. The cylinder is purged with an inert gas, either nitrogen or argon. An electric current, in three stages, is passed through the cylinder walls to evaporate the solvent, to ash the sample and finally to raise the unit to incandescence to atomize the sample. When the metal is atomized, a transient absorption signal is measured on a recorder. The time spent by atoms in the light path as they diffuse down the graphite tube is on the order of 2-3 sec. Very small amount of samples can be analyzed by Carbon Rode Atomizer (Fig. 2.3.). CRA technique is a very quick and sensitive method. (8)

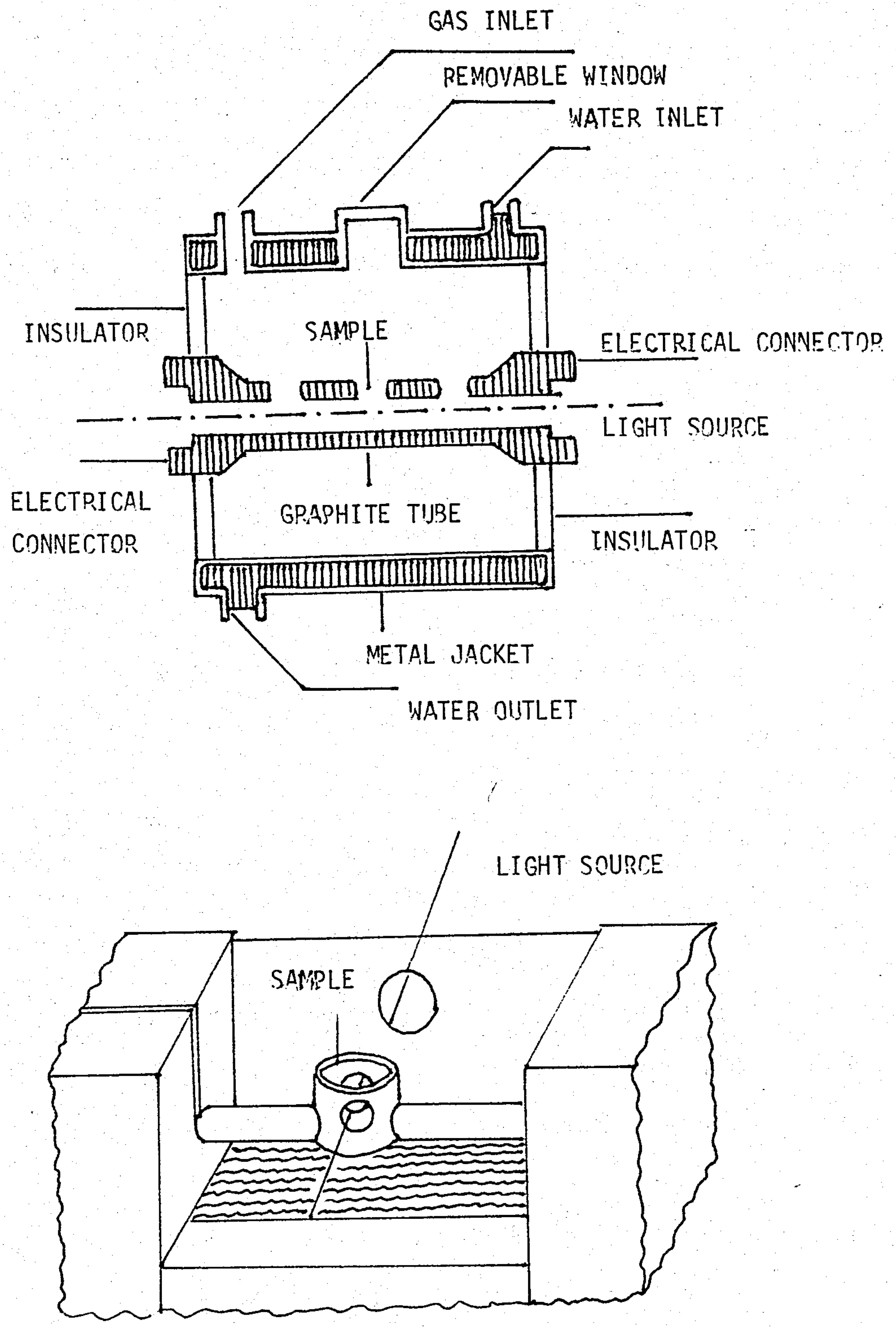


Fig. 2.3 Carbon Rode Atomizer

Atomic Absorption spectroscopy has important characteristics which make it suitable for trace element analysis. Versatility is an important feature which makes it particularly suited for the analysis of archaeological objects. Lists of available hollow cathode lamps for AAS show over 65 elements available (9). This method is also highly sensitive, because for the majority of the elements amenable to AAS, the analytical sensitivity is high and concentrations in the parts per million (ppm) range in solution can be readily determined. Alloys of copper, tin, lead, silver, gold, silicate materials comprising clays, ceramics, glass, glazes and minerals are all sensitive to this method. Typical sample requirements are two to ten mg. In order to indicate the sensitivity of atomic absorption methods, the minimum measurable concentrations in solution for typical elements which are important in archaeology are listed in Table 2.3. With a flameless atomizer, there are dramatic improvements in detection limits and this option is particularly useful in the analysis of bronze, (for e.g.) for arsenic, antimony, bismuth, cobalt and so on. For this purpose it is assumed that the amount of sample from an object available for analysis is 10 mg. and the dilution is 25 ml. (9)

The accuracy also is very high, even with quite small sample (10 mg) accurate results can be obtained. Each element is determined separately; for major elements an accuracy of ± one percent can be expected. In the case of minor and trace elements, for elements present at concentrations between o.5 and 0.05 wt. percent, the accuracy can be ± five percent, and for elements at concentrations below 0.05 wt. percent, the accuracy can be ± 15 percent. However, for elements present below 0.05 wt. percent an accuracy of ± five percent can be maintained, even down to relatively low concentrations, with the use of a flameless atomizer unit. (9) This is also a very quick method.

TABLE 2.3. Typical Atomic Absorption Detection Limits of Archaeologically Important Metals

Element	HGA (ppm)	Flame (%)
Antimony	0.5	0.01
Arsenic	0.25	0.025
Bismuth	0.25	0.006
Copper	0.125	0.00025
Gold	0.25	0.0025
Iron	0.05	0.0013
Lead	0.125	0.0025
Nickel	2.5	0.0005
Silver	0.0125	0.0005
Tin	2.5	0.0025
Zinc	0.0025	0.00025

HGA : Graphite furnace

Not : Typical sample is 10 mg in 25 ml

The time taken to obtain a concentration reading for a solution is usually under 20 sec. Including sampling of the objects concerned, one operator can analyse over 20 bronze samples in five days for ten different elements. (9)

This method can be readily applied to copper alloys. Pure copper, arsenical copper, bronze (including leaded bronze) and brass are all included in this category and dissolve readily in aqua regia(one vol.conc.nitric acid:three vols conc. HCl) including even trace metals as silver, because of the small weight (ten mg.) and relatively high acid concentration. Care must be taken to ensure that tin has dissolved completely in the acid mixture, a gentle heating of the acid (60°C) has been found to bring tin into solution in a very short time. Tin can be lost by evaporation if the acid solutions are heated to dryness. After dissolution and appropriate dilution to volume the solutions can be transferred to polythene screw-cap bottles for storage.

When experiments were carried out on standart solutions of several metallic elements containing known concentraiton of metals, it was found that the presence of copper enhanced the atomic absorption signals of the other elements (9). This enhancement is approximately in the order of eight to ten percent.

Several years experience of the application of AAS to the analyses of ancient materials for archaeology has shown that it is a valuable technique for analysing with good accuracy, a range of different materials. The technique complements others already in use for either analysis or examination in that AA analysis provides the internal composition of an object rather than an analysis of its surface (9). Thus internal and surface analysis complement each other, and both are of value in interpreting the structures of materials as seen with the various forms of microscopy. With AA it is possible to detect very small quantities of elements, and the range of a spectrometer can be greatly extended with one of the recently introduced flameless atomizers. Techniques have been worked out, tested and checked by analysis of standart materials of known composition. Ancient copper alloys, ceramics, a range of other metals and non-metals can be analysed by this method.

2.2. Copper

2.2.1. Native Copper

Various archaeological finds have shown that copper and copper alloys had a special place in human history. It is a metallic body, livid, with a dusky redness, ignitable, fusible, extensible under hammer. It is the earliest useful metal of mankind and its production is the earliest branch of metallurgy. It was with it that the early man learnt to discover the changes that fire works on it.

Copper occurs in the native state in many places of the world. In the native form it is known to man since 8000 B.C. First man treated it like any other stone (10, 11), but later when copper technology began between the years of 5000-2000 B.C., this metal was used as a commercial good and gained economic importance. The most important step in copper technology is the smelting process, because after this step, melting, casting and alloying processes developed and copper became widespread in human life, so became important commercially.

There are three ways one can transform native copper into useful artifacts (12).

1. The cold hammering; which is to hammer a branch of native copper into the desired shape.

2. Annealing and hammering; which is shaping with heat

3. Melting of native copper, fallowed by casting to give the. desired shape.

Objects made from unworked native copper and refined copper may show unique differences (13). The degree of purity and the hardness cannot be used in the identification of unworked native copper, because impurities depend on geological origin varying from area to area, whereas the hardness is affected by the nature, amount, size and distribution of impurities. However, copper oxide particles, grain size and twins, which appear as parallel bands within a single grain are distinctive indication of native copper. In fact, native copper which has not been melted or smelted can be free of copper oxide. The size of a grain may also be used to identify unworked or cold hammered native copper from that which has undergone heat treatment, in fact grain size is a function of heat, pressure and time. Large grains indicate unworked native copper. Lastly long and thin twins which are produced by geological phenomena at low temperature and over great period of time are the most distinctive indication of native copper. (12)

2.2.2. Copper Ores

Copper is found native, but most of it is smelted from various ores, among which are: The oxide, the carbonates, the sulphides and ores containing arsenic. Different copper ores are given with their formula and common impurities in Table 2.4. (13)

Nearly all copper ores contain sulphur, antimony, arsenic or lead and a small percent of zinc. Nickel is very rare because it is not genetically connected with copper ores. The three nickel bearing copper ores Algodonite,

TABLE 2.4. Different Copper Ores and their Common Impurities

Ore	Formula	(%) of Copper	Trace Elements %					
			Fe	Zn	Co	Ni	Ag	As
Cuprite	Cu_2O	89	traces	traces				
Melaconite	Cu_2O	89	traces	traces				
Malachite	$CuCO_3Cu(OH)_2$	55	0,09-6.2	4.5-27				
Azurite	$2CuCO_3.Cu(OH)_2$	55	traces	0.1-5.3				
Atacamite	$CuCl_2.3Cu(OH)_2$	59						
Algodonite	Cu_6As					0.08		
Whitneyite	Cu_9As					0.44-0.61		
Mohawkite	Cu_3As	61-68	traces			3.3-9.2		28
Chalcocite	Cu_2S	80	9.9	11.5	2.4		16	
Covellite	CuS	66.5		6.0				
Eurobescite (Bornite)	$3Cu_2S.Fe_2S_3$	56	17					
Chalcopyrite	$Cu_2S.Fe_2S_3$	35	30	4			trace	
Enargite	$4Cu_2S.(SbAs)_2S_3$	45		6			trace	13.3
Tetrahydrite	CuSbS	30-48	4	traces			trace	

Whitneyite and Mohawhite are very rare. The sulphide ores which are in the lower part of Table 2.4 contain higher percentage of iron as well as arsenic, antimony, zinc, nickel and silica which enter the copper metal in proportions depending on smelting conditions.

The diagrammatic section accross a copper lode is shown is Fig. 2.4. (14). Copper weins are found in regions of hydrothermal activity, such as contact metamorphic zones. In the copper lode four parts are seen. The primary enrichment zone, the secondary enrichment zone, the leached zone and the upper cap or gossan. The primary sulphides of copper and iron; bornite and chalcopyrite associated with pyrite, are situated in the primary enrichment zone. Copper sulphides are very unstable and are oxidized. The oxides and carbonates of copper are leached in the secondary enrichment zone where native copper is also found. If this enriched zone lies below the water table, the oxides are replaced by enriched sulphides of copper; covellite and chalcocite. The upper cap or gossan, which consists of oxidized iron ores such as limonite, is seperated from the enriched zone by a sterile leached zone having soluble minerals in it.

The physical characteristics of native copper and various copper ores, observed in the copper lode (Fig. 2.4.) are as fallows:

a. Native Copper: It is copper-red with a metallic lustre, the surface may be tarnished and dull, sometimes with a black or a greenish colour. The specific gravity is 8.8 and its hardness ranges from 2.5 to three (14). It is malleable and ductile, can be hammered into shape. Repeated hammering hardens the metal and renders it brittle. On reheating it becomes malleable again. The m.p is 1100°C. Hammering copper brings Brinell hardness from 87 to 135, that is more than is achieved by the alloying with the normal ten percent of tin to make bronze and it approaches the hardness of mild steel.

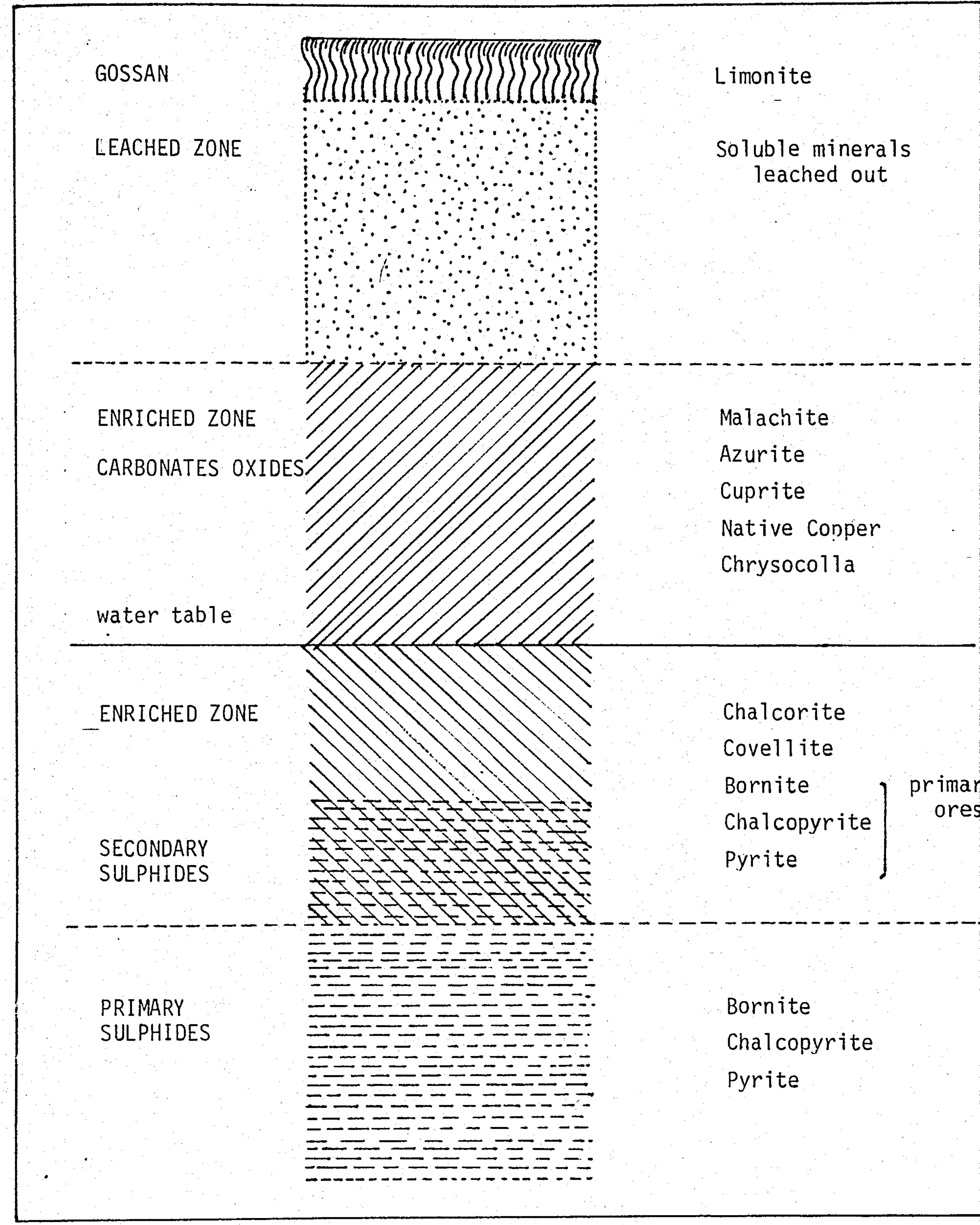


Fig. 2.4 Diagrammatic section accross a copper lode

This hardness is temporary and the operation must be repeated regularly.(14)

b. Cuprite: Cu_2O, 89 percent Cu. It is bright and dark red. The specific gravity is 5.8 to six. The hardness is 3.5 to four.

c. Melaconite: It is a black copper oxide, has 89 percent Cu. It's specific gravity is 6.3 and its hardness is three to four (14). They occur as a dull black mass or as a fire black powder.

d. Malachite: Hydrated carbonate of copper $CuCO_3 . Cu(OH)_2$, has 56 percent Cu (13). It is brilliant green, has a specific gravity of four (14). The hardness is 3.5 to four.

e.Azurite: Less hydrated form of copper carbonate. $2CuCO_3 . Cu(OH)_2$. It is brilliant blue. It's specific gravity is 3.7. It is less common than malachite, has 55 percent of Cu.

f. Chalcopyrite, Copper Pyrite: $CuFeS_2$ with 34.5 percent Cu (13). It is brass yellow with a metallic lustre. It s specific gravity is four to 4.3. The hardness is four.

g. Bornite: A sulphide of copper and iron. Its composition being variable has no chemical formula. It is richer in copper and poorer in iron than chalcopyrite. It has a reddish golden colour with a high metallic lustre, but on exposed surfaces it tarnishes to green and blue. It's specific gravity varies from five to 5.5. The hardness is 3.3. It has 55.5 percent Cu. (13

h. Chalcocite: Rich copper sulphide, Cu_2S with 80 percent Cu. Fe is present in it as an impurity. The colour is black or lead grey. The specific gravity is 5.5 and the hardness is 2.5 to three (14).

i. Covelline, covellite: CuS, a sulphide with 66.5 percent copper (13). It's dark-black in colour with a high metallic lustre and slight irridescence The hardness is 1.5 to two and the specific gravity is 4.5.

j. Chrysocolla: It has a variable composition containing a hydrated silicate of copper. $CuSiO_3.2H_2O$. It varies in colour from bluish green or turquoise to sky blue. The specific gravity is two to 2.2. The hardness varies from two to four. The copper content is variable but may yield up to ten percent on smelting, using limestone as a flux to melt the silica (14).

As a summary, the physical properties of copper ores and native copper are grouped in Table 2.5.

2.2.3. Stages of Early Copper Metallurgy

Stages of early copper metallurgy till Bronze Age are illustrated in Table 2.6 where five major stages can be classified.

a. Shaping of native copper

This stage is fixed at the seventh or eighth millennium B.C. (11). Hammering, cutting, bending, grinding and polishing all belong to this stage. Shaped native copper is not useful because it is soft, with poor ductility. It can embrittle and cause cracks.

b. Annealing of native copper

It consists of alternately heating and hammering native copper. Until this discovery copper was used for small ornaments, but by annealing it was possible to shape it into further forms without making it too brittle. Both discoveries; the malleability and the fusibility of copper are done in this stage. The fusibility of copper made the melting and casting of metal possible (15, 16).

TABLE 2.5. Physical Properties of Native Copper and Copper Ores

Name	Formula	Copper (%)	Colour	Specific Gravity	Hardness
Native copper	Cu		copper-red	8.8	2.5-3
Cuprite	Cu_2O	89	dark-red	5.8-6	3.5-4
Tenorite, Melaconite	Cu_2O	89	black	6.3	3-4
Malachite	$CuCO_3.Cu(OH)_2$	56	green	4	3.5-4
Azurite	$2CuCO_3.Cu(OH)_2$	55	blue	3.7	
Chalcopyrite	$CuFeS_2$	34.6	brass yellow	4-4.3	4
Bornite	no chemical formula	55.5	reddish golden	5-5.5	3.3
Chalcocite	Cu_2S	80	black or lead grey	5.5	2.5-3
Covelline	CuS	66.5	dark black	4.5	1.5-2
Chrysocolla	$CuSiO_3.2H_2O$		turquoise or sky blue	2-2.2	2-4

TABLE 2.6. Stages of Early Copper Metallurgy

a. Shaping of native copper (hammering cutting, bending, grinding polishing)

b. Annealing of native copper (heating and hammering)

c. Smelting oxyde and carbonate ores

Smelting ore
regulus ← → slag (thrown away)

d. Melting and Casting Copper

e. Smelting Sulphide Ores

1. Roasting the ore
2. Smelting roasted ore
   copper matte (copper-iron sulphide) ← → slag
   ↓
3. Roasting copper matte
   ↓
4. Smelting roasted matte
   blue metal (rich is copper) ← → slag (rich is Fe and Cu)
   ↓
5. Roasting blue metal
   ↓
6. Smelting roasted blue metal
   black copper ← ↓ rich copper matte → slag (rich is copper)
   ↓
7. Melting black copper
   refined copper ← → slag (rich is copper)
   ↓
   Fashioning refined copper by casting etc.

c. Smelting of Oxyde and Carbonate Ores

Together with the melting and casting of copper, this stage forms the beginning of individual copper metallurgy. The reduction temperature of oxyde and carbonate was fairly high (1085°C)

d. Melting and Casting Copper

This stage became widespread about 4000-3500 B.C. Unsuitable old tools were remoulded, so recasting process was realized.(15, 16).

e. Smelting of Sulphide Ores

The preliminary roasting is carried out prior to the smelting process. The principles of roasting are connected with the production of lead and silver from galena. The smelting operation is conducted in three stages (13)

1. To produce a copper matte of 30-40 percent Cu content.
2. To make a blue metal of 65 percent Cu content.
3. To make a black copper of 95-96 percent Cu content.

After having produced a copper matte with 30-40 percent copper content the blue metal is smelted. The smelting of blue metal is generally done is "blast furnace" and in an oxidative medium which is coal and silicate. Coal reduces the CuO in order to form "Black Copper" with 95-97 percent copper content. At this stage certain amount of Au, Ag, Fe, Pb, As, Sb, Ni, Co, Zn and Sn may still remain as trace elements in copper metal. (17) During the final smelting with charcoal and blast air the final product, "tough-pitch copper" of over 99.5 percent purity is obtained. However, part of the air used in smelting may form CuO which makes copper brittle (13). The copper oxide is reduced by inserting greenwood in it. The slag which is formed is called "melting slag" and may have as high as 20-28 percent copper in it. Because of this, the analysis of trace elements in slag can help to find out the ore source.

The refining process discovered in Antiquity was very gradually developed until the twentieth century. New methods were introduced, among which the following can be observed; concentration of the ore by flotation, furnace treatment, combination of roasting and smelting in the convertor process, hydrometallurgical treatment, and electrical refining (17). But still there is always a tendency to return to older methods because the copper produced by modern mass methods is not always of the quality required.

In its simplest form, the operation consists of a series of roasting and smelting followed by refining. People of antiquity used different metallurgical techniques for their daily and long-term needs. Today technological data are easily obtained by using different methods of chemical analysis. It must be noted that, these metallurgical studies which have been used, are developed and are being used in all regions of the world. With minor technical improvements, ancients could obtain a good and pure copper alloy without too much difficulty, however, too much copper was left in the slag compared to modern methods. (13)

2.2.4. Smelting Process

The smelting process is the reduction of an ore body to metal in an atmosphere of carbon monoxide. Fuels and fluxes are used besides the minerals as is illustrated in Fig. 2.5.

The essential component of the fuel is carbon which creates the atmosphere of carbon monoxide. Carbon monoxide reduces the metal ore via the reaction: (14)

$$MO + CO \longrightarrow M + CO_2$$

where M = metal

MO = The oxide of that metal

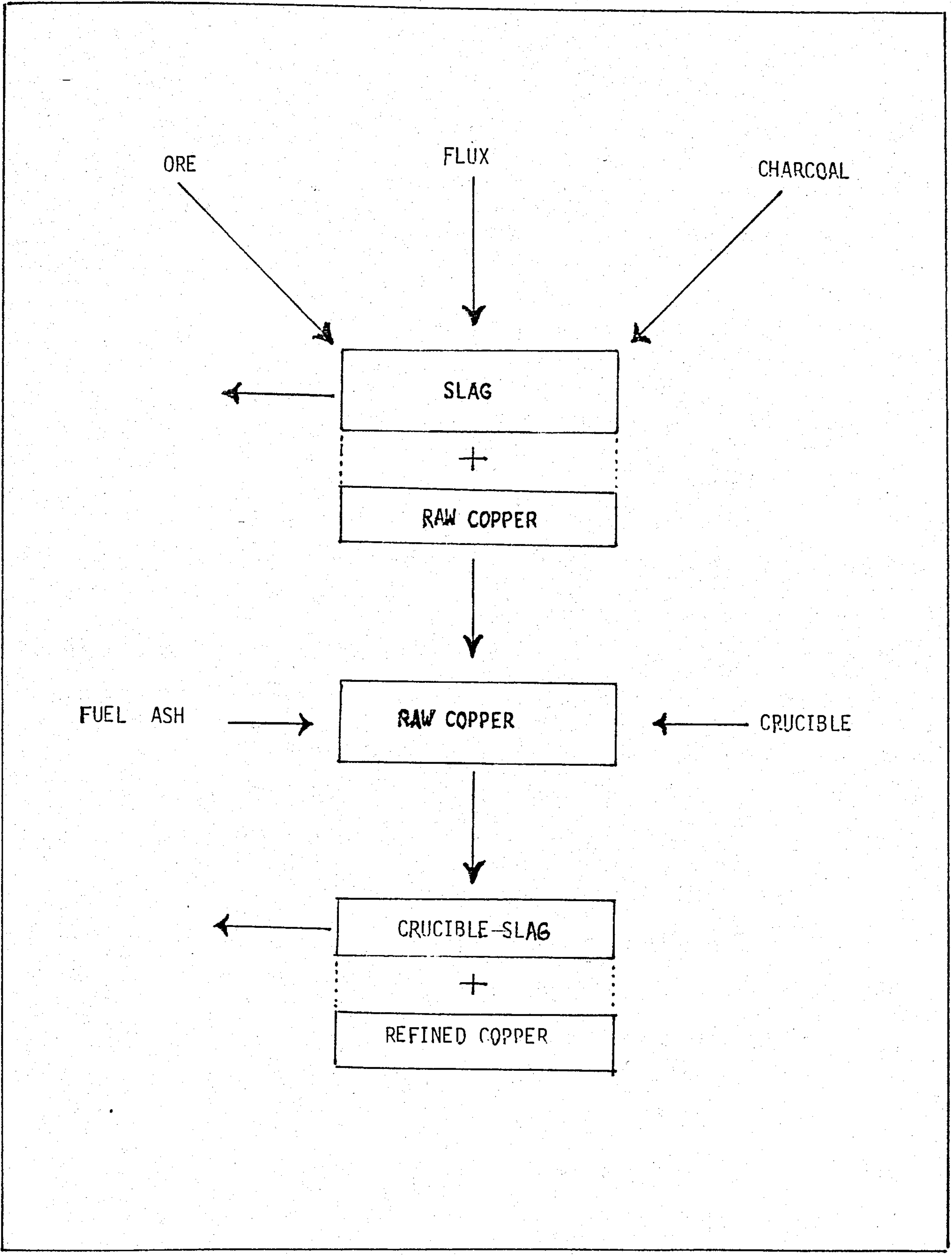


Fig. 2.5 Flow chart of the smelting process

The carbon dioxide so created is converted back to carbon monoxide via the reaction.

$$CO_2 + C \longrightarrow 2CO$$

Ores are mixtures of the desired mineral and the unwanted mineral or "gangue" high in silica. The 80 percent of gangue has to be fluxed and removed from the copper as a liquid "slag".

Fluxing was known since fourth millennium B.C. (18) Pure minerals such as cuprite (with 89 percent Cu), melaconite (with 89 percent Cu) and chalcocite (with 80 percent Cu) can be smelted without fluxing, because there are sufficient quantity of minerals in these ores and they can be readily leached. On the other hand, siliceous (oxide) ores, which have excess silica, need to be fluxed with FeO and the ferruginous ores (sulphides) which have exces iron, need to be fluxed with silica, SiO_2 (18). In both cases the liquid slag will be the same: fayalite (2 $FeO.SiO_2$) with a free running temperature of 1150°C-1250°C.

Slags obtained by this process can be characterised by their high viscocity, (500-2000 cP) as compared to that of mattes (ten cP) and liquid copper (three cP). The presence of solid magnetite or excess solid silica increases slag viscosity even further (17). Liquid slags are ionic. They are made of cations (e.g. Ca^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}) and anions (O^{2-}, SiO_4^{4-}, and large silicate chains and rings). Smelting slags are classified in three groups: acidic, basic and neutral according to their silica content. Basic slags are simple in structure and are fluid whereas acidic slags have high viscosity (17). Slags can be classified according to their types in the following manner (19): a. Glassy slags, black and obsidianlike, uniform b. Ripple slags, less uniform than the former, can vary in colour from grey to black c. Chunky slags, not homogeneous, may contain bits of ore, charcoal and also copper prills, some areas may have a rusty appearance due to oxidation of some of the iron percent. It is very brittle, a freshly broken surface may show some matte areas (19).

There are two techniques for reduction of an ore body to metal.

a. Hydrometallurgy

If the oxidized minerals are too lean in a copper ore, they are treated by hydrometallurgical techniques. It is the leaching of the ore with sulphuric acid, followed by precipitation or electrowinning of the copper from solution. The overall reaction for copper electrowinning is as fallows (17).

$$CuSO_4 + H_2O \xrightarrow{2v} \underset{\text{cathode}}{Cu^0} + \underset{\text{anode}}{\tfrac{1}{2}O_2} + H_2SO_4$$

The copper is not very pure because of the contamination from the lead anode which is not completely inert.

b. Pyrometallurgy

When the oxidized minerals are present in sufficient quantity in the ore, they can be reduced pyrometallurgically to impure copper (20).

Pyrometallurgy consists of three stages: (17) 1. Roasting 2. Matte smelting 3. Converting to blister copper

The copper ores mined today are too lean in copper (one percent copper) to be smelted directly. For economical smelting, copper minerals in the ore must be concentrated by "froth flotation" technique (17). Copper minerals are rendered hydrophobic and are removed mechanically from the top of the flotation cell. The gangue minerals are left in water avid at the bottom of the pulp. Typical concentrates contain 20-30 percent Cu.

1. Roasting

Roasting is a partial oxidation of copper sulphides with air. It is carried out for two main reasons depending upon the method of copper extraction. First in hydrometallurgical extraction, roasting is necessary because copper minerals are not easily leached, whereas their sulphates are soluble in water and their oxides are soluble in dilute sulphuric acid. Thus a controlled roasting of sulphides can produce a readily leachable calcine. Second in pyrometallurgical extraction, roasting is done prior to matte smelting in order to utilize the heats of roasting, to dry and heat the charge before it is added to the smelting furnace, and also in order to increase the concentration of copper in the smelting product i.e. in the liquid matte (21).

During this process temperature must be between 500-700°C (17). Some examples of the roasting reaction are as fallows:

$$CuFeS_2 + 4O_2 \longrightarrow CuSO_4 + FeSO_4$$

$$2CuS + \frac{7}{2}O_2 \longrightarrow CuO.CuSO_4 + SO_2\uparrow$$

$$2CuFeS_2 + \frac{13}{2}O_2 \longrightarrow 2CuO + Fe_2O_3 + 4SO_2\uparrow$$

In the roasting reactions sulphur is eliminated in the form of SO_2 and also, volatile elements like As, Sb are decreased if present in the medium. The roaster product "calcine" is a mixture of oxides, sulphates and sulphides. Oxidation reactions are exothermic, so once ignition takes place the roaster operates autogenously (20).

2. Matte Smelting

It consists of melting concentrates or partially roasted concentrates at 1150° - 1250°C to produce two immiscible liquid phase (17): the first phase is a copper-rich matte, (sulphide, containing all the copper) and the second phase is the slag (oxyde, free of copper). The main disadvantage of the method is its contamination with SO_2 gas.

The matte phase consists principally of $Cu_2S.FeS$ matte (35-65 percent Cu). Beside these two sulphides, the matte phase also contains small amount of Co_3S_2, Ni_3S_2, Pbs and ZnS. The matte is also an excellent solvent for precious metals like Ag, Au, Pt which enter the phase along with As, Sb, Se, Te (17).

The slag contains mainly copper and iron oxides (FeO, Fe_3O_4) and also other oxides like Al_2O_3, CaO, Mgo, SiO_2. These are added as flux or are present in the original concentrate. It is the iron, copper, sulphur, oxygen and these oxides which control the chemistry and physical constitution of the matte slag system.

The first purpose of matte smelting is to transform all forms of copper into Cu_2S and this is ensured by FeS, which tends to sulphidize the non sulphidic copper (17).

$$FeS(l) + Cu_2O(slag) \rightleftharpoons FeO(slag) + Cu_2S(l)$$

Oxidized copper may be present in various forms as: CaO, $CuSO_4$, $CuO.CuSO_4$ or $CuO.Fe_2O_3$. All of them form Cu_2S at the end. So it's impossible to smelt copper metal without having iron in the medium. Iron regulates also the distribution of heat at microscobic level.

The second important thing is the silicated flux (13). The smelting operation must be carried out by bringing the slag to near saturation with SiO_2 (35-40 percent silica). When silica is absent it is impossible to seperate the matte from slag, because they form a miscible system together (17). In such a system the oxides and sulphides combine into one covalently bonded, semiconducting phase Cu-Fe-O-S phase. But when silica is present, it combines with the oxides to form strongly bonded silicate polymer anions: (17)

$$2FeO + 3SiO_2 \rightleftharpoons 2Fe^{2+} + Si_3O_8{}^{4-}$$

All these, group together to form the slag phase. The sulphides show no tendency to form these anions and hence remain as a distinct covalent matte phase. Thus two immiscible layers are created. Lime and alumina can stabilize matte-slag immiscibility. They are beneficial up to about ten percent concentration.

3. Converting to Blister Copper

It consists of oxidizing (with air) the liquid matte from smelting stage. It removes the iron and sulphur from the matte and yields the crude (99 percent Cu) blister copper. This operation is accomplished at 1100°C.

This conversion is carried out in two sequential stages: The first stage is the FeS elimination or slag forming stage, i.e.

$$2FeS + \underset{\text{air}}{3O_2} + \underset{\text{flux}}{SiO_2} \longrightarrow 2FeO.SiO_2 + 2SO_2$$

whereas the second is the blister copper forming stage, i.e.

$$Cu_2S + \underset{\text{(air)}}{O_2} \longrightarrow 2Cu + SO_2$$

The second stage begins when the matte contains less than about one percent Fe, so that almost all of the iron is removed as slag before the beginning of copper production (17).

The product of the converting process is blister copper which contains 0.02-0.1 percent sulphur. Oxidation of the copper is not a problem because copper oxide occurs when the sulphur content is below 0.02 percent (17).

Most of the nickel and precious metal, which were in the matte enter the blister copper. Iron and zinc are oxidized into the slag, while antimony, arsenic, cadmium, and lead tend to vaporize. SO_2 is a by-product and can be removed as H_2SO_4 because its concentration is high (greater than five percent SO_2).

The blister copper is then electrochemically refined to produce high purity (99.99 percent Cu) cathode copper. Electrorefining consists of the electrochemical dissolution of copper from the impure anodes, and the plating of pure copper (without the anode impurities) into copper cathodes. The electrolyte is an aquous solution of H_2SO_4 (200 kg/m^3) and $CuSO_4$ (50 kg/m^3) usually with a trace amount of chlorine.

After the development of the five stages in copper metallurgy, (Table 2.6) Bronze Age began. Especially in the Anatolian sites arsenical bronze is seen earlier than tin bronze, so alloying copper with tin indicates a more advance in metallurgical evaluation. Then man began to add trace elements into copper, in order to obtain superior properties as compared to copper. Thus alloying process began after the development of the smelting process.

2.2.5. Alloys

Over 50 percent of the world production of copper is used in the electrical industry, nine percent in the automobile industry and 11 percent for building and architectural purposes. The electrical industry uses either pure copper or copper alloys, so the greater part of the produced copper is used in the form of alloys with other metals. Alloys replaced native copper in many areas because they have superior properties compared to pure copper. Many specific alloys are developed for special applications.

a. Copper Arsenic Alloy

Many researches showed that in the Early and Middle Bronze Age, arsenic was intentionally added to copper to produce an alloy with superior casting and mechanical properties (21, 22, 23). Arsenic reached from 0.25

percent to as high as ten percent in the alloy and diminished in bronzes when tin gained more importance in later periods.

Arsenic bearing minerals can be identified by the garlic odour given off when struck by a hard implement or stone (19). If an artifact is found to contain an appreciable amount of arsenic (more than about three percent) then the arsenic is said to be intentionally added as an alloying element (20). It is thought that the ancients mixed enargite (Cu_3AsS_4) or other arsenical minerals with copper pyrites and prepared a metal rich in arsenic, then they noticed that the alloys prepared in this manner, were taugher and stronger than usual.

Arsenical copper has superior properties than copper: It is a good deoxidant and has a greater affinity for oxygen, hence, it renders copper suitable for casting. Even one percent of arsenic functions as a mild deoxidant. In the cold working conditions, arsenic increases the strength and hardness of copper, however, in the hot working conditions such as annealing at 700^{o}C, it softens the metal, thus copper can be worked without difficulty. The effects of work hardening process i.e. cold working by hammering and annealing on arsenical copper are illustrated in Table 2.7. As is observed on the table, an arsenical copper alloy with 7.92 percent As content could crack when it is compressed by work hardening process, however, anealing it at 700^{o}C would soften the metal, thus copper could be worked more easily. (20)

It is also observed that alloys with seven percent As posess remarkable ductility and have corrosion and erosion resistance (20).

Cu-As alloys are formed with the association of sulphide copper minerals and some other complex minerals containing As (24). These are given in Table 2.8.

TABLE 2.7. Effect of Work Hardening and Annealing on Arsenical Copper

Condition of Metal	Arsenic		
	4.2%	5.94%	7.92%
as cast	83	85	163
compressed 100% work hardening	195	220	224
annealed at 700°C	55	63	64

TABLE 2.8. Complex Minerals Containing Arsenic

Name	Formula	Composition (%)
Enargite	Cu_3AsS_4	19% As and 46% Cu
Tennantite	Cu_3AsS_3	21% As and 53% Cu
Tetrahedrite	$Cu_5(SbAs)_2S_7$	
Orpiment	As_2S_3	
Realgar	As_2S_2	

Among these minerals orpiment and realgar are non cupriferous arsenic which form arsenical copper alloy when they are simultaneously smelted with copper ore (24).

Arsenic minerals can also provide silver coloured coatings on copper, producing an artificial silver. This kind of luster tarnishes less rapidly than silver. The silver colour is due to a copper-arsenic alloy containing at least 12 percent of arsenic. It has been shown that the Ancient Egyptiens prepared silver coloured coatings on copper and used this high arsenic copper alloy as a mirror (25). Also in Turkey, arsenical copper objects containing up to 12.6 percent arsenic are found at İkiztepe and are analyzed by Doç.Dr. Hadi Özbal from Boğaziçi University (26).

Later, however, The Early Man began to use tin instead of arsenic, because of the high risk of poisoning due to As and its high volatility (27) which lead to uncertain metal composition.

b. <u>Copper-Tin Alloy (Bronze)</u>

Stannite (tin sulphide) or cassiterite (tin oxide) were used for the production of copper-tin alloy. The early bronzes contain all kinds of contamination, because matte or black copper is smelted with tin ore, but later bronzes avoid contamination because they are prepared by smelting pure copper with tin ores.

Tin-bronze is the most suitable metal for casting. In fact closed moulds are one of the consequence of the development of bronze metallurgy, because the addition of tin checks the absorption of oxygen and other gases, acting as a deoxidizing agent. The strength and hardness of this alloy are very improved, only steel and iron can surpass tin-bronze in many physical properties (4). The physical properties of bronze are illustrated in Table 2.9.

TABLE 2.9. Physical Properties of Bronze

	TENACITY (tons per square inch)	HARDNESS (Brinell number)
Cast Copper	10	80
Tin bronze with 10% of tin	15	
when hammered		120-130
Tin bronze with 9.31% of tin		136
when hammered		257

As is observed in Table 2.9., the addition of 10 percent of tin to the cast copper, brings the tenacity from ten to 15 tons per square inch, whereas the addition of 9.31 percent of tin on copper brings the hardness from Brinell number 80 to 136. It is also observed that hammering increases further the hardness of tin bronze to the figure of Brinell number 257 (1).

As an alloying element tin is superior to arsenic and zinc. All three make copper more fluid and thus easier to cast, but tin in a quantity of about ten percent makes copper harder and stronger and brings greater corrosion resistance to copper than zinc and arsenic. It also reduces the m.p. of copper from 1085°C to 1020°C by addition of about ten percent, while five percent arsenic reduces the m.p. by about 25°C and adding ten percent zinc lowers by about 30°C (10).

In the earlier period the tin content was between five and 15 percent (10), but later bronzes contain anywhere from eight percent up to 33 percent of tin. The most widely used of the modern bronzes is "gunmetal" containing ten percent of tin (10).

There are two general methods of producing copper-tin alloys (28). In the first case tin is smelted from the oxide cassiterite with charcoal which is very simple because of its low m.p. (232°C) (21). This smelted tin is added to smelted copper to produce bronze. In the second case, copper ores and cassiterite ores are mixed before smelting and are smelted together. The second method produces alloys with variable tin percentages, but it is not likely because it requires shipping tin ores to copper sources. It is unlikely because ore has a greater bulk than a smelted metal, therefore the first method was perhaps widely used (21).

In Ancient Anatolia tin was used for bronze manufacture, despite the fact that Anatolia was believed to have very little tin deposits. In the beginning of the second millennium, B.C., it is believed that tin was imported in exchange of copper, gold and silver.(29). Examples of even an earlier period are found at Alacahöyük (Çorum, Sungurlu) and Horoztepe (Tokat-Erbaa) in the third millennium B.C. (28). Sometimes the surface of bronzes are plated and inlayed with electrum (gold-silver) and also inlayed with arsenic. This indicates the perfection of the technical skill in metallurgy (28, 15, 16).

c. Copper-Zinc Alloy "Brass"

Brass is a yellow alloy of a more golden colour than bronze. It can be manufactured by melting copper together with calamine (zinc carbonate), cadmia (zinc oxide) and also by simply using metallic zinc (30). But calamine brass is believed to be superior in mechanical properties to brass made by using metallic zinc (4).

Brass which contain from 15 percent to 20 percent of zinc possess the greatest ductility. Such an alloy was also used in jewellery. Thin sheets of brass were used in the imitation of gold. (2). Also in ancient times brass was used for ornamental purposes (4).

The method used in the preparation of calamine brass is very simple. The calamine is grounded and mixed with charcoal and copper, in granules or small fragments. This mixture is placed in a crucible and is carefully heated to a temperature sufficient to reduce the zinc in the ore to the metallic state, without melting the copper. The zinc being volatile, its vapor permitted the copper to be converted into brass. The temperature was then raised and the molten brass was poured out of the crucible into moulds. The alloy obtained is called "calamine brass". Later, copper used in the manufacture of calamine brass for objects of art is purified (2). This purification was especially necessary to remove lead, because lead is found to be contaminating brass.

Beside arsenic, tin and zinc, other trace elements also are added into copper. These trace elements have some unique effect on the properties of copper (31): Bismuth, having a very low solubility in copper, forms inclusions in copper and copperalloy casting and causes brittleness. Lead, at a small amount, aids in effective casting and reduces the brittleness of tin-bronze and arsenical copper alloys. However, at higher concentrations, lead behaves like bismuth and renders copper brittle (31). The concentration of nickel on the other hand, generally does not exceed one percent. It is less common in copper and hardens without causing brittleness.

2.2.6. Variation and Partitioning of Trace Elements Between the Ore, Flux, Slag and Metal

It is not easy to distinguish native copper from smelted copper. Native copper has in many cases the properties of the smelted metal, it can be as pure as smelted copper or considerably less pure. In certain cases a large percentage of gold, silver, iron and antimony indicates a native origin and sometimes the presence of arsenic, lead, zinc, tin, nickel and sulphur indicate that the metal in question is a smelted copper (10).

Copper whether native or smelted has a percentage of impurities. Trace impurities can serve as clues to the possible ore sources of the metal. Metals like iron, manganese, zinc, aluminium, chromium pass to the slag, thus minor quantities remain in metallic copper (13). Upon smelting, arsenic and antimony present in the ore, mainly remain in metallic copper, but since arsenic is very volatile, its concentration in the objects varies widely. Zinc and cadmium are also volatile, their occurence in copper varies according to the smelting method used. Tin has a high solubility is copper and passes into the metal during smelting. Other elements such as "phosphorous, silicon, calcium, arsenic, sulphur and antimony have a tendency to pass on to the reduced metal if they are present in the ore (13).

The proportion of impurities present in the ore is not constant and varies with particular smelting conditions. Similarly, the same ore source may show wide differences in the trace element distribution. During smelting, for example, arsenic and antimony can diminish since they are highly volatile. On the other hand, the presence of nickel may indicate that the metal in question is a smelted copper, because nickel is not seen in the native copper.

Trace elements in the ore, partitione between the flux, slag and metal during the smelting process, Tylecote and Boydell carried out experiments to show that the conditions of smelting, melting and refining processes, (32) changed the distribution of trace elements. For this purpose, they have smelted different types of ores in a primitive smelting furnace and studied the effect of the changes in the laboratory conditions on the trace element distributions

It is evident that iron always can be found in impure copper. It can vary from less than 0.2 percent to over 24 percent due to ferruginous slag, but can be refined out. It s solubility in copper is very low. If there is more than one percent of Fe in the copper, it becomes ferromagnetic. Iron is seperated from the copper as fayalite, ($FeO.SiO_2$) which is the slag. Manganese and cobalt are related to iron and also pass into slag and are easily seperated. Nickel and zinc are related both to iron and copper so they are equally distributed between the iron and the copper. Silver, is copper related and mainly remains in copper. Arsenic, antimony, bismuth and lead, are all highly volatile and their proportion varies according to the temperature used during smelting.

The trace element partitioning of a synthetic copper ore between slag and metal after a primitive smelting procedure is shown in Table 2.10.

From this study (32) some important conclusions were made:Among the oxides, CaO, Na_2O and K_2O are found to come from the charchoal ash , whereas As and Mn are introduced into the metal from the fluxes. The principle impurities are S, O_2 and Fe. As for Ni and Ag, they are observed in copper from oxidized ores. When two tuyeres are used, such high smelting temperature can cause a reduction in the level of Zn, Sb, Pb and Bi in the copper. A roasting process is necessary for sulphide ores at 850^{0}C before the smelting process. Slags obtained after the smelting process can contain up to 40-50 percent of FeO and their analysis can give clues about the source of an ore.

2.2.7. Heterogeneity and Sampling Problem

The purpose of trace element analysis is to determine possible ore sources. Especially some of the elements found in the ore remain in copper, alter the smelting. However, as mentioned before, different parts of a given ore source may show wide differences in trace element distributions. Thus such applications should be done with care. Along with this problem, the distribution of the trace element in a given piece of metal may not be uniform as well. Taking 25 mg. sample from an artifact, which weighs a few kilograms may not give the overall distribution of the trace elements. (33, 34)

Trace element distribution may change during smelting, melting, alloying and casting processes (33). It is possible that in the past new artifacts were also made by melting the older ones. These artifacts showed neither the real distribution nor the ratio of the ore sources.

TABLE 2.10. Partitioning of Trace Elements in an Ore Between Slag, Raw and Refined Copper

Composition %			Element % in Metal			
	Ore	Slag		Ore	Raw Smelted Copper	Refined Copper
CuO	50.0	0.08	Cu	40.0	73.15	85.9
MnO_2	5.0	4.75	Mn	3.16	0.05	0
As	2.88	0	As	2.88	4.20	2.0
ZnO	5.00	2.50	Zn	4.03	2.20	1.0
NiO	5.00	0	Ni	3.89	9.75	5.3
PbO	5.00	1.34	Pb	4.65	2.02	1.5
Sb	4.20	0	Sb	4.20	5.30	3.0
Bi_2O_3	3.72	0.09	Bi	3.72	1.01	0.8
$FeO+Fe_2O_3$	0	51.36	Fe	0	2.32	0.5

Researches done show that, there isn't a homogeneous distribution of trace elements in metallic artifacts (33). Precious metals and their fine alloys are homogeneous, but more common metals like copper are not. Thus, a small sample taken from an object will not give the complete distribution of trace elements. Some of the investigators have suggested that the greatest heterogeneity may be due in part to the segregation of components on ageing, by reason of diffusion, crystal growth or phase change. However, investigation showed that such events happened with silver-lead or silver-copper, lead alloys and lead precipitated even at room temperature. Such segregation is found to be negligible (33).

There are several reasons for the heterogeneous distribution of trace elements in metal objects (33). First of all phase of low solubility may precipitate out during manufacture. This problem is observed in bronzes which contain high proportion of lead, where lead forms a seperate phase in the form of globules of different size. Likewise, when an alloy is not prepared at a high temperature or when melting is done under unsufficient heat, some trace elements are distributed as bulky groups at various regions. Guilding artifacts with some valuable metals can effect the homogeneity. Objects can be manufactured in the form of a plating of a precious metal on a core of base metal. Thus, a sample from the surface of such an object can't reflect the composition of the whole.

Oxides and slag can also be introduced into an alloy during smelting and melting processes. This is the main cause for the beginning of corrosion, which is one of the main causes of heterogeneity. Especially erratic and extensive intergranular corrosion effects the trace elements distribution in great proportion. The percentage of arsenic and antimony are generally higher in a corroded portion of an object as compared to non-corroded parts(33).

As the object gets bigger, the heterogeneity similarity increases.

The analysis of a single sample taken at random is not sufficient for a good result. Samples should be taken systematically from various parts and either analyzed separately or combined into one representative sample to determine the average compositon (33).

Sometimes the metal is so corroded that samples of unaltered metal cannot be obtained. The results of analysis of such objects will not add up to 100 percent. The visible surface corrosion products should be just removed by mechanical treatment. Then the clean metal should be washed with alcohol and acetone to remove possible oil and grease contaminants. After metal is dried in an oven and accurately weighed, it is placed in a solution of one to one nitric acid. After five minutes it is removed, washed successively with water ethanol and acetone, dried and reweighed. The difference between mass is the amount of metal dissolved in the acid. This could be a useful sampling method for small objects like coins. However, the major problem of this method is that only samples from the surface are taken for analysis. Also if the object is highly corroded the acid solution may demage the whole specimen.

The best way to obtain samples from a metal object is by drilling method. In order to avoid necessary demage to the appearance of objects, drill bits of small diameter are used. Drilling taken from different points are combined into one representative sample (33).

2.2.8. Types of Smelting Furnaces

Detailed information cannot be given for the earliest smelting furnaces in which copper oxide ores were smelted, because these furnaces when cooled down were destroyed, in order to extract the copper (35, 35).

The furnace shown in Fig. 2.6. which the excavator, Rothenberg, dates to the Chalcolithic period, can give an idea about the furnaces used in ancient times. This is modelled on the type of furnace found on Site 39 at Timna, Israel, at about 3300 B.C. (32, 37). The model consists of a cylindrical hollow hole with 23 cm. diameter and 30 cm. depth. It is made from fire bricks, surrounded by sand and insulating brick. First, a single tuyere was used, then a second one was added. With the intention of burning the unburnt carbon monoxide given off at the top. Both tuyeres were supplied with air at a rate of 150 l/mn. The mixed ore, flux and charcoal were added to the furnace in 200 gr. charges maintaining a (flux ore)/ fuel ratio of one to two.

Today, however, smelting is most often performed in conventional reverberatory furnaces. Blast furnaces are also used in locations, where lump ores are available and electrical furnaces are used in locations, where power is inexpensive (11). A newer process "flash smelting" replaces the other processes for its low fuel requirement.

Blast furnaces were used in the past for producing large quantities of matte for lump sulphide ores. They are unable to treat finaly grounded flotation concentrates directly because the combustion gases below the particles out of the furnaces (17). Reverberatory furnaces, however, were the most widely used method for producing copper matte. Its virtues are its simplicity and versatility. The greatest problem is the production of large volumes of gases with low concentrations of SO_2. The use of such furnaces declines gradually because of the big air polution caused by SO_2 gas. Electric furnace system, has the advantage of good temperature flexibility and control, and because there are no combustion gases, good control over oxidation conditions is possible. Consequently low losses of copper occur in the smelting slags and there is an excellent control of slag properties.

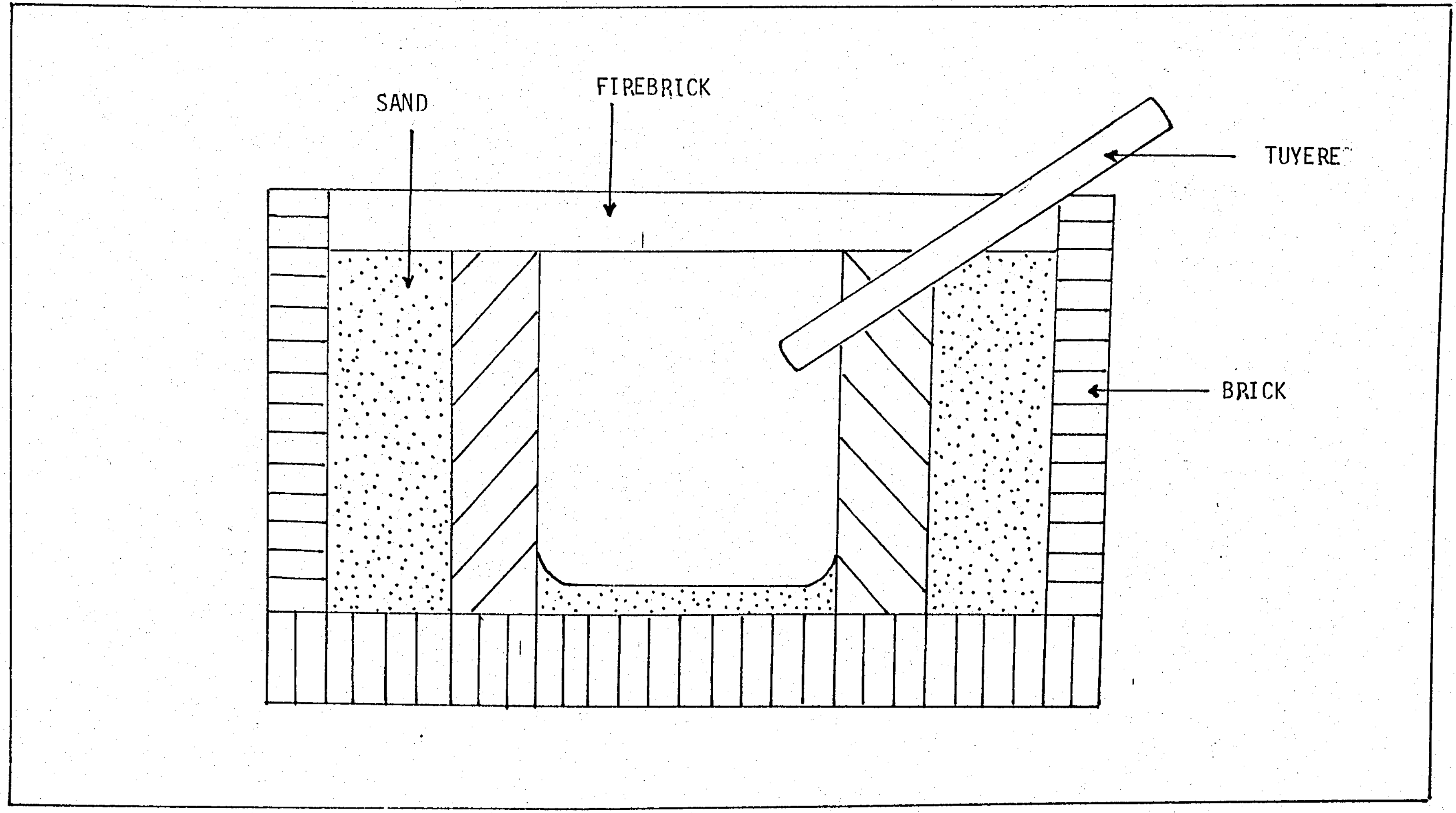


Fig. 2.6. Shape of the Chalcolitic Furnace

Since small quantities of gas and SO_2 are produced in this type of furnace, electric furnaces replaced reverberatory furnace in regions where electrical energy is inexpensive.

The first three types of furnaces use hydrocarbon fuel or electrical energy, flash furnace on the other hand uses the energy obtained in the oxidation of its sulphide charges (17). This liberated heat is also used for the melting of matte and slag. The combustion reaction is as fallows:

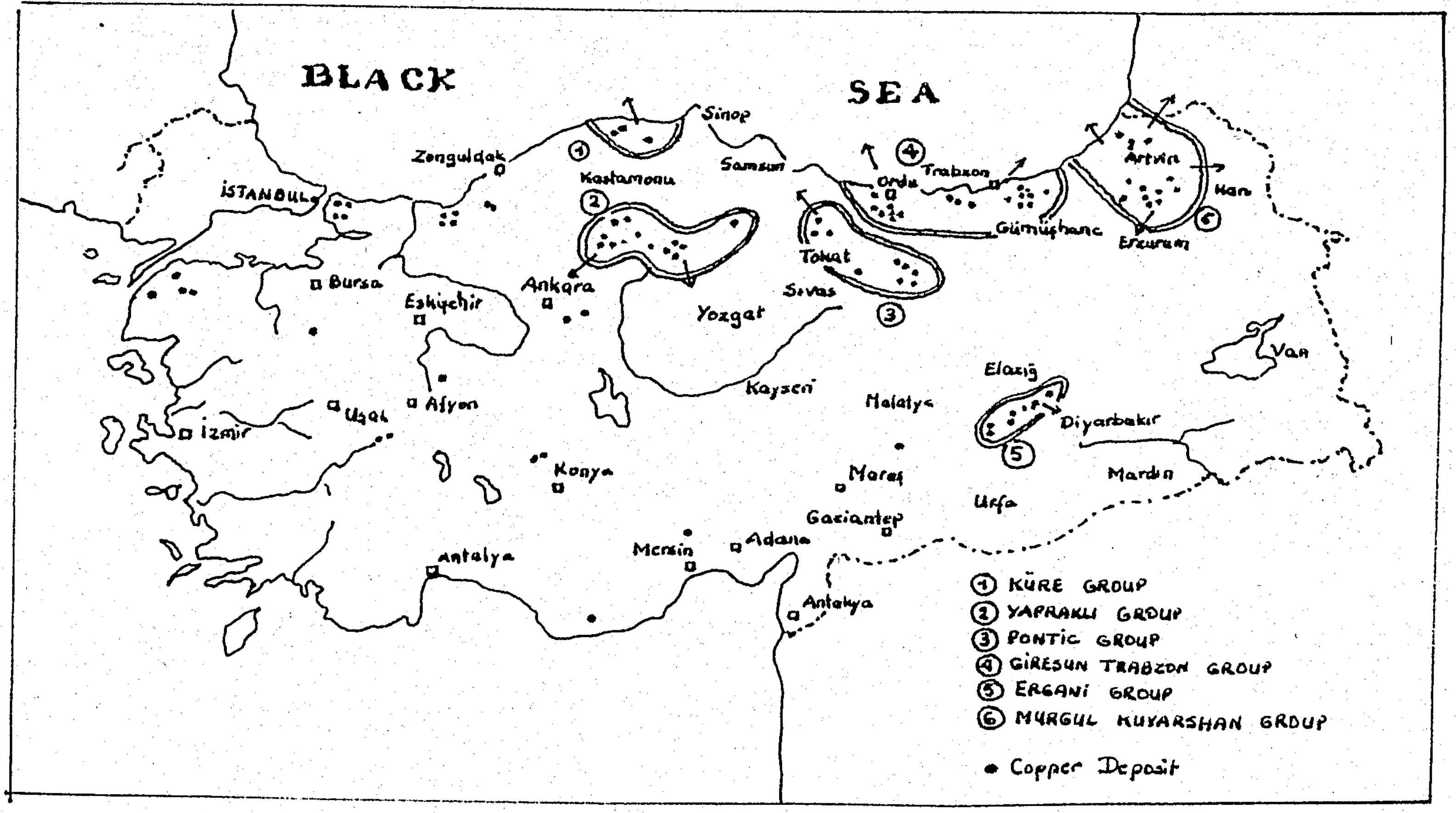
$$\underset{\text{(Chalcopyrite)}}{2CuFeS_2} + 5O_2 + \underset{\text{flux}}{SiO_2} \longrightarrow Cu_2S.FeS + FeO.SiO_2 + 2SO_2 + \text{heat}$$

This reaction provides much or all of the heat required for heating and melting. A considerable quantity of SO_2 is produced by this furnace. Its concentration is high enough (greater than ten percent SO_2) to be removed as H_2SO_4.

The main advantages of this kind of furnace are: its law hydrocarbon fuel requirement and the ease and efficiency with which the SO_2 can be removed from their effluent gases. However, high loss of copper may occur in slag which can be recovered by recycling.

2.2.9. Metallurgy in Turkey

Copper ore is relatively abundant in Turkey. It occurs in various form and its distribution encompasses a large area of the country (19). The most prevalent type of copper mineral available today is chalcopyrite. It is often associated with lead and zinc to the extent that all three metals (lead, copper and zinc) can be mined and smelted from the same ore body. Although copper ore is widely distributed (Fig. 27) only a few areas in Turkey today are mined for it. There are six suggested areas of intensive copper exploitation in the past (19, 38, 39).



Fiq. 2.7 Sources of copper in Turkey

1. Küre group (Middle of Black Sea region including Sinop)
2. Yapraklı group (Middle Anatolian side, near Yozgat and Ankara)
3. Pontic group (Area including Tokat and Erbaa)
4. Giresun-Trabzon group (Area including Giresun, Trabzon and Ordu)
5. Ergani group (South eastern part of Anatolia including Diyarbakır)
6. Murgul-Kuvarshan group (East of Black Sea Region including Artvin)

The Ergani group is the most famous deposit because it has been exploited for a long time. In antiquity a certain amount of oxidized ore was available at Ergani, judging from present remains. The Ergani copper deposit has always maintained a special interest for archaeologists, because of its strategic location in eastern Anatolia on the main route between Central Anatolia and Assyria, and also because of its continued wealth. (11, 15).

The Küre mining area continues to be an important source of copper today. Copper ore is no longer extracted at the Küre mine itself but at the near by site of Aşıköy (9, 36). The ore here is chalcopyrite with pyrite and some bornite.

Near Artvin, the Murgul-Kuvarshan Mines are also important. (39) Mining at Kuvarshan Maden has ceased, but Murgul is still in operation. Chalcopyrite is the principal mined ore, but there are secondary mineralizations of bornite, chalcocite, covellite as well as chalcopyrite.

The Pontic mining area was also an important source of copper. The ores were noted as malachite, azurite, chalcopyrite, cuprite and native copper. The prehistoric smelters probably smelted ores of carbonates and oxides which were the easiest to treat and were the nearest to the surface (19). During their work Enargite (Cu_3AsS_4) has been found near Gümüşhane (19). There are also arsenopyrite deposits in the West of Turkey often associated with gold.

In Antiquity native copper was probably much more abundant in surface outcrops than it is today (10), although copper nodules can still be picked up in a number of copper producing areas in Turkey.

The distribution of copper deposits accross Turkey from the Caucasus to the Troad provides a number of opportunities for copper exploitation by earlie periods people. Two types of mining activities have been practiced in historic Turkey. One was the intensive exploitation of a particular site, such as at Ergani and at Murgul and the second was small-time exploitation along the Black Sea Coast in Gümüşhane, Giresun and Trabzon Provinces (19). Most of the mines however have caved in and were covered with rubble and top soil, leaving behind only slag dumps. Possible ancient copper mines are shown in Fig. 2.8.

Copper deposits are found on the banks of the Copper Stream (Bakır Çay) in Amasya Province (Site 17). Also at Ağaca Ağaçlı, south of Artova in Tokat Province (Site B) a mine covered with rubble has been exposed (38).

The Kozlu mine south of Erbaa in Tokat Province (Site C) which was an important source of copper ore, was also filled. Horoztepe, 15 km north of Kozlu was an important site for copper objects(19). In Kastamonu Province near Taşköprü (Site D) several tons of slag attest to active copper smelting in the past. Karaeli, 60 kms. southeast of Ankara (Site E) and Hisarcıkkaya near Eldivan in Çankırı Province (Site F) showed the remains of smelting furnaces, and lastly (Site G) showed two neighbouring smelting sites in the Eldivan Mountains to the west of Hisarcıkkaya.

The most spectacular smelting site was that of Gümüş (Site A). A large sector of the village is built on the slag layer. The area is known for its lead deposits, but upon analysis the slag showed upto 30 percent of arsenic (19). Appreciable quantities of iron and lead were also present.

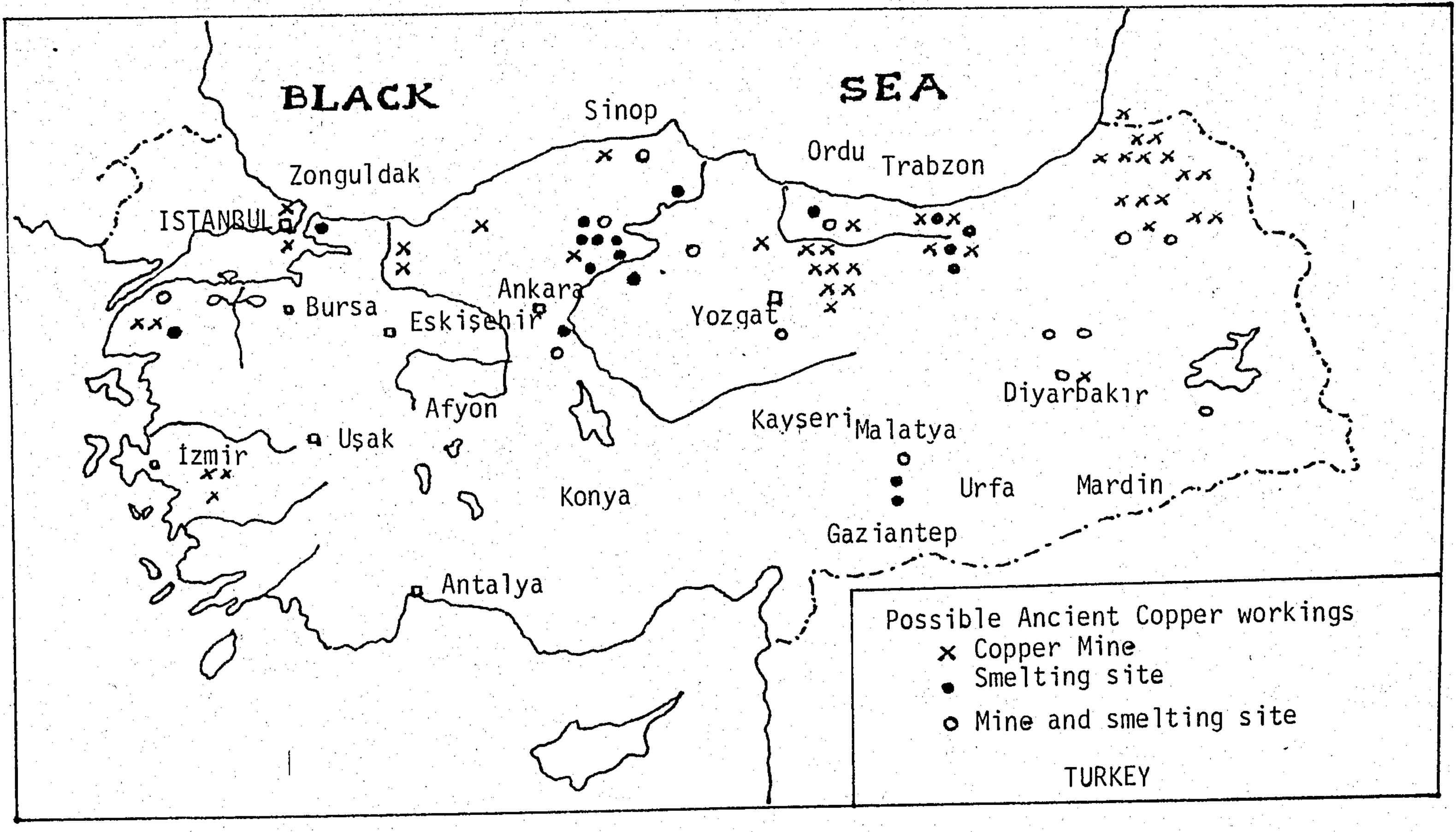


Fig. 2.8 Ancient mines in Anatolia

These copper slag dumps give and idea of the extent of ancient Metallurgical production in Turkey.

The term "Stone Age" and "Copper", "Bronze" and "Iron" Ages are used in archaeological literature to distinguish periods before and after the discovery of metal. In Copper, Bronze and Iron Ages, metals became available and proved superior to stone for many purposes. The use and manufacture of metal marked advances in technology. It is difficult to set a fixed date for the first extraction of metal from ores, but every new discovery pushed the event farther back in time.

An archaeological site in Anatolia called Çatal Höyük dated to 6000 B.C. has yielded a metal which did not occur in the native state,this metal found at Çatal Höyük was lead (15, 16). Lead is rarely found in nature, in native state. Native lead is extremely rare and only tiny particles in rock have ever been found in Sweden (40). In general, the metals found in the native state are copper, gold, sometimes silver, platinum and a meteoric iron-nickel alloy. In early times, pure native copper as huge boulders as well as small pieces were very abundant.

Earliest use of metal was simply hammered native copper(31,16)to shape needed articles, but too much hammering caused the metal first to harden and then to crack. The problem could be remedied by warming, because heat softened the metal so that it could reworked. This change with heat encouraged man to apply the same treatment to other stones. Most stones cracked and broke apart, but when galena (lead sulphide) was put in the fire, a new substance "lead" formed at the end. This extraction of lead from galena was the basis of all pyrometallurgical processes.

Metal ores were also abundant in prehistoric times, but Galena required the simplest treatment to extract lead from it and was reduced at a much lower temperature than copper ores. Thus, lead can be said to be the father of all metals and was the starter of the Metallotechnological Age. However lead did not play an important role in the development of ancient metallurgy but the more functional ones such as copper did. Lead was smelted for its by products which were litharge as a glaze and silver as a metal. Lead-glazed artifacts have been found dating from 5000 B.C. (40) and the number of excavated silver artifacts rapidly increases from this date on. During the third millenium B.C. in the Black Sea Region at Mahmatlar, the process known as cupellation was used to obtain the silver from the lead sulphide ore "galena" (14).

Copper, was first used for ornamental purposes because when rubbed it showed a bright colour. All extremely old copper articles are cold worked or hammered because they are free of copper oxides which are formed only when copper is melted and absorbs oxygen from the air (40). The earliest find of copper is from an excavation at Çayönü in Turkey dating to 7000 B.C. The smelting of copper from ore is believed to be first accomplished at about 6000 B.C. at Çatal Höyük (31). Tin bronze artifacts with 11,5 percent tin were first made by about 3500 B.C. and tin objects appeared 500 years later.

Early settlements appear to have evolved in the regions of Anatolia and the surrounding areas, and in these areas the greatest number of stone, ceramic and metal objects have been found together. Three tiny copper pins were found at Çayönü Tepesi dated from 7000 B.C. (31) The source of this native copper is considered to be the Ergani mine region (41) which is at about twenty kilometers from Çayönü Tepesi. Another important site for early metal working was Çatal Höyük. Copper objects mainly beads, tubes, rings and small tools were found in that region located in the Konya plain, mostly in the graves of women (around 6400 B.C.) (31, 16). Beycesultan and Gedikli Höyük are interesting sites giving information about the third millennium metallurgy of Anatolia (29). In addition, many spectrographic analysis were executed and statistically tested on objects found in the "Royal Burials" at Alaca Höyük, Horoztepe, Mahmutlar, Troy, Tarsus,and Alishar Höyük. All these are major third Millennium sites in Anatolia (31). Spectrographic analysis on diverse objects from these Anatolian sites are executed by Prof.Ufuk Esin from İstanbul University (42).

2.2.10. Gedikli Excavation

Gedikli Höyük is located in the South eastern Anatolia, 23 km. west of Gaziantep on the plain of Sakçagözü. The analyzed materials are from an excavation made by Professor U. Bahadır Alkım in 1964. (43). The excavation had lasted for 3 years between 1964-1967 (44).

This excavation showed very rich findings belonging to the Early Bronze Age and according to these finds it can be said that a very rich culture was present in Gedikli. This period is characterized by an orange red ware (43). In addition to this special pottery called Buttle Orange ware, metallic objects and especially pins were discovered among the finds.

The analyzed objects belong to the Cremation burials dated to the end of Early Bronze Age and the beginning of Middle Bronze Age. Cremation was prevalent in the Gedikli Tombs and burnt areas were very important and were separated with a stone division in the cemetary.Corpses were burnt in a special place in a tomb. (43) Without waiting to the end of this procedure the fire was extinguished with a special liquid. The bones remaining behind were, wrapped into a cloth and this cloth was held together by different kinds of pins (kefen iğnesi) and then they were placed in pots. These pots were buried with the gifts given to the dead person.

106 samples are taken from the different types of objects found in the cremation burial site of Gedikli. Among these objects, which are mainly

pins, are also different kinds of gifts given to the dead person, such as awls, rings, bracelets, and axes. The trace element analysis of these samples were made to find the composition of these objects. and to trace the possible ore sources, from which these objects are made and also to estimate possible date. In addition to this such analysis will give light about the technique of manufacture, the commercial relationship, the culture and metallurgical skill of Gedikli site.

III. MATERIALS AND METHOD

3.1. Material

3.1.1. Context

GEDİKLİ, 1964 Season. Cremation Burials

3.1.2. Chemicals

Chemicals used in this experiment were obtained from: Fisher and Merch

3.2. Method

Atomic Absorption Spectrometry and carbon rode atomisation are used for the determination of trace elements. Ten to twenty mg. of copper alloy drillings are weighed to an accuracy of ±0.02 mg. and transfered to a 25 ml. pyrex beaker. In a fume cupboard one ml. (±0.1 ml.) of aqua regia is added and the beaker is placed on a hot plate (60°C) until solution is complete (There is no need to boil the solution and to prevent loss of tin, prolonged heating is inadvisable). The beaker is removed, allowed to cool and an additional one ml. aqua regia and ten ml. distilled water are added. The solution is quantitatively transfered to 25 ml. volumetric flask and is diluted to volume with distilled water. It is mixed and transfered to a screw-cap polythene bottle. (9)

CHAPTER III

MATERIALS AND METHOD

Before the analysis of the samples, a series of concentrated standart solutions containing 1000 ppm of each element to be measured are prepared. The standart solutions are diluted with water to prepare the desired concentratio Dilute standarts are made up relatively frequently. Four standarts for each element was usually sufficient, the samples are kept within their range, i.e. the calibration graphs were not extrapolated. Conditions and AA parameters for the analysis of all trace elements used in this study are illustrated in Table 3.1.

Once the concentration of the element has been determined on a sample solution, in terms of ppm. of the element in solution, the weight percentage in the object itself is calculated as fallows (9).

$$\text{weight \% in the original alloy} = \frac{CV}{W}$$

where C = concentration of element in solution (in ppm)

W = weight of sample (in mg)

V = volume of original solution (in mls)

The calibration curve is prepared by using the least square method and concentrations of the samples are obtained from the calculator. Results are also compared with a reference sample with known trace element distribution and concentration. Two samples from the reference are taken for each set of elemental analysis.

TABLE 3.1. Instrument Parameters in the Analysis of Copper Alloys

		Lamp Current	Fuel	Support	Flame Stochiometry	Wavelength	Spectral Band Pass (slit)	Working Range ($\mu g/ml$)	Dilution (ml)
AAS Method	Cu	4 m.A	acetylene	air	oxidizing	324.7	0.2	1-8	2500
	Ag	3 m.A	"	"	"	328.1	0.2	1-5	25
	Fe	5 m.A	"	"	"	248.3	0.2	2-8	25
	Ni	5 m.A	"	"	"	232.0	0.2	1-8	25
	Pb	6 m.A	"	"	"	217.0	1.0	5-20	25
	Sb	10 m.A	"	"	"	217.5	0.2	1-4	25
	Sn	8 m.A	"	"	reducing	286.3	0.2	20-80	25
	Zn	5 m.A	"	"	oxidizing	213.9	0.2	0.1-1	2500
	Co	5 m.A	"	"	"	240.7	0.1	2-8	25

		Lamp Current	Wavelength	Spectral Band Pass (slit)	Working Range (mg/ml)	Dry	Ash	Atom	Dilution
CRA	As	6 m.A	193.7	0.5	0.025-0.2	$110^{o}/22$	900/15	2100/2.1/300	25 625

CHAPTER IV

RESULTS AND EVALUATION

IV. RESULTS AND EVALUATION

Among the 106 samples taken from the Cremation Burial sight of Gedikli Hoard diverse objects are seen. They can be classified according to their types as: pins, awls, rings, bracelets, iron samples, a silver ring and others. The pins are classified according to their shape as: headed pins with hole, headed pins, spiral headed pins and umbrella headed pins. These are listed in Table 4.1.

Also various shapes of each type of artifacts are illustrated in Fig. 4.1. - Fig. 4.8.

Samples are tried to be taken from the uncorroded side of metallic artifacts, but sometimes it was not possible. Since the objects were very small and thin, only single sample is obtained by drilling from each object due to possibility of breakage. It is known that the best way of sampling is to take two or more samples by the drilling method from different parts of a single object and then mix these to make a composite sample. Some of the pins and awls being very delicate and thin broke down during drilling. Generally drilling bids of 1.0 mm or smaller are used. Thus only a single sample was taken from each artifact at the most convenient place. Dots on the objects in Fig. 4.1. - Fig. 4.8. indicate places where samples are taken.

4.1. RESULTS

Copper, tin, arsenic, lead, zinc, antimony, nickel, cobalt, silver an iron content of the samples are determined by the methods described in section 3.2. As can be seen from Table 4.1. 95 of the 106 samples are copper and copper alloys. The number of samples of the other types were not large

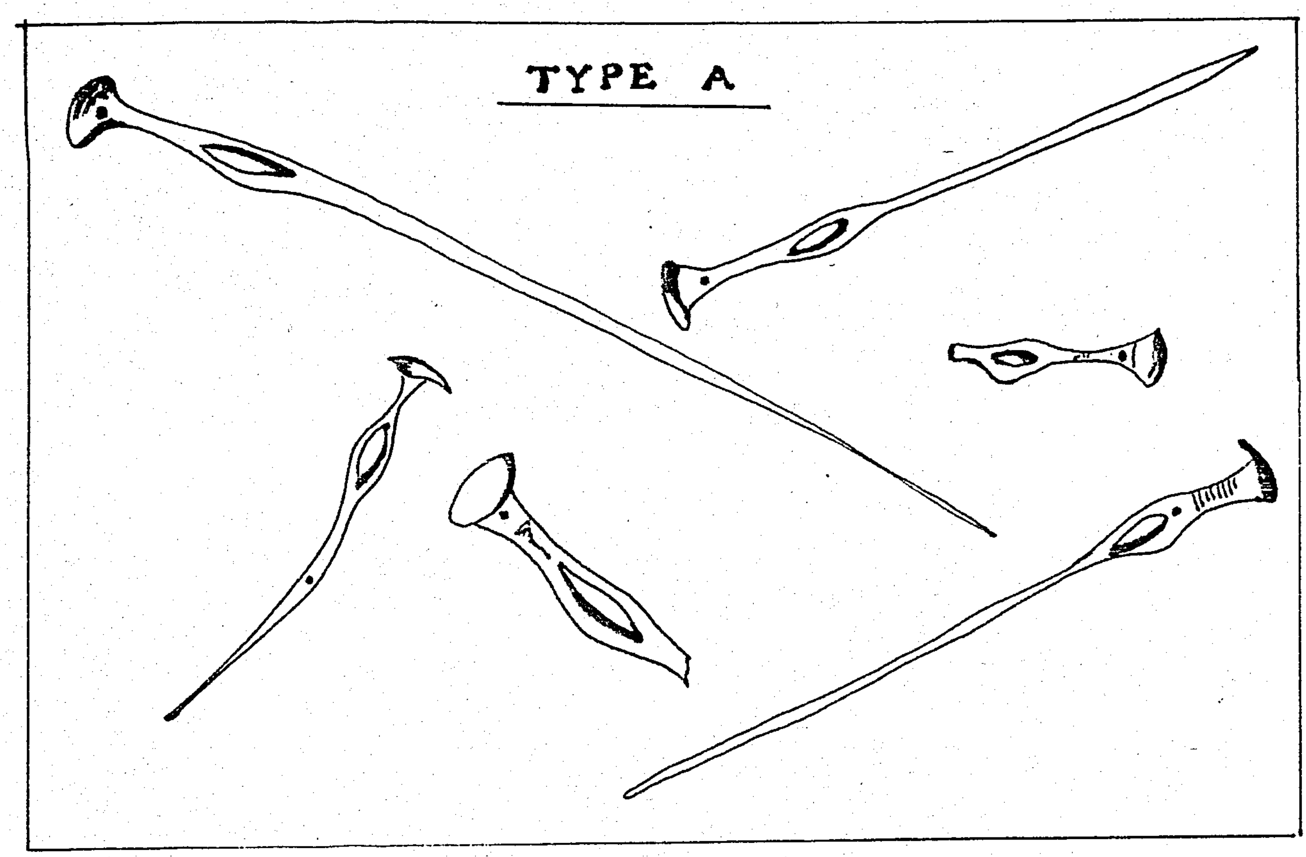


Fig. 4.1 Shapes of Type A (Headed pins with hole) samples

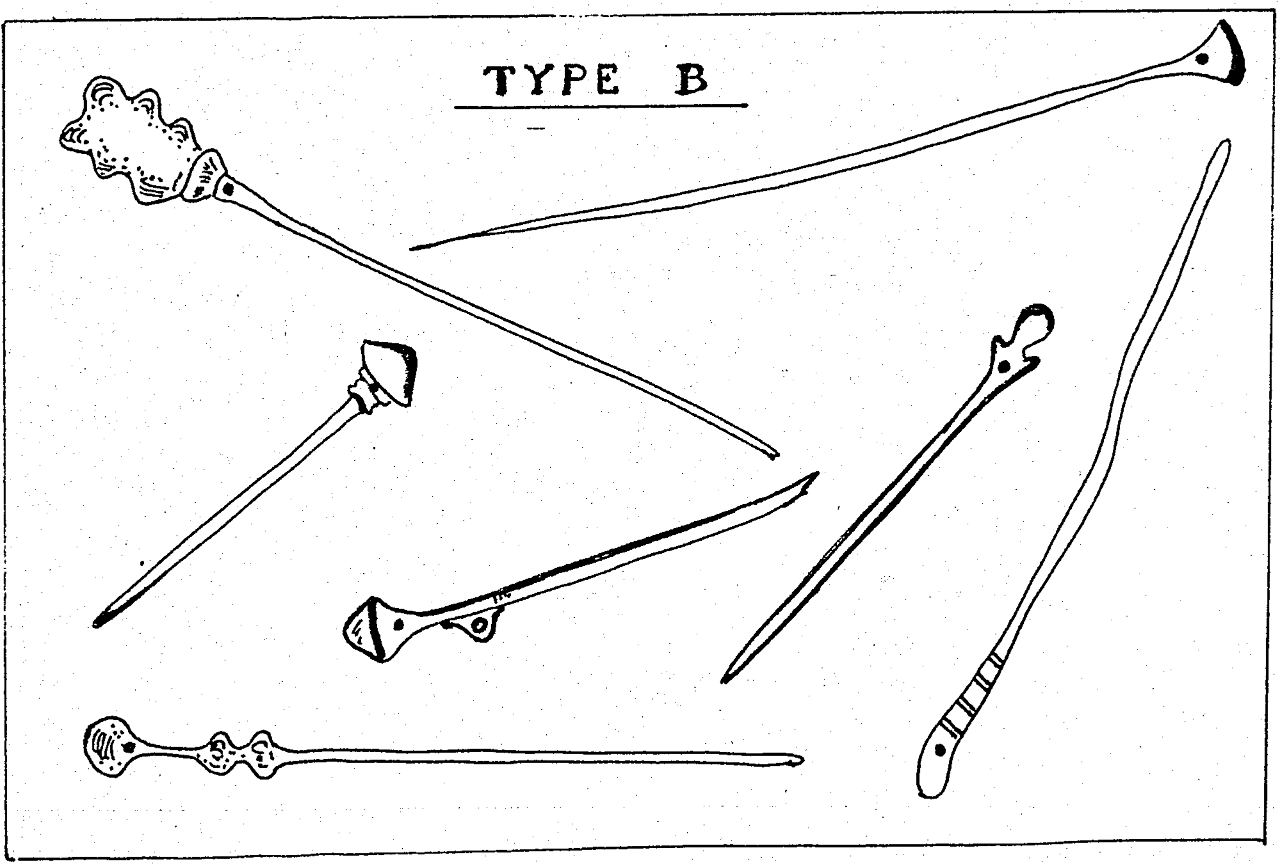


Fig. 4.2 Shapes of Type B (headed pins) samples

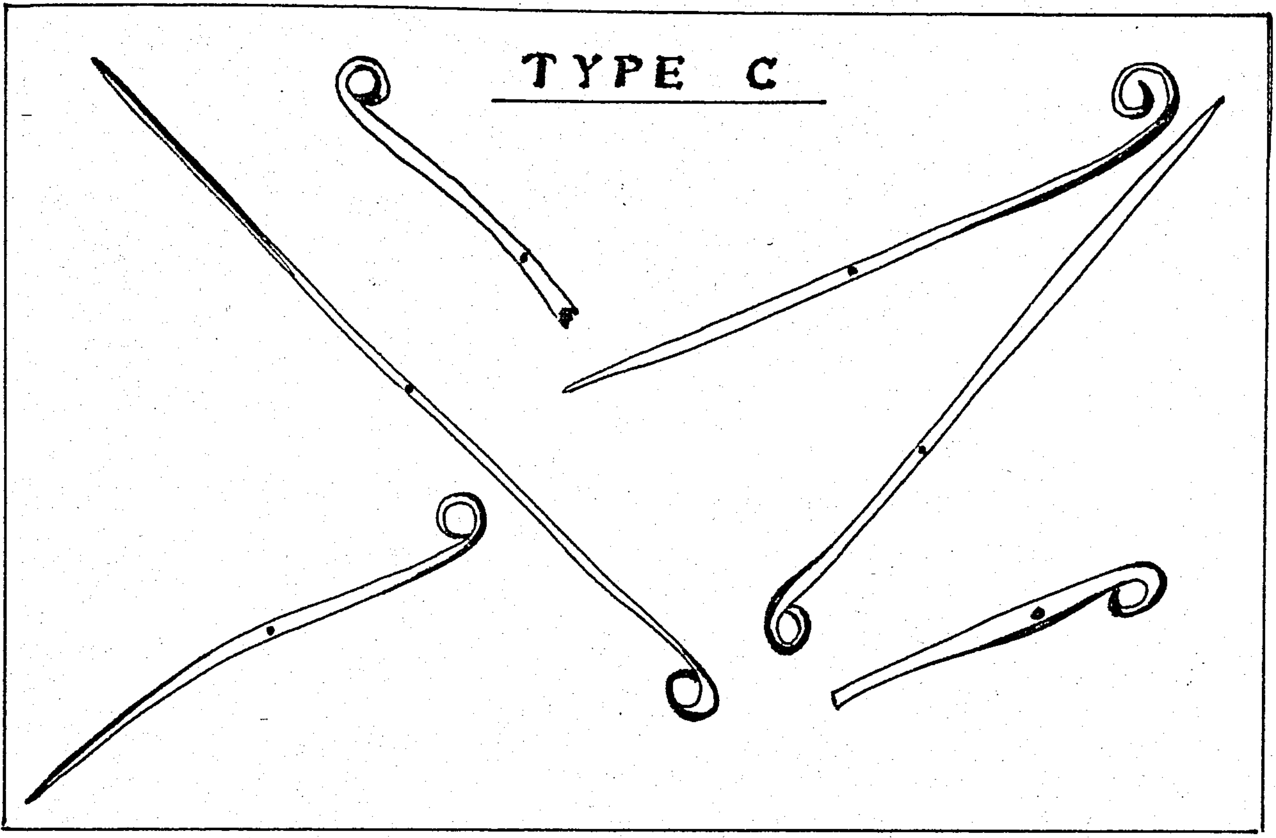


Fig. 4.3 Shapes of Type C (Spiral headed pins) samples

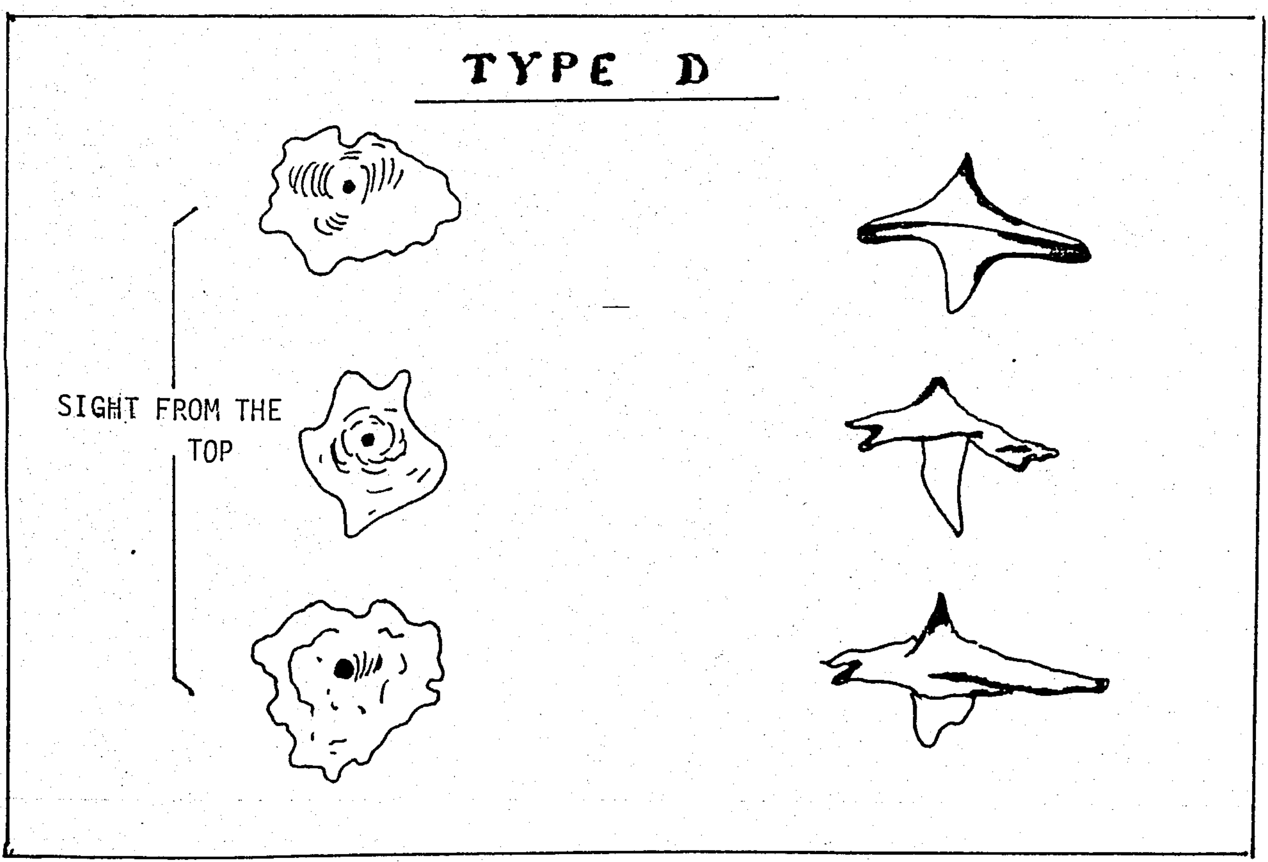


Fig. 4.4 Shapes of Type D (Umbrella headed pins) samples

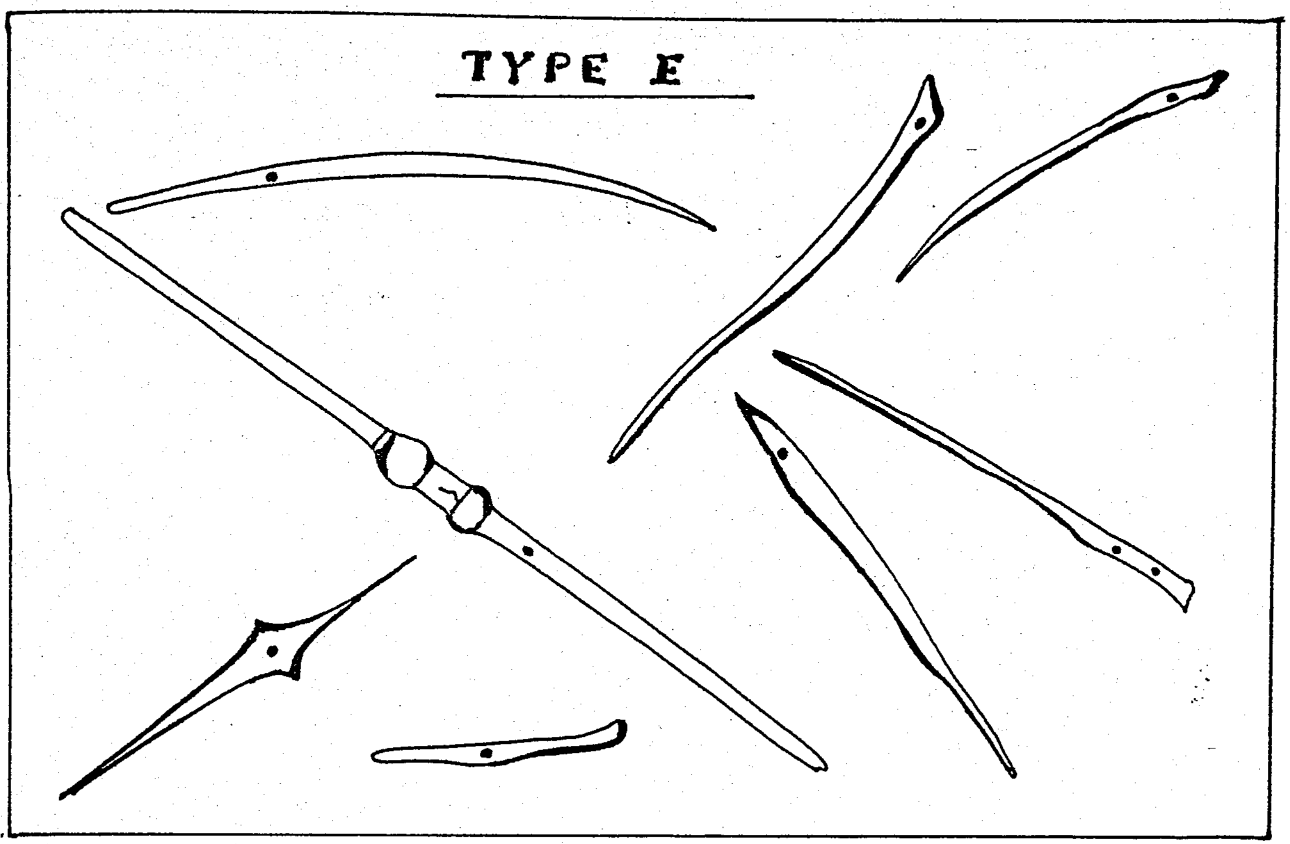


Fig. 4.5 Shapes of Type E (Awls) samples

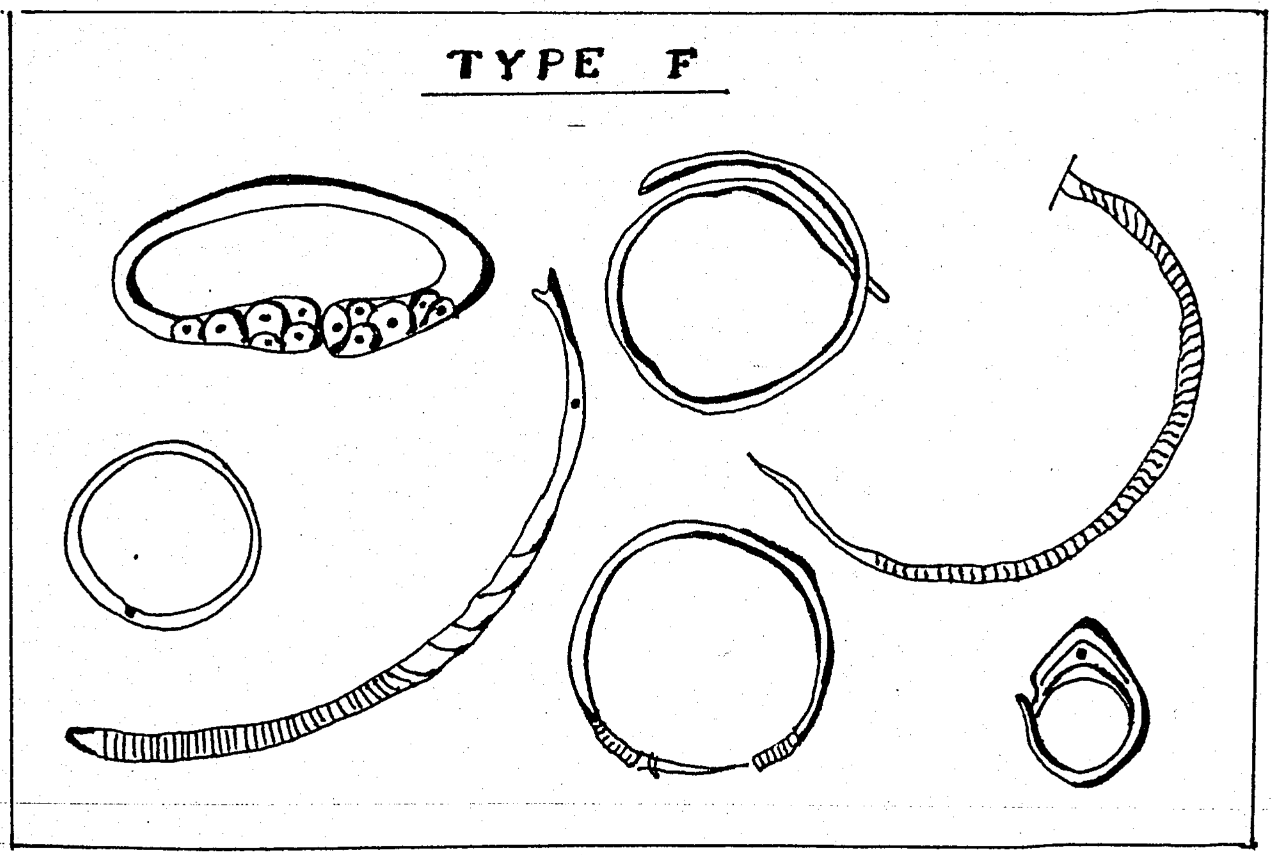


Fig. 4.6 Shapes of Type F (Rings and bracelets) samples

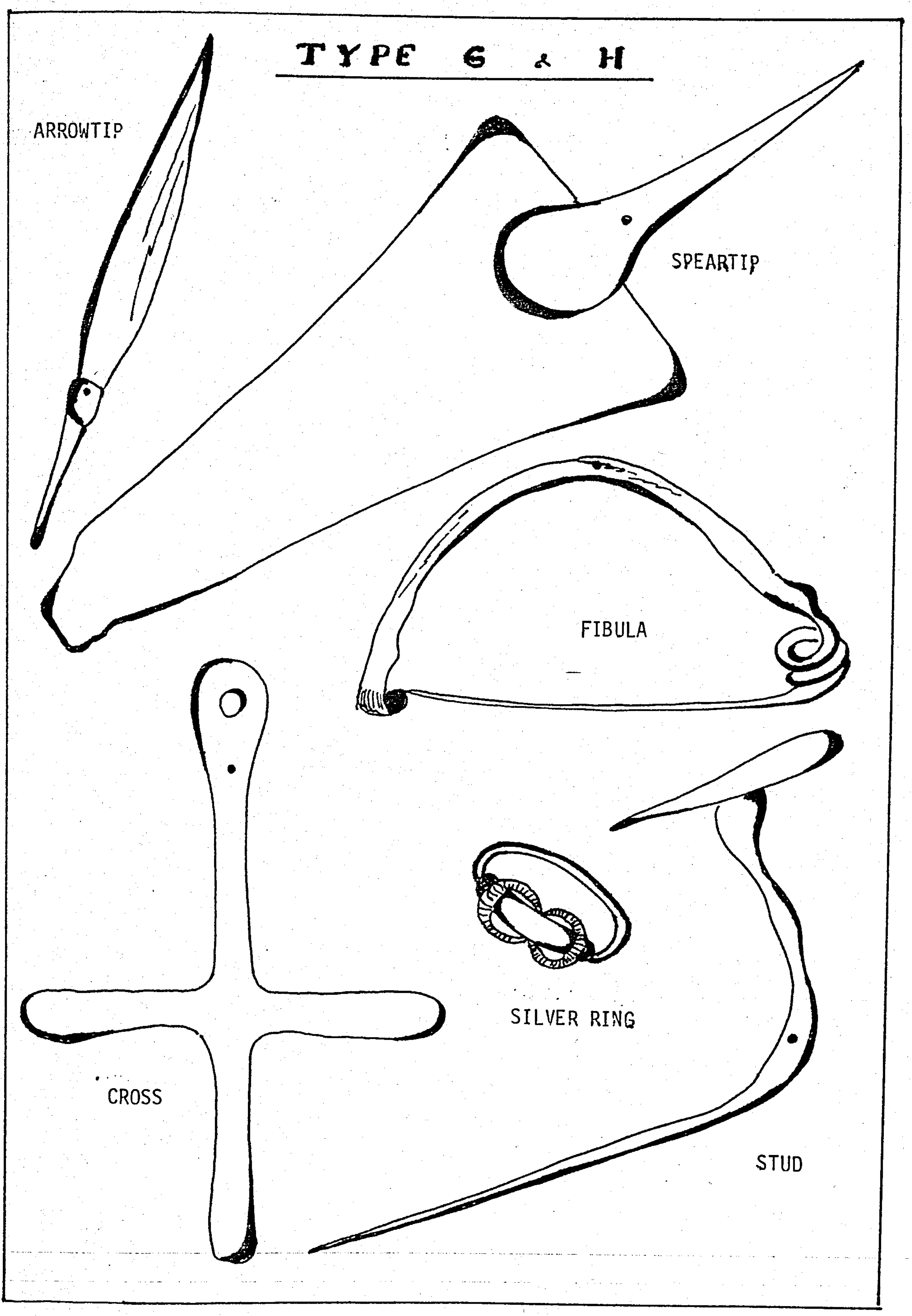


Fig. 4.7 Shapes of Type G and H (Iron samples and a silver ring) samples

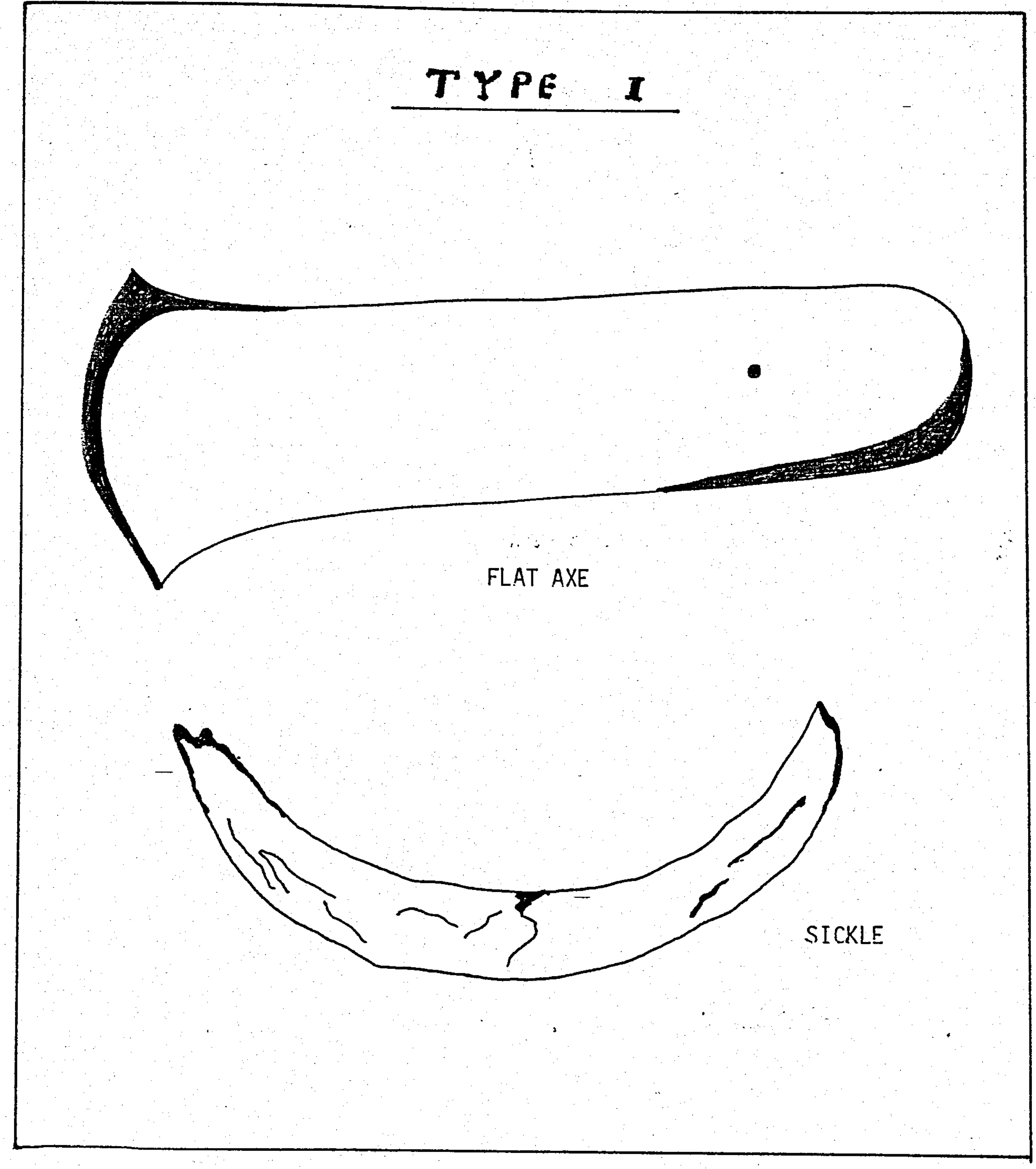


Fig. 4.8 Shapes of Type I (others) samples

enough to make any stasitical evaluation. Results of the trace element distribution of all samples are given in Table 4.2. - Table 4.9,, and the statistics are illustrated in Table 4.10.

TABLE 4.1. Classification of Samples According to Their Types

Type of Sample		Number
I. Pins		
Headed pins with hole	Type A	35
Headed pins	Type B	18
Spiral Headed pins	Type C	10
Umbrella Headed pins	Type D	5
II. Awls	Type E	14
III. Rings an Bracelets	Type F	11
IV. Iron Samples	Type G	10
V. A silver ring	Type H	1
VI. Others	Type I	2
TOTAL		106

TABLE 4.2. Trace Element Distribution of Type A Samples (%)

Sample No	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
G/541	68.3	0.92	-	0.94	-	-	0.41	-	0.29
G/537	93.1	-	-	1.03	0.16	0.08	0.12	-	0.76
G/882	65.2	7.99	0.43	0.69	-	0.02	-	-	0.2
G/701	73.4	2.32	-	1.86	0.43	-	0.29	6.37	0.74
Ga-K/211	77.9	0.67	0.06	0.9	0.34	0.02	0.05	-	1.24
G/891	86.2	-	-	0.54	0.07	0.04	0.02	-	0.46
G/588	67.5	4.69	-	0.68	0.02	0.07	-	-	0.25
G/201	83.6	0.35	-	1.07	0.13	0.09	0.24	-	0.86
G/310	84.7	-	-	1.02	0.2	0.16	0.06	-	1.03
G/183	90.9	-	1.15	0.54	-	-	-	0.72	0.35
G/189	89.1	-	-	1.14	0.08	0.01	-	-	0.63
G/620	89.9	-	-	0.89	-	0.02	0.2	-	0.94
G/190	83.8	-	-	1.05	-	0.01	0.21	-	0.11
G/371	87.2	0.11	-	0.91	0.1	0.19	0.03	-	0.8
G/93	82.5	0.05	0.49	0.91	0.11	0.09	-	-	0.26
G/245	77.4	8.4	0.88	0.77	-	0.04	-	0.34	0.29
G/828	82.9	5.32	1.75	0.74	-	0.18	0.75	-	0.34
G/891	84.9	0.3	-	0.7	0.09	0.07	0.04	-	0.42
G/193	89.2	-	0.03	0.87	0.09	0.04	0.51	-	0.2
G/913	90.1	0.14	-	1.31	0.07	0.06	0.25	-	0.43
G/206	81.3	-	-	0.65	0.09	0.08	0.01	-	0.32
G/627	75.7	6.93	0.11	0.74	0.08	0.05	0.13	2.3	0.18
G/622	81.6	8.41	2.39	0.75	-	0.03	0.41	-	0.18
G/192	78.8	11	-	0.6	-	-	0.23	-	0.21
G/925	77.3	8.41	0.23	0.1	-	-	0.05	-	0.38
G/194	82.3	-	0.52	0.81	-	0.01	-	-	0.47
G/250	41.6	2.24	-	1.21	-	0.04	0.4	1.9	0.26
G-K/195	61.7	0.91	-	0.6	0.45	0.01	-	-	0.42
G/893	80.7	8.19	0.6	0.38	-	0.02	0.36	-	0.15
G/887	76.9	7.34	0.14	0.6	0.07	0.04	0.01	-	0.33
G/187	75.9	-	0.04	0.52	0.02	0.04	-	-	0.56
G/623	87.5	-	0.98	0.76	0.07	0.07	-	0.86	0.54
G/222	83.6	1.3	-	0.8	0.12	0.01	0.06	1.49	1.21
G/532	86.3	-	-	0.7	0.6	0.06	-	0.78	0.54
G/224	86.9	0.13	-	0.5	0.34	0.07	-	-	0.97

TABLE 4.3. Trace Element Distribution of Type B Samples (%)

Sample No	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
G/393	89.4	0.05	-	0.61	0.05	0.16	-	-	0.53
G/520	85.1	0.24	-	0.51	0.02	0.09	2.09	-	0.15
G/922	91.8	-	-	0.73	-	0.59	-	-	0.62
G/699	84	0.05	-	0.82	0.51	0.17	0.01	0.5	1.57
G/609	88	0.24	-	0.4	0.19	0.12	0.02	-	0.46
G/921	86.1	-	-	0.89	0.49	0.09	1.27	-	0.29
G/920	93.5	-	-	0.61	-	0.01	0.15	0.08	0.18
GK/148	91.4	-	0.74	0.56	-	0.19	-	-	0.42
G/549	82.3	1.06	-	0.7	0.92	0.05	-	1.4	0.35
G/699	78.9	-	-	0.61	0.09	0.03	0.22	1.6	0.19
G/492	82.7	2.18	0.07	0.4	0.22	0.02	0.03	1.66	0.35
G/883	72.1	0.69	-	0.9	0.09	-	0.08	0.12	0.24
G/403	84.1	-	-	1.16	0.14	-	0.22	1.43	1.11
G/216	83	0.75	-	0.9	0.24	0.03	0.04	1.02	0.27
G/217	84.9	-	-	1.29	0.09	0.05	0.04	1.65	0.7
G/215	82.3	0.95	0.58	1.53	0.05	0.02	2.34	-	0.42
G/885	89.2	-	-	0.8	0.03	0.04	0.09	-	0.74
G/241	86.6	-	-	0.57	0.22	0.08	0.14	-	0.44

TABLE 4.4. Trace Element Distribution of Type C Samples (%)

Sample No	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
G/215	75.4	8.58	0.05	0.16	0.08	0.29	0.22	-	0.24
G/372	80.9	0.89	-	0.73	0.12	0.01	0.05	-	0.6
G/231	85.1	1.89	0.27	0.64	0.04	0.06	0.08	1.23	0.23
G/818	82.3	3.69	0.28	1.95	0.05	0.03	0.17	1.26	0.15
G/668	95.6	-	-	0.04	0.08	0.01	-	1.58	0.56
G/880	82.5	-	-	0.63	0.11	0.13	0.11	1.54	0.71
G/539	82.4	0.74	-	0.83	0.1	0.04	0.45	1.34	0.61
G/378	86.1	1.43	-	0.78	0.1	0.03	0.04	1.2	0.3
G/240	81.4	8.76	0.34	0.48	0.16	0.01	0.33	1.19	0.23
G/234	81.9	-	-	0.72	0.14	0.004	0.08	1.6	0.75

TABLE 4.5. Trace Element Distribution of Type D Samples (%)

Sample No	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
GC-K/933	81.3	7.11	--	4.78	-	0.03	0.44	-	0.23
GC-K/934	67.6	9.92	-	0.33	-	0.01	0.05	-	0.11
GC-K/935	85.8	5.15	0.17	1.36	-	0.06	0.29	1.87	0.15
G/22	80.9	7.21	0.13	0.63	-	0.02	0.24	-	0.73
Ga-K/235	81.1	5.31	0.06	2.04	-	0.07	0.13	0.44	0.15

TABLE 4.6. Trace Element Distribution of Type E Sample (%)

Sample No	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
GK/179	70.9	-	6.72	0.09	0.1	0.04	0.02	27.4	0.45
GC-K/927	95.6	-	-	0.09	-	0.001	-	-	0.48
G/917	87.7	-	-	0.55	0.1	0.01	0.2	1.21	0.66
G/919	87.6	-	0.81	1.36	0.12	0.16	-	-	0.11
Ga-K/402	88.9	1.52	-	1.5	-	0.02	-	-	0.62
GC-K/937	89.7	-	-	0.17	-	0.005	1.17	-	0.21
GC-K/926	90.3	-	-	-	-	-	-	0.25	-
Gb-K/714	91.5	-	-	4.85	-	0.04	-	-	0.66
Gb-K/556	91.2	0.65	-	0.24	0.22	0.23	0.01	-	0.05
GK/47	78.8	7.38	0.31	0.62	-	0.05	0.14	-	0.23
Gb-K/530	86.5	-	-	0.62	0.74	0.07	-	-	0.64
Ga-K/311	88.6	0.91	0.18	0.99	0.33	0.29	0.15	1.83	0.3
Ga-K/368	88.6	-	-	0.25	-	0.02	0.3	1.62	0.63
Gb-K/533	85.8	1.24	0.17	1.3	-	0.03	-	-	1.5

TABLE 4.7. Trace Element Distribution of Type F Samples (%)

Sample No	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
GK/17	72.9	-	-	0.08	0.15	0.09	-	19.3	0.71
Gb-K/709	85.8	1.44	0.54	0.32	0.09	0.09	0.33	-	0.41
Ga-K/315	95.1	10.6	-	0.1	-	0.02	0.29	-	0.24
G-24	86.9	-	-	0.19	0.07	0.05	-	-	0.53
Ga-K/357	88.7	-	-	0.5	0.35	0.1	-	-	0.14
Ga-K/373	84.9	1.76	0.02	0.75	-	0.12	0.1	1.64	0.32
GK/56	75	0.26	15.5	0.25	0.19	0.16	-	11.5	0.87
Gb-K/542	93.4	5.53	0.14	6.21	-	0.08	0.33	-	0.43
Gc-K/930	115.1	-	-	0.23	-	0.01	-	-	0.11
G-8	94.8	0.39	-	0.16	0.19	0.08	0.23	-	0.1
G-K/178	72.7	2.9	9.04	-	0.24	0.08	-	2.07	0.34

TABLE 4.8. Trace Element Distribution of Type G and F Samples (%)

Sample No	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
Ga-K/405	-	-	-	-	0.11	0.34	-	-	98.7
Ga-K/406	-	-	-	0.004	0.07	-	-	0.24	87.9
Ga-K/404	-	-	-	0.007	0.04	-	-	0.27	73.9
Gc-K/36	-	-	-	-	0.05	-	0.2	-	102
G-K/179	-	-	-	0.002	-	-	-	-	117
G-9	-	-	-	0.006	0.07	0.004	-	-	85.9
GK/24	-	0.62	-	0.06	-	0.35	-	-	77.7
G-K/29	-	0.42	-	-	-	-	-	-	81.05
GK/23	-	-	-	0.06	-	-	-	0.68	60.91
Gb-K/654	-	-	-	0.05	-	-	-	-	103
Gc-K/932	32.2	4.77	0.73	0.2	-	8.19	-	0.76	0.2

TABLE 4.9. Trace Element Analysis of Type I Samples (%)

Sample No	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
GC-K/939	89.9	-	-	0.09	-	12.6	0.12	1.46	0.05
GC-K/940	88.6	-	-	4.4	0.07	0.006	1.34	-	0.04

TABLE 4.10. Statistical Findings for All Trace Elements

	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
# of samples	95	55	35	93	61	87	65	37	94
% sample	100	58	37	96	67	91	68	39	98
mean	83.6	3.43	1.31	1.49	0.18	0.07	0.28	2.86	0.
st. deviation	8.81	3.44	3.08	4.29	0.18	0.08	0.42	5.42	0.

In the analyzed samples, no Cobalt has been detected. This is unique because, cobalt has been reported to be a characteristic trace element of Anatolian copper artifacts (19). Tin was observed in about half of the samples with an average of 3.43 percent. This is too high to be an impurity, yet too low to be considered as a tin bronze. Many of the samples had tin content less than one percent which may come as an impurity rather than intentionally prepared alloys. As will be noted in Fig. 4.9., tin content in copper increases gradually in Anatolian culture and reaches to about ten percent by the end of Bronze Age. The answers to this question, however, can be found after a complete excavation at the site.

Almost all samples showed some amounts of arsenic, however mostly less than one percent (aver. 1.49 percent). This is a good indication that arsenic is introduced into copper mainly, during the smelting of arsenic containing copper ores. Large standart deviation ($\sigma = 4.29$) also indicates that it is difficult to maintain arsenic concentration constant at some desired level.

Lead is found in 37 percent of the samples, generally at low concentrations. Except in few samples, lead is also an inpurity, and may indicate a particular ore source. Similarly 39 percent of the samples contained zinc (an average of 2.86 percent) however, variation of zinc content was quite large ($\sigma = 5.42$) zinc and lead are generally associated in nature and 15 samples contain both of these elements. On the other hand, 38 samples had both no zinc and lead. Analysis of the surrounding copper ores for trace elements may lead to possible source identification.

Silver is another element that was observed at high percentage, (Table 4.10). It is related to copper and has a tendency to accumulate in the molten copper during melting. All the ore sources therefore must contain some silver.

Antimony is also observed at low concentration (average of 0.18 percent) in 67 percent of the samples. Like silver and lead, it is related to copper and tends to accumulate in it.

Nickel is observed in 68 percent of the samples at rather low (average of 0.28 percent) concentrations. Since it is mainly introduced to copper during smelting from the flux, it cannot be used as a source indicating element.

Finally iron is observed in almost all samples at trace amounts. It is introduced into copper from flux and can be easily removed in purification methods with the slag. Lower iron contents, indicate better purification and refining technology. Small amount of iron percent in Gedikli samples reflect an advanced metal technology.

The use of copper and copper alloys in Anatolia has a long history. The development in metal technology can be assigned to specific ages. Analysis of large number of metal artifacts carried out in Anatolia (45) shows that older samples were arsenical copper and later tin replaced arsenic as an alloying element Fig. 4.9.

Arsenic is generally observed in copper artifacts at concentrations of about one percent or lower. This is certainly not an intentionally prepared alloy but a result of impurities left from smelting, arsenic containing copper ores. However, the arsenic content of artifacts found during the Early Bronze Age II, reaches upto about five percent. At this time it is difficult to specify if metallic arsenic is added to refined copper or

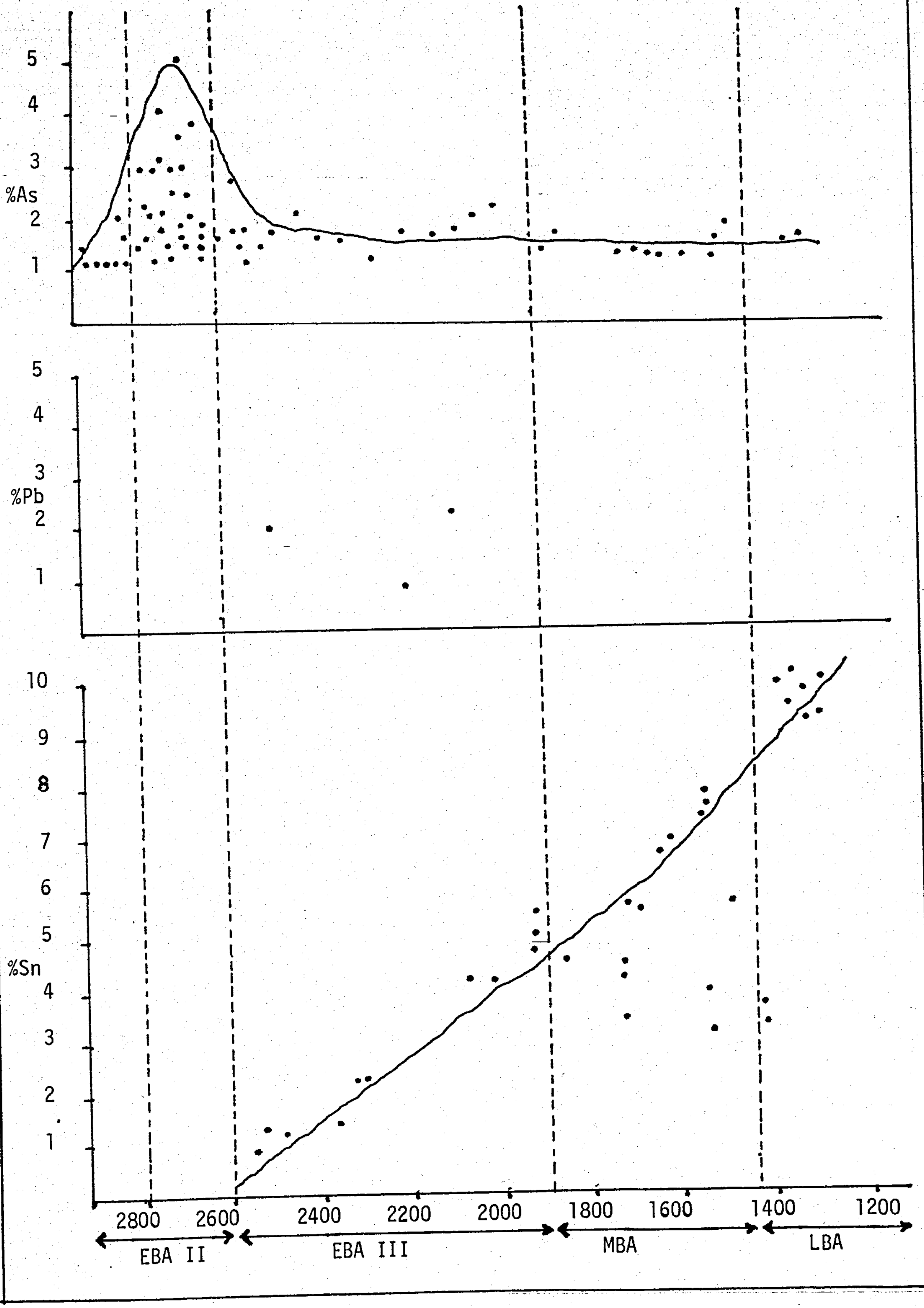


Fig. 4.9 Distribution of arsenic and tin in Anatolia during Bronze Age Period

arsenic and copper ores were smelted together, however, latter seems to be more probable.

Since tin is believed to be lacking in Anatolia, development of arsenical copper technology is quite understandable (29). However, by early bronze age III and middle bronze age, the first examples of tin bronzes are also seen in Anatolia. Origin of tin in these artifacts are still quite debatable. However, it should be emphasized that the metal technology in Anatolia was very advanced. By late bronze age, tin content of bronzes has reached around ten percent in many cases, with still traces of arsenic present.

At times, copper artifacts with high concentration of lead and zinc are also observed. However, the number of such objects are small to make satisfactory historical pattern.

Within this broad perception of the historical development of metal technology in Anatolia one may attempt to place Gedikli Hoard to its historical niche.

4.2. Histograms

The main purpose of this section is to find the distribution of the trace elements determined in the metallic objects, obtained from Gedikli. Thus histograms of the five major trace elements mainly As, Sn, Pb, Zn, and Sb are prepared for all copper samples. Fig. 4.10 - Fig. 4.14.

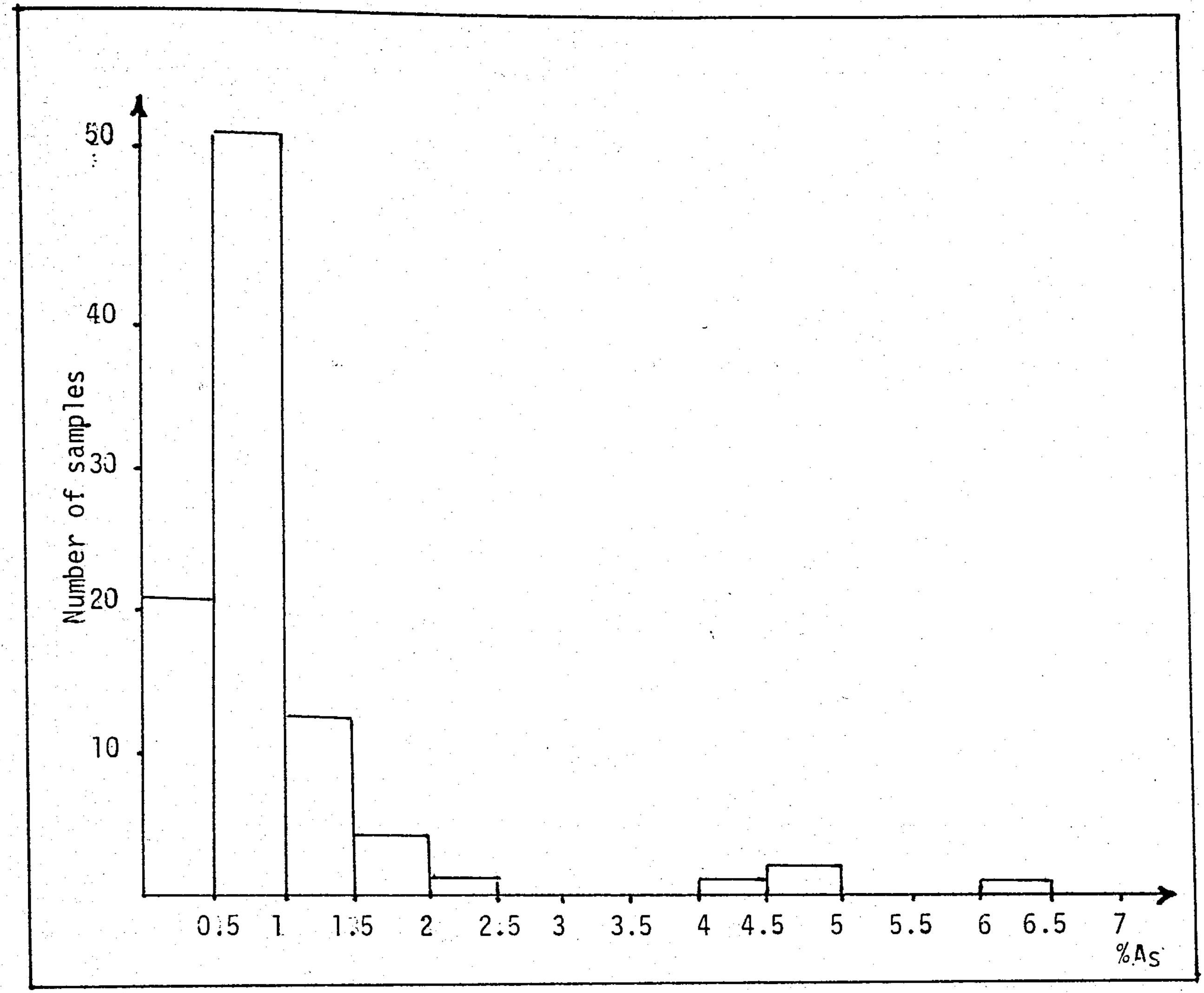


Fig. 4.10 Histogram of arsenic distribution in all samples

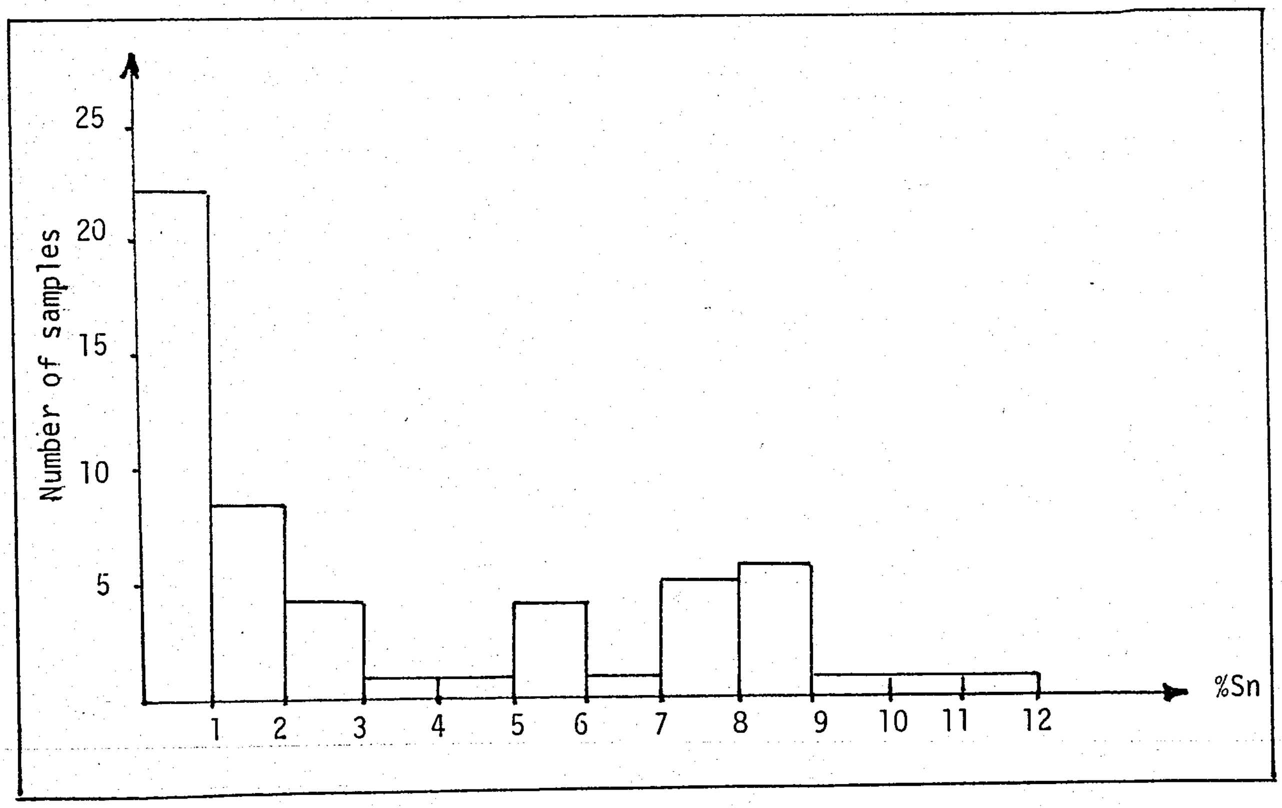


Fig. 4.11 Histogram of tin distribution in all samples

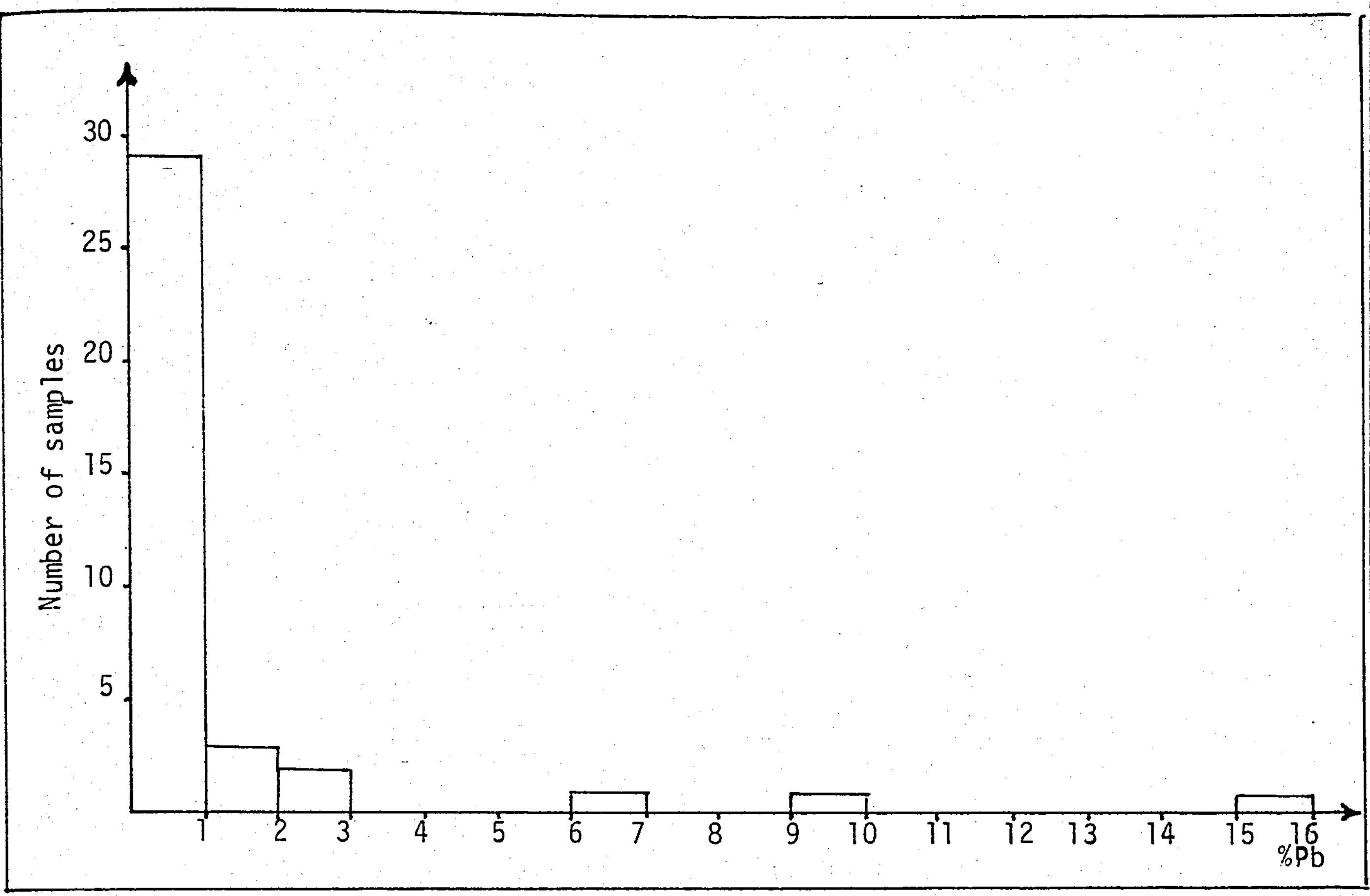


Fig. 4.12 Histogram of Lead Distribution in all Samples

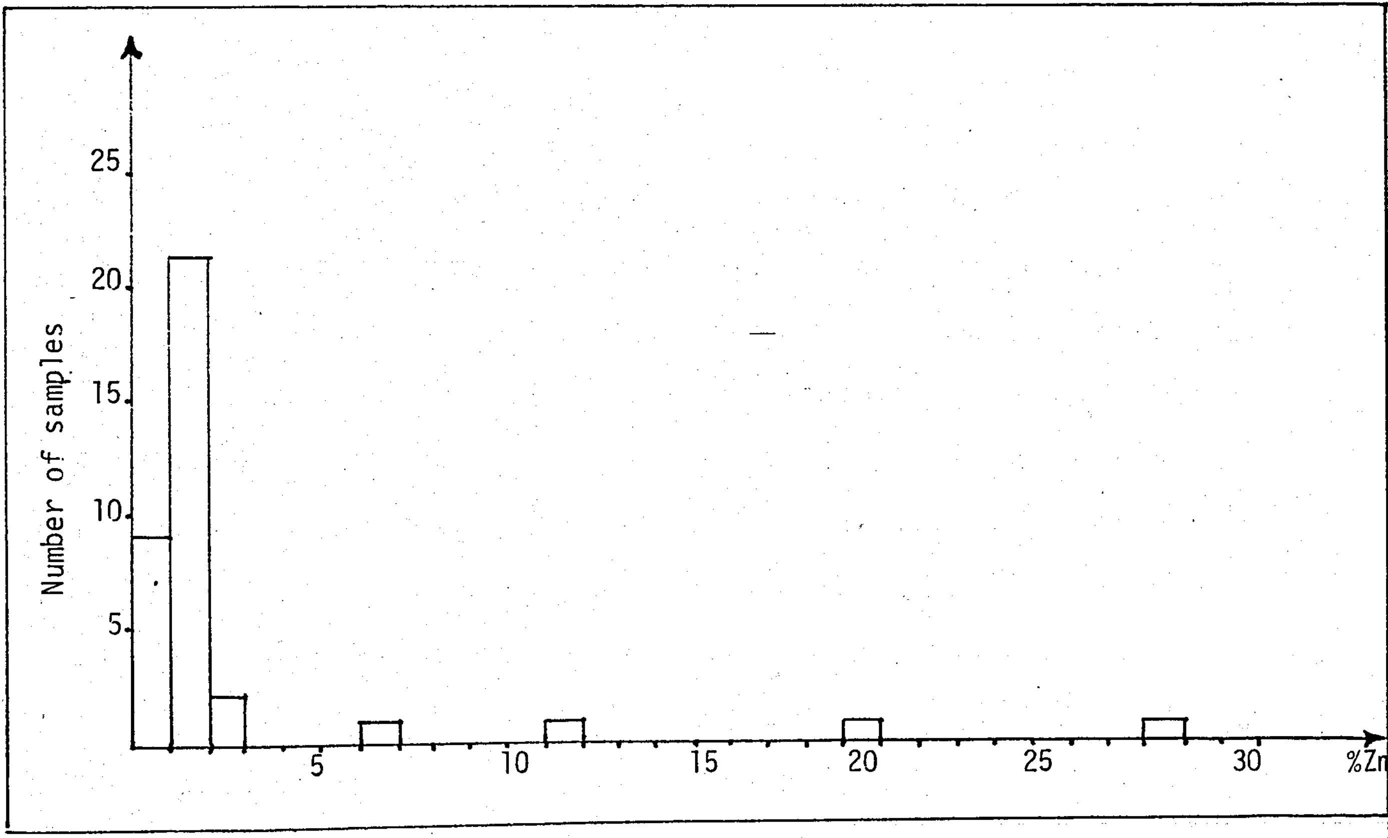


Fig. 4.13 Histogram of Zinc Distribution in all Samples

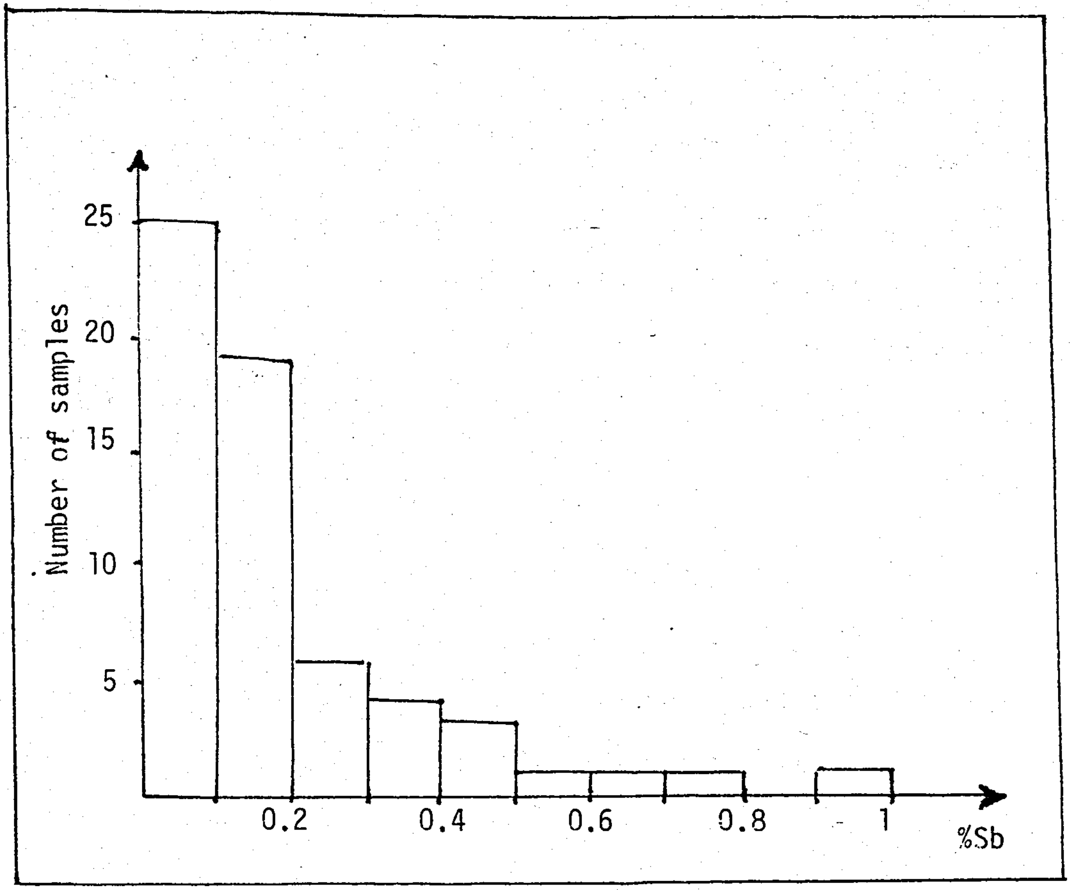


Fig. 4.14 : Histogram of Antimony Distribution in All Samples

4.2.1. Arsenic

Of all the copper artifacts, 93 (96 percent) contained arsenic (Fig. 4.10) however, majority of the samples (78 percent) had arsenic less than one percent. The origin of the arsenic observed at such concentration must be coming from the arsenic content of the copper ore. Only four samples, an umbrella headed pin, an awl, a bracelet and a sickle had over four percent arsenic. Since addition of about five percent arsenic improves the strength and casting properties of copper the awl in Type E (Gb-K/714) and the sickle in Type I (GC-K/940) are samples which are expected to have high As content. Umbrella headed pin in Type D samples (GC-K/933) not only contains 4.78 percent arsenic, but 7.11 percent tin. In fact all pins of this type have over five percent tin content. It is difficult to estimate if these samples are manufactured by casting or by hammering. Due to their unique design, the umbrella headed pins may be manufactured by casting in which case it is expected to be an alloy of copper. The bracelet, Gb-K/542 containing 6.21 percent As also contains 5.53 percent tin. It is unique from other rings and bracelets.

4.2.2. Tin

Fifty five (58 percent) of the samples contained tin, from trace amounts to as high as over 11 percent. Majority of the samples (30 in Table 4.11.) has Sn less than two percent, 19 samples, however, have Sn content over five percent indicating specially prepared bronzes. Except all the umbrella headed pins (six samples) tin bronzes are randomly distributed among other types of objects. As discussed in section 4.2.1., all umbrella headed pins contain high percentage of tin. It is difficult to rationalize the distribution of tin bronzes among other samples, because as discussed in section 4.1. tin is believed to be lacking in Anatolia. Then samples may belong to a slightly different time scale, for example, objects with higher percent of tin are the ones which belong to the later transition period (Fig. 4.9), or perhaps a special alloy mixture may be used by a certain metal smith. Likewise, samples may be obtained from other cultures through trade. For these reasons it is difficult to rationalize the distribution of tin among these samples.

4.2.3. Lead

Of all the copper artifacts, 35 (37 percent) contained lead. Majority of the samples (31 on Fig. 4.12) had lead less than two percent, three samples however have lead content over six percent, indicating an intentionally addition to reduce brittleness and for better casting properties. The samples with high lead content are two bracelets and an awl. The owl GK/179 containing 6.72 percent Pb (Type E) and the bracelet GK/5^{6} with 15.5 percent Pb (Type F) have no or trace amount of Tin, however the bracelet G-K/178 in Type F, not only contains 9.04 percent Pb but also 2.9 percent Sn indicating that it may belong to a later period of the early bronze age.

4.2.4. Zinc

Thirty seven (39 percent) of the samples contained zinc. Majority (33 on Fig. 4.13) contains less than three percent of zinc, however in four examples zinc is found at a higher concentration (above six percent). It is known that the addition of ten (or more) percent of zinc improves the ductility of copper alloys, thus they can be worked with greater ease. A pin, an awl, a ring and a bracelet are found to contain high percent of zinc. Pin, G/701 in Type A has 6.37 percent of Zn, owl, GK/179 in Type E has 27.4 percent zinc, and ring, GK/56 in Type F has 11.5 percent of Zn. In these samples zinc may be added to improve ductility. But in the fourth sample which is from a decorated bracelet, GK/17 with 19.3 percent zinc content, zinc may be obviously intentionally added for working more easily on its decorations.

4.2.5. Antimony

61 (67 percent) samples have antimony, all are less than one percent (Fig. 4.14). Antimony generally occurs with copper and lead ores and is not used as an alloying element. It is somewhat volatile and its concentration in the refined copper depends on smelting and purification conditions. Its presence or absence could be more important for source identification rather than how much is present in an object. Gedikli Hoard contains objects with and without antimony indicating that there are different sources for them.

4.3. Linear Regression Analysis for All Copper Samples

It is assumed that if the ore source used in the manufacture of these objects are the same, the variations in the concentration of some of the trace elements should be due to variations during smelting operation. Since the smelting parameters during early smelting operation cannot be accurately controlled, wide distribution in the trace element concentration is expected. However, if the trace elements are correlated among each-other, it is possible to see some similar trends.

Linear regression analysis carried out between each pair of trace elements for all the samples determine the correlation coefficient for each pair. Accordingly, a correlation coefficient close to +1, indicates a direct relationship between the pair of particular elements, whereas correlation coefficient of -1 indicates an inverse relationship. Correlation coefficient around zero, however, indicates that the concentration of the two elements are not at all related. Such linear regression analysis are carried out among all the copper and copper alloy samples as well as according to particular types of objects and selected groups.

The correlation coefficients of the linear regression analysis on the trace element pairs of all copper and copper alloys are given in Table 4.11. In Table 4.11 pairs without any relationship are not included. The results show that when all the samples are considered together, of the possible 28 pairs, only 6 pairs have same relationship to a certain degree. A fairly good correlation is observed between Ni and zinc. Generally nickel is introduced into copper through flux since it is not associated with copper ores. Once introduced, it is a trace element, like zinc, it is difficult to eliminate. There are 25 objects which contained the two elements which may indicate possible ore source or manufacturing similarities.

Correlation coefficients of about 0.4-0.5 are observed between Zn and As, Ag and Sb , and Fe and Pb. Among these three pairs Ag and antimony together with lead are generally associated with each other in nature. However, among the samples it may not be statistically significant.

Since the correlation coefficients including all the samples did not yield any significant result, objects are devided into subgroups according to types, and according to the presence or absence, or high concentration of a certain element.

4.4. Linear Regression Analysis Between Subgroups

4.4.1. According to types

The total objects as seen in Fig. 4.1.-Fig. 4.8., are devided into subgroups according to shapes and intented use. Among the types classified as A to F, only type D samples, classified as umbrella headed pins were significant. (Table 4.5) Even though there are five objects of this type, similarities of trace element analysis are significant. As mentioned before,

TABLE 4.11 Correlation Coefficients of the Linear Regression Analysis of all Samples

Element Pair	Sample	Correlation Coefficient
As vs Fe (without Zn)	12	0.91
As vs Fe (All)	93	0.05
Ni vs Zn	25	0.51
Zn vs As	32	0.42
Ag vs Sb	60	0.49
Fe vs Pb	35	0.43

they are all tin bronzes with tin content between 5.15-9.52 percent. Like wise no antimony is observed for all of them. Lead was either absent or was present at trace amounts well below the average, observed for all the samples. Zinc in these samples were also either absent or well below the average. Just simple examination of Table 4.5 shows that all the samples are very closely related. They may belong to the same age, be manufactured by the same metal smith or the same ore source is used. Even though there were only five samples present in this group, linear regression analysis is carried out between Sn, As, Ag, Ni and Fe as pairs. Among the possibilities only two, between Sn vs Ag (corr. coef.= - 0.91) and As vs Ni (corr. coef. = 0.77) showed some correlations. There is an inverse relation between Sn and Ag, e.i. as tin content increases, the Ag content decreases. It is surprising to find such a relationship since Ag is associated with copper ore, and tin is introduced by itself as an alloying element, especially in these tin bronzes. Nickel and arsenic have direct correlations. However, in both cases due to overall number of samples, correlations may be statistically insignificant.

4.4.2. According to Presence or Absence of Certain Trace Element

a) 40 samples containing no Sn, showed three element pair with high correlation coefficient. (Table 4.12)

Pb and As are inversly related which is unexpected, because both elements have relatively high volatility. Thus if As decreases Pb should also decrease. There is also good direct relationship between Pb and Zn as we would expect. However among the samples without any tin, only three had both Pb and Zn and the result has no statistical significance. Relatively good relationship is seen between Antimony and Iron, in this group however, again since iron may be also introduced from the flux, the relationship may not be used for source identification.

b) 58 samples containing no zinc showed only relationship between Pb and Sb (corr. coef.=- 0.58). Even though there were only nine such samples, since Pb and Sb may be related as possible ore source, this group can be significant.

c) 25 samples containing Sn above two percent yielded several relationships which may be significant(Table 4.13)

Of the element pairs listed in Table 4.13, only three pairs had enough samples to have statistical significance. An inverse relationship between Sn and Fe is unique. Iron is an unwanted impurity in copper and as smelting and refining technology is improved, its concentration in copper decreased. Likewise tin content of copper objects generally increased as metallurgy advanced. In this case it is seen that as Sn content increases, Fe decreases, which colud be reflecting this metallurgical development. An important direct relationship is seen between Ag and Ni. These two elements have tendency to accumulate in copper in smelting operations. For this reason these two samples have high probability of being from the same ore source.

d) 23 samples contained Zn between 1.00 - 2.00 percent, and yielded several relationships (Table 4.14). There were only four pairs with relatively high correlation coefficients, however, since the number of samples were small, the results cannot be statistically significant.

e) There were five samples with Ni content over 1.0 percent. Since Ni is not associated with the copper ore and is introduced by the fluxing agent, these samples are expected to show some similarities. Since no statistically significant correlation can be made among five samples, general trace element distributions are considered (Table 4.15).

TABLE 4.12. Correlation Cofficients of the Linear Regression Analysis of Samples Containing no Tin.

Elements Pair	Sample	Correlation Coefficient
Pb vs As	8	-0.64
Pb vs Zn	3	0.99
Sb vs Fe	27	0.78

TABLE 4.13. Correlation Coefficients of the Linear Regression Analysis of Samples Containing Sn Above Two Percent

Elements Pair	Sample	Correlation Coefficient
Sn vs Sb	9	-0.54
Sn vs Fe	25	-0.53
Pb vs Sb	7	0.63
Pb vs Ni	16	0.57
Sb vs Ni	7	0.59
Sb vs Zn	6	0.84
Sb vs Fe	9	0.89
Ag vs Ni	19	0.96

TABLE 4.14. Correlation Coefficients of the Linear Regression Analysis of Samples Containing Zn between 1.00 - 2.00 percent

Element Pair	Sample	Correlation Coefficient
Zn vs Pb	7	-0.69
Sn vs Pb	8	0.59
Pb vs Ni	8	0.57
Pb vs Fe	8	-0.51

TABLE 4.15. Trace Element Distribution of Samples with Ni above 1.0 percent (%)

Sample No	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
G/520	85.1	0.24	-	0.51	0.02	0.09	2.10	-	0.15
G/921	86.1	-	-	0.89	0.49	0.09	1.27	-	0.29
G/215	82.3	0.95	0.58	1.58	0.05	0.02	2.34	-	0.42
G-K/221	89.7	-	-	0.17	-	0.01	1.69	-	0.21
GC-K/940	88.6	-	-	1.4	0.07	0.01	1.34	-	0.04

Strikingly none of the samples have zinc. Lead is non existent except in one. Tin is also quite low or non existent. Antimony is present in four and silver in all. Such similarities may be an evidence that these objects are made from the same ore source, using very similar smelting procedures.

f) There were eight samples with As content over 1.5 percent. Again linear regression analysis was insignificant, thus trace element distribution are considered. (Table 4.16)

These samples have also some trends. Except one sample, all have none or very little antimony. Most of them also have high tin content (between 0.95 - 7.11 percent). However, there were large variation in lead, nickel and zinc content. Since arsenic is such a volatile element, it is difficult to suggest particular trend in this group.

4.5. Cluster Analysis

The main purpose of this section is to find clusters containing groups of samples having similar composition. Therefore, such an analysis is made in order to find clusters coming from the same ore source, or clusters prepared by the same metalsmith or by similar smelting process conditions.

In this analysis, all the trace element percentages are plotted against each other in pairs. The object was to see if there were main clusters of data points. Most of the element pairs yielded a very random distribution. However, graphs of elements of tin versus nickel, of arsenic and lead yielded two major clusters Fig. 4.15, Fig. 4.16 and Fig. 4.17 respectively.

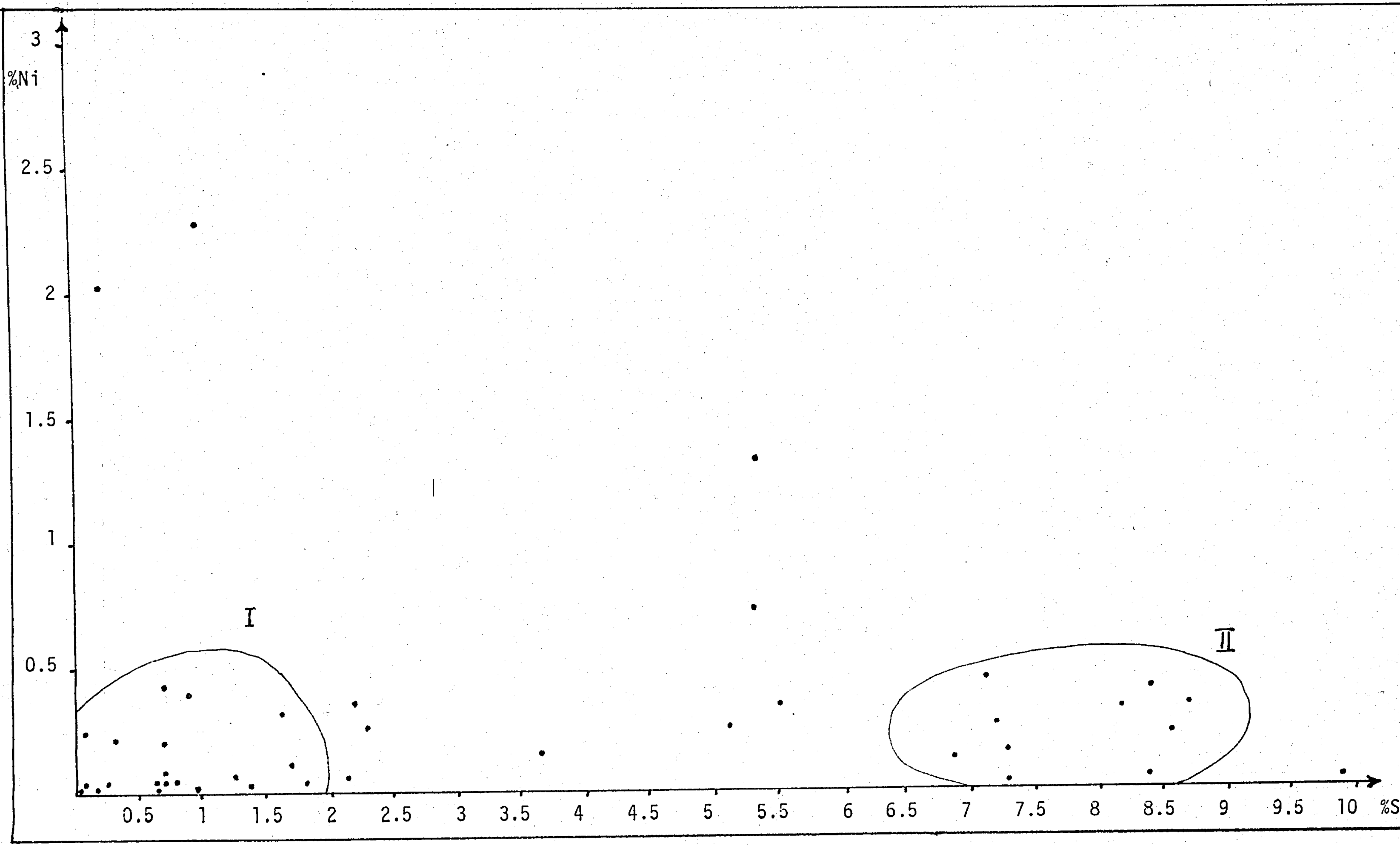


Fig. 4.15 Graph of tin versus nickel (Graph A)

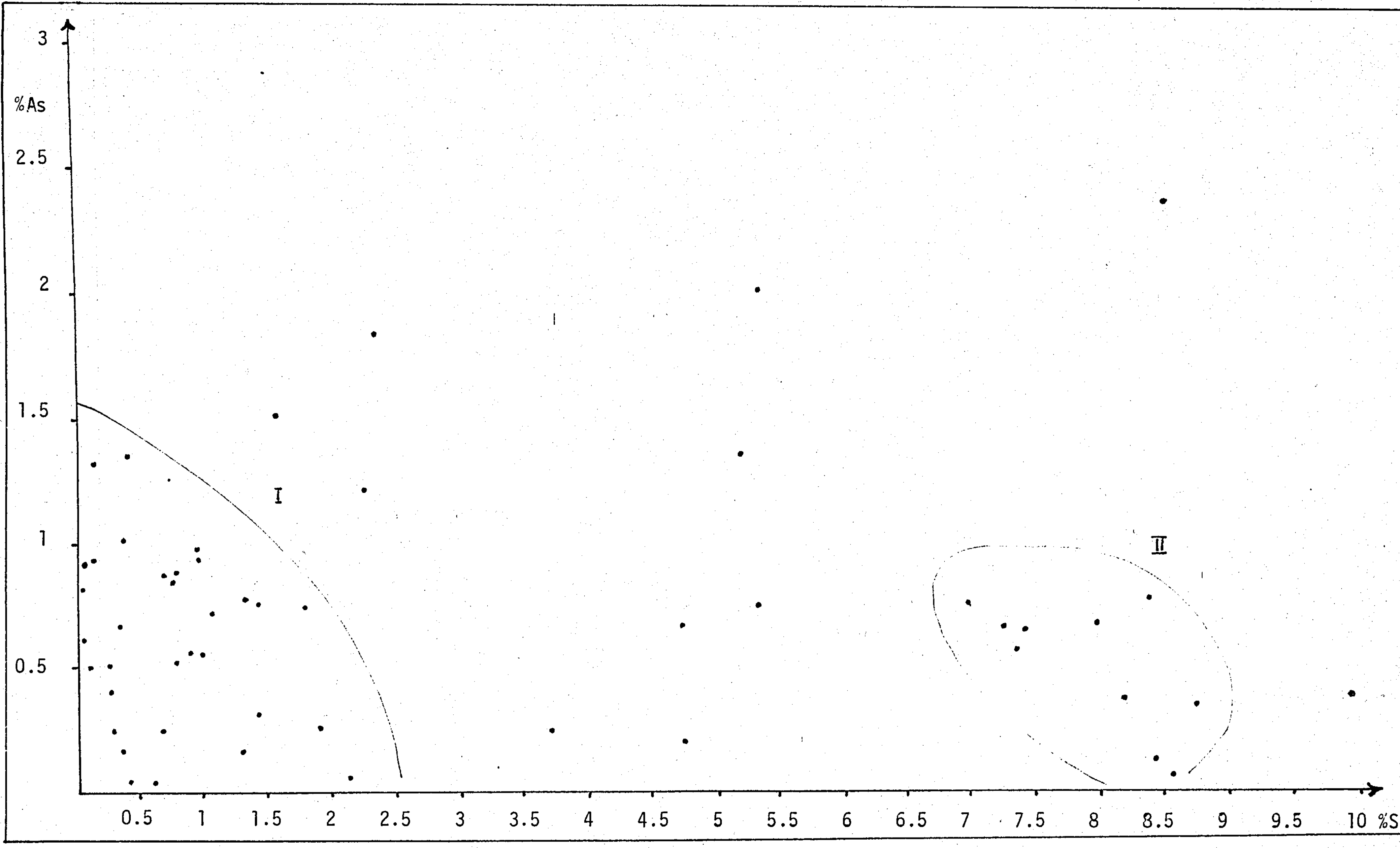


Fig. 4.16 Graph of tin versus arsenic (Graph B)

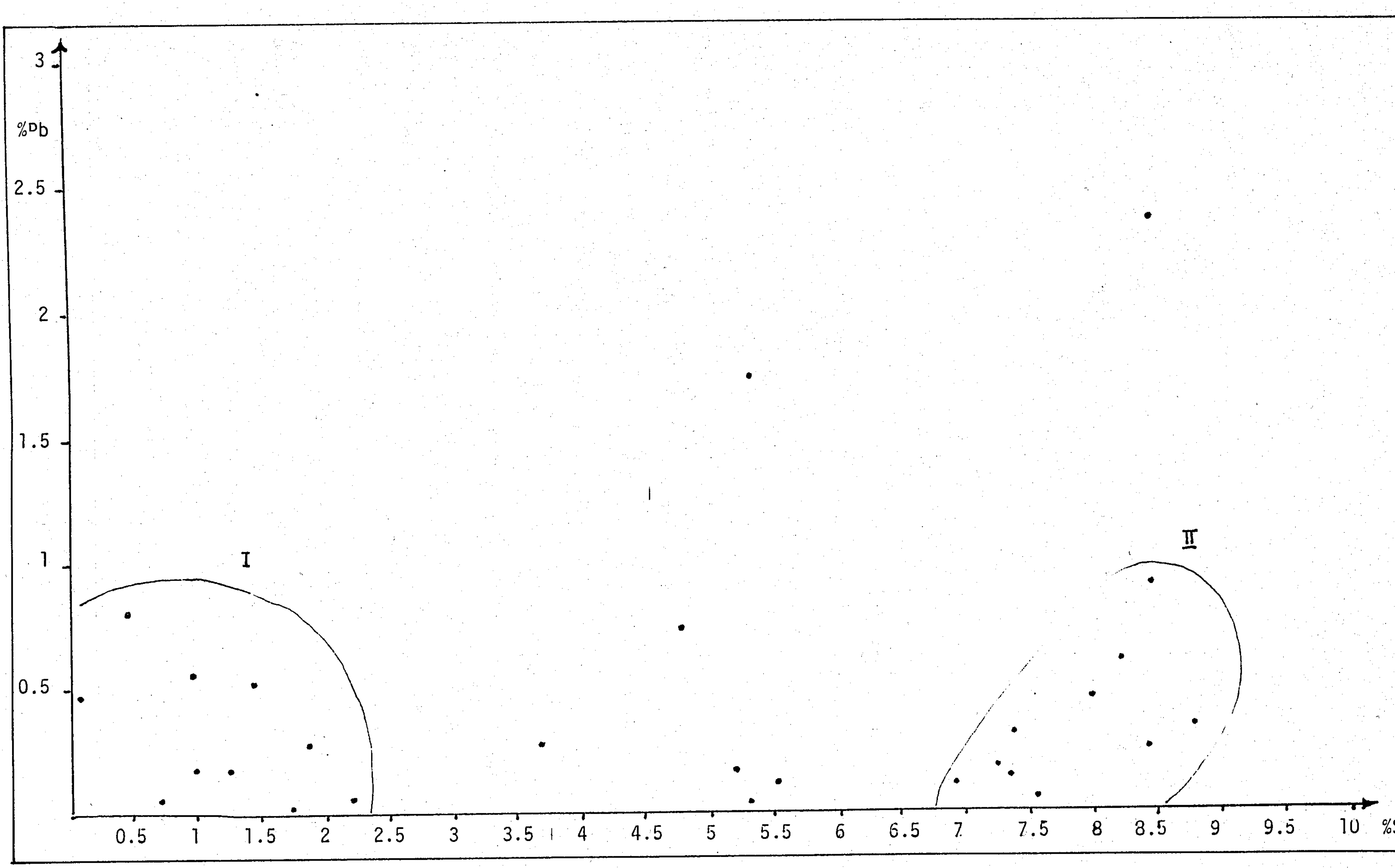


Fig. 4.17 Graph of tin versus lead. (Graph C)

The two clusters,(Cluster I) for low concentration of tin and (Cluster II) for high concentration of tin are observed with some data randomly distributed in between. The number of data points in each of the clusters in the three graphs are given in Table 4.17.

The next question was to find,how many samples yielded the data points in the same cluster, in all three graphs. Similar numbers are also determined for samples yielding data points in the same cluster in pairs of graphs. The results are summerized in Table 4.18.

It can be seen from Table 4.18 that there are five samples in Cluster I (Group 1) and six samples in Cluster II (Group 2) that belong to the same cluster in all three graphs. Groups 3-8 in Table 4.18 give the number of samples belonging to cluster I and cluster II in pairs of graphs, e.i. A and B, A and C, and B and C.

The trace element distribution of samples that belong to Group 1 and Group 2 are given in Table 4.19 and Table 4.20 respectively.

Since there are only five samples in Group 1, the results cannot be statistically very significant. Likewise the members of this group belong to four different sample types. In this group Sn, Pb, As and Ni are expected to be similar since they belong to the same cluster. However, the other trace elements (Sb, Ag, Zn and Fe) show large deviation relative to average values. Thus it is difficult to relate these samples to the same source.

Group 2 has also small number of samples (6), however, examination of Table 4.20 shows that the samples are closely related. First of all, the samples are pins, with four of them of the same type. Elements other than Sn, Pb, As and Ni are also closely related. Sb is not present, and those that have are well below average. Zinc is absent except in two samples. Fe is present in all without much variations. The samples in this group may have some possibility of coming from the same source.

TABLE 4.16. Trace Element Distribution of Samples with As above 1.5 percent (%)

Sample No	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
G/701	73.4	2.32	-	1.90	0.43	-	0.29	6.37	0.73
G/215	82.3	0.95	0.58	1.60	0.05	0.02	2.34	-	0.42
G/818	82.3	3.69	0.58	2.00	0.05	0.03	0.17	1.26	0.16
GC-K/933	81.3	7.11	-	4.78	-	0.03	0.44	-	0.23
Ga-K/235	81.1	5.31	0.06	2.04	-	0.07	0.13	0.44	0.15
Gb-K/714	91.5	-	-	4.85	-	0.04	-	-	0.66
Ga-K/402	88.9	1.52	-	1.50	-	0.02	-	-	0.62
Gb-K/542	93.4	5.53	0.14	6.20	-	0.08	0.33	-	0.43

Table 4.17. Clusters with the Number of Their Data Points in Three Graphs

Graph	Cluster	Data Points
Graph A (Fig. 4.15)	I	21
	II	10
Graph B (Fig. 4.16)	I	36
	II	9
Graph C (Fig. 4.17)	I	10
	II	10

TABLE 4.18. Number of Samples in Various Groups Obtained from the Cluster Analysis

Group	Number of Samples
1. Samples belonging to Cluster I in A+B+C	5
2. Samples belonging to Cluster II in A+B+C	6
3. Samples belonging to Cluster I in A+B	13
4. Samples belonging to Cluster I in A+C	5
5. Samples belonging to Cluster I in B+C	4
6. Samples belonging to Cluster II in A+B	6
7. Samples belonging to Cluster II in A+C	7
8. Samples belonging to Cluster II in B+C	8

TABLE 4.19. Type and Trace Element Distribution of Group 1 (%)

Sample No	Type	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
Ga-K/211	A	77.9	0.67	0.06	0.9	0.34	0.02	0.05	-	1.24
G/492	B	82.7	2.18	0.07	0.4	0.22	0.02	0.03	1.66	0.35
G/231	C	85.1	1.89	0.27	0.64	0.04	0.06	0.08	1.23	0.23
Gb-K/709	F	85.8	1.44	0.54	0.32	0.09	0.09	0.33	-	0.41
Ga-K/373	F	84.9	1.76	0.02	0.75	-	0.12	0.1	1.64	0.32

TABLE 4.20. Type and Trace Element Distribution of Group 2 (%)

Sample No	Type	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
G/627	A	75.7	6.93	0.11	0.74	0.08	0.05	0.13	2.3	0.18
G/925	A	77.3	8.41	0.23	0.1	-	-	0.05	-	0.38
G/893	A	80.7	8.19	0.6	0.38	-	0.02	0.36	-	0.15
G/887	A	76.9	7.34	0.14	0.6	0.07	0.04	0.01	-	0.33
G/240	C	81.4	8.76	0.34	0.48	0.16	0.01	0.33	1.19	0.23
G/22	D	80.9	7.21	0.13	0.63	-	0.02	0.24	-	0.73

Even though only three elements (Sn, Ni and As) are related, group 3 (Table 4.18) has the largest number of samples, 13 in all. List of type and trace element distribution of Group 3 elements are shown in Table 4.21.

Strikingly lead is absent in all of them. Zn is also either absent or present at concentrations well below the general average. In all samples, since only 67 percent (Table 4.10) contained Sb, in this group only one out of 13 has no Sb.

The distribution of Ag and Fe is similar to those observed for all the samples. Again it may be possible to conclude that these samples may originate from the same source.

Group 4 and Group 5 belonging to cluster I have only five and four samples respectively. These groups have certain similarities, however, the number of elements are small to reach any statistically important conclusions. Since group 6 has the same elements as those of group 2 (Table 4.20), the discussions that apply to group 2 can be also applied to group 6.

Group 7 which has 7 samples is listed in Table 4.22.

In this group Sn, Pb and Ni are expected to be similar. Arsenic is present in all members with similar values averaging around 0.6 percent. Silver is generally lower than observed for all samples. Iron as expected, varies within normal limits. Sb and Zn are either present or absent without any particular trend. Samples in all can be considered to be closely related.

The trace elements of Group 8 which involves elements Sn, Pb and As are listed in Table 4.23.

There are good similarities between Group 7 and Group 8. Silver is present in the samples, but at lower concentration compared to general average. Zn is present only in three samples with concentration lower than

TABLE 4.21. Type and Trace Element Distribution of Group 3 (%)

Sample No	Type	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
G/541	A	68.3	0.92	-	0.94	-	-	0.4	-	0.29
G/201	A	83.6	0.35	-	1.07	0.13	0.09	0.24	-	0.86
G/371	A	87.2	0.11	-	0.91	0.1	0.19	0.03	-	0.8
G/891	A	84.9	0.3	-	0.7	0.09	0.07	0.04	-	0.42
G/913	A	90.1	0.14	-	1.31	0.07	0.06	0.25	-	0.43
G/222	A	83.6	1.3	-	0.8	0.12	0.01	0.06	1.49	1.21
G/699	B	84	0.05	-	0.82	0.51	0.17	0.01	0.5	1.57
G/609	B	88	0.24	-	0.4	0.19	0.12	0.02	-	0.46
G/883	B	72.1	0.69	-	0.9	0.09	-	0.08	0.12	0.24
G/216	B	88	0.75	-	0.9	0.24	0.03	0.04	1.02	0.27
G/539	C	82.4	0.74	-	0.83	0.1	0.04	0.45	1.34	0.51
G/378	C	86.1	1.43	-	0.78	0.1	0.03	0.04	1.2	0.3
Gb-K/556	E	91.2	0.65	-	0.24	0.22	0.23	0.01	-	0.05

TABLE 4.22. Type and Trace Element Distribution of Group 7 (%)

Sample No	Type	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
G/627	A	75.7	6.93	0.11	0.74	0.08	0.05	0.13	2.3	0.18
G/925	A	77.3	8.41	0.23	0.1	-	-	0.05	-	0.38
G/893	A	80.7	8.19	0.6	0.38	-	0.02	0.36	-	0.15
G/887	A	76.9	7.34	0.14	0.6	0.07	0.04	0.01	-	0.33
G/240	C	81.4	8.76	0.34	0.48	0.16	0.01	0.33	1.19	0.23
G/22	D	80.9	7.21	0.13	0.63	-	0.02	0.24	-	0.73
G-K/47	E	78.8	7.38	0.31	0.62	-	0.05	0.14	-	0.23

TABLE 4.23. Type and Trace Element Distribution of Group 8 (%)

Sample No	Type	Cu	Sn	Pb	As	Sb	Ag	Ni	Zn	Fe
G/245	A	77.4	8.4	0.88	0.77	-	0.04	-	0.34	0.29
G/627	A	75.7	6.93	0.11	0.74	0.08	0.05	0.13	2.3	0.18
G/925	A	77.3	8.41	0.23	0.1	-	-	0.05	-	0.38
G/893	A	80.7	8.19	0.6	0.38	-	0.02	0.36	-	0.15
G/887	A	76.9	7.34	0.14	0.6	0.07	0.04	0.01	-	0.33
G/882	A	65.2	7.99	0.43	0.69	-	0.02	-	-	0.2
G/22	D	80.9	7.21	0.13	0.63	-	0.02	0.24	-	0.73
G/240	C	81.4	8.76	0.34	0.48	0.16	0.01	0.33	1.19	0.23

the average. The other elements e.i., Sb, Ni and Fe, however, are withing the ranges observed for all the samples, no particular pattern can be deduced.

Cluster analysis unfortunately didn't yield too many possible correlations with large number of samples. This may be mainly due to limited member of similar samples analyzed. However, the patterns of trace elements observed for Groups 2, 3, 6 and 7 can be considered to come from same period or ore source or metalsmith workshop.

CHAPTER V

CONCLUSION

V. CONCLUSION

The results obtained from the analysis of Gedikli copper samples have shown great diversity. Majority of the samples were smelted copper with few percent impurities of arsenic, iron, nickel and other trace elements. There were also samples which can be considered pure arsenical bronze and pure tin bronzes. Few samples were also very rich in lead and zinc.

Since all these objects were found from a particular burial sight, with about 250 burials , the time span is not expected to be very long. If this assumption is true, this may indicate that the society used different quality metal objects at about the same time. Since complete archaeological excavation of Gedikli has not been done, we do not have any evidence that these objects are actually manufactured there. If they were the smelters and metal smiths, it is certain that they used different ore sources. To see both arsenical and tin bronzes together as well as copper with high lead and zinc content may indicate that their supply of raw materials varied from time to time. They may have used whatever new material available.

Again if these objects were manufactured by the local population, their metallurgical technology can be considered to be quite advanced. First of all, the quality of the metal artifacts showed excellent workmanship. Whether shaped by casting or hammering, the delicate skill in the manufacture of these small objects is clearly visible.

Secondly the quality of the metal changed among different types. High tin content of all the umbrella headed pins is an excellent indication that they knew all about copper alloys.

Their smelting and purification technology is also quite advanced. The average Fe content of all samples was about 0.46 percent. Low iron content indicates the proper ratios of flux components as well controlled smelting and purification temperatures.

The distribution of trace elements indicates that different ore sources were available for them. Arsenic and silver were the most common trace elements, and were introduced most likely from the ore. Likewise no trace of cobalt could be detected. These three elements should represent the general character of the majority of the local ore sources.

On the other hand, lead and zinc were present only in some of the objects and they are also contaminants from the ore. This indicates that some of the local copper deposits were rich in lead and zinc while others had none.

Tin is generally an alloying element and is expected to be present at levels over five percent for true bronzes. If it is present at levels about two percent or less, this may indicate a copper source with some tin as trace element. It may also mean that copper and copper alloys from different sources were melted and a composite metal is obtained. The analysis of the possible ore deposits of the area is necessary to obtain the true picture.

If these objects were not locally manufactured, the overall picture should be further extended to the neighbours of the community and look for possible trade relationships.

The results obtained from the 106 objects from the cremation cemetary in Gedikli can be considered only as a preliminary work on this important historical center. Complete archaeological excavation of Gedikli,will give the true picture. In such an excavation it may be possible to find furnaces for smelting, slags, ore samples as well as other metal artifacts. Complete analysis of these materials will yield the true picture of Gedikli culture.

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