CHEMICAL ANALYSIS AND CHARACTERIZATION OF FIRST MILLENIUM B.C. ARROWHEADS FROM TARSUS

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CHEMICAL ANALYSIS AND CHARACTERIZATION OF FIRST MILLENIUM B.C. ARROWHEADS FROM TARSUS

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ABSTRACT

CHEMICAL ANALYSIS AND CHARACTERIZATION OF FIRST MILLENIUM B.C. ARROWHEADS FROM TARSUS

This study was related to the metal artifacts from Tarsus/Gözlükule which was an important urban center from the Chalcholitic to Ottoman Periods. Tarsus is located at the southern end of the Cilician Pass and was able to control trade between Central Anatolia and Mesopotamia. It was also an important port where contacts with Cyprus, Eastern Mediterranean as well as Western Anatolia. Tarsus also had access to the ore sources of Central Taurus ranges as well as Kestel tin.

The objective of this study was to chemically analyze, typologically categorize and determine their production technologies of 82 metal arrowheads from Late Bronze II (LBII), Iron Age (IA) and Hellenistic-Roman (H-R) periods covering a time span between 1400 BC. and 400 AD. The chemical composition of the 82 arrowheads is determined by Atomic Absorption Spectroscopy. The results indicate that pure copper was used extensively in all three periods. Arsenical copper and bronze was used during the LBII and IA. Bronze along with pure copper was the main metal utilized during the H-R Period. The arrowheads were stylistically grouped in three categories depending on how they are attached to the shaft, namely socketted, straight pin and butted pin. There was a definite preference in the use of different type of arrowheads in these periods. Straight and butted pin arrowheads were used in the EBII. During the IA, however, there was almost exclusive use of socketted arrowheads. During the H-R period, straight pin arrowheads were in use. 26 socketted arrowheads from the IA constitute a very standard group with a mass of 6.0 ± 1.0 grams. Chemical analysis showed that these socketted arrowheads contained lead over 1.0%. The source of lead is the lead metal that was added to the cavity of the blade to increase the mass of the arrowheads. Socketted arrowheads were cast generally by two piece clay or metal molds.

ÖZET

M.Ö. BİRİNCİ BİNYIL TARSUS OKUÇLARININ KİMYASAL ANALİZİ VE SINIFLANDIRILMASI

Bu çalışma Kalkolitik çağlardan Osmanlı dönemine kadar önemli bir yerleşim bölgesi olmuş olan Tarsus/Gözlükule'deki metal buluntuları üzerinedir. Tarsus, stratejik olarak Kilikya Geçidi'nin güneyinde yer alır. Orta Anadolu ile Mezopotamya arasındaki ticareti kontrol etmiştir. Tarsus aynı zamanda Kıbrıs, Güney Akdeniz ve Batı Anadolu ile bağlantılı önemli bir liman kentidir. Tarsus, Orta Toroslardaki metal cevherlerine yakın olduğu gibi Kestel kalayınada ulaşma imkanına sahiptir.

Bu çalışmanın amacı, M.Ö. 1400 yıllarından, M.S. 400 yıllarına kadar uzanan bir dönemdeki, Geç Bronz II (GBII), Demir Çağı (DÇ) ve Helenistik-Roma (H-R) dönemlerine ait olan 82 adet metal okucunun kimyasal analizi, tipolojik katagorizasyonu ve üretim teknolojilerini anlamaktır. 82 adet okucunun kimyasal bileşimleri atomik absorpsiyon spektroskopisi kullanılarak belirlenmiştir. Sonuçlar göstermiştir ki; saf bakır her üç dönemde de yaygın olarak kullanılmıştır. GBII ve DÇ.' nda, arsenikli bakır hem de bronz kullanılmıştır. H-R döneminde ise, saf bakır ve bronz, okucu üretiminin temelini oluşturmaktadır. Okuçları, şaft bölümüne bağlanma durumlarına göre; kovanlı, düz iğneli ve boğumlu iğneli olarak üç grupta katogorize edilmiştir. Bu çalışmadaki dönemlere ait okuçlarında bariz farklılıklar bulunmaktadır. GBII döneminde yalnızca düz ve boğumlu iğneli okuçları kullanılmıştır. Buna rağmen, DÇ'nda, sap delikli okuçlarının kullanımı yaygındır. H-R dönemi boyunca, düz iğneli okuçları tercih edilmiştir. DÇ'na ait 26 adet kovanlı okucu ağırlıkları 6.0±1.0 gram olan oldukça standart bir grup oluşturmaktadır. Bu kovanlı okuçlarına ait kimyasal analizler bu okuçlarının 1.0% üzerinde kurşun içerdiğini göstermektedir. Bu kurşunun kaynağı, okucunun bıçak kısmında bulunan bir oyuk içerisinden okuçlarının ağırlıklarını arttırmak amacıyla eklenen kurşun metalidir. Sap delikli okuçları, iki parçalı kil veya metal kalıp kullanılarak dökülmüştür.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS iii
ABSTRACT iv
ÖZET v
LIST OF FIGURES ix
LIST OF TABLES xiii
LIST OF SYMBOLS / ABBREVIATIONS xiv
1. INTRODUCTION 1
2. HISTORICAL BACKGROUND 3
  2.1. Ancient Anatolian Metallurgy 3
    2.1.1. Before 5000 B.C. 3
    2.1.2. 5000-4000 B.C. 5
    2.1.3. Late Chalcolithic and Earliest Alloys (4000-2700 B.C.) 6
    2.1.4. Bronze Technology during the Bronze Ages (2700-1200 B.C.) 8
  2.2. Metallurgy at Tarsus/Gözlükule 11
    2.2.1. Neolithic and Chalcolithic Period 11
    2.2.2. Bronze Ages 12
3. ANCIENT COPPER METALLURGY 14
  3.1. Copper Ores 14
  3.2. Ancient Unalloyed Copper Metallurgy 16
    3.2.1. Copper Utilization before Extractive Metallurgy 16
    3.2.2. Exractive Metallurgy 16
    3.2.3. Distrubition of Trace Elements During Smelting 21
  3.3. Copper Alloys 23
    3.3.1. Copper-Arsenic Alloy (Arsenical Copper) 26
    3.3.2. Copper-Tin Alloy (Bronze) 28
    3.3.3. Cu-As-Sn Ternary Alloy 30
    3.3.4. Other Alloys of Copper 30
  3.4. Ore Sources around Tarsus 32
    3.4.1. Central Taurus Range 32

3.4.2. Amanos Range 33
3.4.3. Kestel Tin Mine 33
4. METHODS USED 35
4.1. Atomic Absorption Spectroscopy 35
4.1.1. Principles 35
4.1.2. Flame Atomic Absorption Spectroscopy 36
4.1.3. Graphite Furnace (Carbon Rod) Atomic Absorption Spectroscopy 36
4.2. Experimental Methods 38
4.2.1. Instruments Used 38
4.2.2. Sample Preparation 38
5. MATERIAL 39
5.1. Definition and Classification of the Arrowheads 39
5.2. Classification of the Arrowheads According to Tang 40
5.2.1. Socketted Arrowheads 40
5.2.2. Straight Pin Arrowheads 42
5.2.3. Butted Pin Arrowheads 42
5.3. Subclassification of Arrowheads According to Blade 43
5.3.1. Cross Section of the Blade 43
5.3.2. Shape of the Blade and Other Morphological Features 45
5.4. Classification and Distrubituon of Tarsus Arrowheads 47
5.4.1. LB II Arrowheads 48
5.4.2. IA Arrowheads 49
5.4.3. Hellenistic-Roman Period Arrowheads 49
5.4.4. Unpublished Arrowheads 49
5.5. A Comparative Classification System of Arrowheads in Anatolia 50
5.6. Arrowhead Technology 51
6. RESULTS AND DISCUSSION 53
6.1. Distribution of Alloying Elements of Tarsus Arrowheads 55
6.1.1. LB II Arrowheads 55
6.1.2. IA Arrowheads 56
6.1.3. Hellenistic-Roman Arrowheads 57
6.1.4. Unpublished Arrowheads 58
6.1.5. Comparative Distribution of Alloying Elements among the Periods 59

    - 6.1.6. Distribution of Arsenic and Tin Concentrations 60
  - 6.2. Trace Element Distributions 62
    - 6.2.1. Distribution of Nickel and Antimony as Trace Elements 62
    - 6.2.2. Lead in Arrowhead 64
  - 6.3. Mass of Arrowheads 68
    - 6.3.1. Mass Distribution According to Periods 69
- 7. CONCLUSION 71
- APPENDIX A: CLASSIFICATION OF THE ARROWHEAD SAMPLES 73
- APPENDIX B: CATALOG OF ARROWHEAD DRAWINGS 76
- REFERENCES 87

LIST OF FIGURES

Figure1.1. Map of Cilicia 2

Figure 2.1. Important Bronze Age sites in Anatolia.................................. 10

Figure 3.1. Cross section of a copper ore deposit.................................. 15

Figure 3.2. Ellingham diagram of metal oxides 18

Figure 3.3. Ancient smelting furnace 19

Figure 3.4. Slagless smelting.. 20

Figure 3.5. Slip planes in an unalloyed metal, Distortion of slip planes in an alloy ... 23

Figure 3.6.Copper-Nickel phase diagram 24

Figure 3.7. Copper-Lead phase diagram 25

Figure 3.8. Hardness of copper and copper alloys 26

Figure 3.9. Phase diagram of the Cu-As binary system 27

Figure 3.10. Phase diagram of Cu-Sn binary system.................................. 29

Figure 3.11. Phase diagram of Cu-Zn binary system.................................. 31

Figure 3.12. Phase diagram of Cu-Sb binary system 32

Figure 5.1. Parts of an arrow 39

Figure 5.2. Arrowhead components 40

Figure 5.3. Cross-section of a socketted arrowhead 41

Figure 5.4. Socketted arrowhead with spur 41

Figure 5.5. Pictures of socketted arrowheads 41

Figure 5.6. Cross-section of a straight pin arrowhead 42

Figure 5.7. Pictures of straight pin arrowheads 42

Figure 5.8. Cross-section of a butted pin arrowhead 43

Figure 5.9. Pictures of of butted pin arrowheads 43

Figure 5.10. Blade morphologies 44

Figure 5.11. Variations in the cross section of arrowhead blades 44

Figure 5.12. Socketted tribolated arrowheads 45

Figure 5.13. Arrowhead blade morphologies 46

Figure 5.14. Percent distribution of arrowheads versus periods....................... 48

Figure 5.15. Reclassification of arrowhead types from Erkanal’s study 50

Figure 5.16. Two piece arrowhead mold 51

Figure 5.17. Socketted bronze arrowhead mold of Mosul 52

Figure 6.1. Distribution of alloy type of LB II arrowheads 56

Figure 6.2. Distribution of alloy type of IA arrowheads.............................. 57

Figure 6.3. Distribution of alloy type of Hellenistic-Roman arrowheads 58

Figure 6.4. Distribution of alloy type of unpublished arrowheads 59

Figure 6.6. Distribution of As and Sn concentration at different periods 61

Figure 6.7. Distribution of Ni and Sb concentrations at different periods 64

Figure 6.8. Epoxy imbeded picture of Acemhöyük arrowhead...................... 65

Figure 6.9. Optical microscope image of Acemhöyük arrowhead.................... 66

Figure 6.10. SEM of Acemhöyük sample 67

Figure 6.11. Cross section of a modern handgun bullet 67

Figure 6.12. Mass Distribution of Arrowheads at different periods 70

Figure B.1. IA samples 81

Figure B.2. Hellenistic-Roman period samples 83

Figure B.3. Unpublished samples 86

LIST OF TABLES

Table 2.1. Trace elements of Can Hasan mace head and Aşıklı Höyük copper beads 5

Table 2.2. Trace element distribution of objects from Mersin-Yumuktepe. 6

Table 3.1. Copper Minerals and their chemical formulas 14

Table 4.1. Typical atomic absorption detection limits of the elements analyzed 37

Table 4.2. Graphite furnace instrument parameters for As and Au analysis 37

Table 5.1. Type codes of arrowheads 47

Table 6.1. Elemental composition of Tarsus Arrowheads 53

Table 6.2. Semiquantitative EDX anaysis of Acemhöyük arrowhead 66

Table 6.3. Mass of Arrowheads 69

Table A.1. Arrowhead samples... 73

LIST OF SYMBOLS / ABBREVIATIONS

A	Absorption
C	Concentration
g	gram
I^o	Intensity of the transmitted radiation
I	Intensity of the unabsorbed radiation
l	Path length of the radiation in the analyte solution
Є	Molar absorptivity

AAS	Atomic absorption spectroscopy
A.D.	Anno Domini
B.C.	Before Christ
C-14	Carbon-14
COMP-image	Compositional image mode
EB	Early Bronze Age
EA	Early Iron Age
SEM	Scanning Electron Microscope
IA	Iron Age
MB	Middle Bronze Age
MI	Middle Iron Age
MIBK	Methly isobuthyl ketone
LB	Late Bronze Age
XRD	X-ray diffraction

1. INTRODUCTION

The utilization of metals by the ancient communities was an important stage of development. The knowledge and the advances in metal work give clues about the technological development throughout the ages. The first utilization of metals appeared in the Near East during pre-pottery Neolithic. These metal objects were very simple implements like pins and beads. They were made out of native copper by hammering. During the Chalcolithic Period usage of copper became much more extensive since it can now be produced from its secondary ores by smelting. During the Bronze Ages arsenical copper alloy is obtained when the complex arsenic containing primary copper ores are smelted. Arsenical copper had a much more superior mechanical properties compared to pure copper. By the discovery of tin, true Bronze Age began in the Near East at the beginning of the third millennium B.C. Together with bronze, lead, silver and gold were also recognized.

Scientific studies on ancient copper and copper based artifacts has become the standard technique to understand the technological developments of metallurgy throughout the ages. Various spectroscopic and other techniques were used to determine the type and quantity of alloying elements such as arsenic and tin as well as the element that are present at trace levels in copper. Presence of alloying elements was a sign of advanced technology. Trace element distributions, on the other hand, were used to understand the type and possible ore sources utilized in their production. Microstructural analysis of metal samples gave important clues about the thermal and physical processes that were applied during the production and shaping of the artifact. Together with metals, analysis of all archaeometallurgical materials such as slags, fluxing agents, furnace or crucible fragments were part of these scientific studies. Finally, lead isotope studies provide information about the possible sources of the ore from which the metal artifacts are made.

In this study, the chemical analysis of copper and copper based arrowheads from Tarsus-Gözlükule belonging to Late Bronze II and Iron Ages is carried out. Tarsus/Gözlükule is located at the southern entrance of the Cilician Gates and played a strategically important role in metal trade route between Central Anatolia and the Mediterranean Coast (Figure 1.1). Excavations at Gözlükule during the 1930s and 1940s showed that the site was a very important cultural center during the Bronze, Iron and Hellenistic and Roman Periods. Numerous metal objects, metal workshops as well as many metal casting molds were recovered during the archaeological excavations. With its strategic location at the southern end of the Cilician pass, Gözlükule probably also had the control of rich copper, silver and gold deposits of Central Taurus Ranges as well as the Kestel tin further to the north (Yener, 2000).

Ancient Tarsus was also a seaport, so it was believed that it had connection with Cyprus, as well as Eastern Mediterranean and Western Anatolia. Metals probably were one of the major trade commodities during the Bronze Ages and Tarsus had an active and important role in its trade.

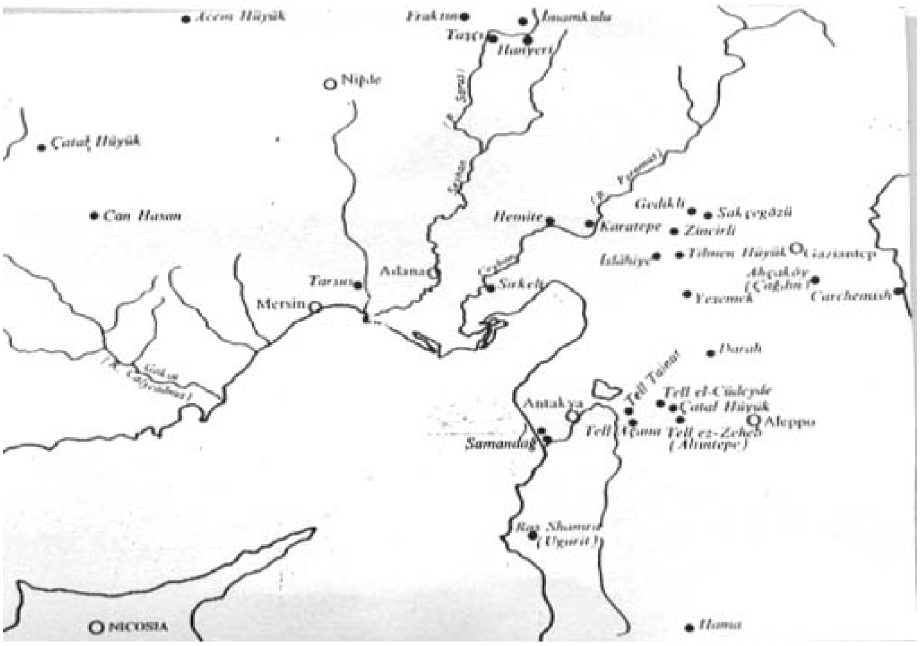


Figure1.1. Map of Cilicia (Yener, 2000)

In this study, atomic absorption spectroscopy (AAS) methods are used to determine the composition of the arrowheads. The composition of the arrowheads is then compared with the results of other contemporary copper and copper based objects from Tarsus, Gözlükule and neighboring sites.

2. HISTORICAL BACKGROUND

2.1. Ancient Anatolian Metallurgy

2.1.1. Before 5000 B.C.

Anatolian mountain ranges, with very rich ore deposits, played a very important role in the development of metallurgy. Hence, it is not suprizing that the first examples of the metal artifacts are found in Anatolia. The metal ores were first used by ancient cultures as pigments and as source of precious stones. With the development of the knowledge of metals and pyrotechnology, the metal utilization started.

The first evidence of metal utilization in human history is documented at the Pre-pottery Neolithic levels of Çayönü Tepesi (Özdoğan and Özdoğan, 1999). This was a turning point in the history of metallurgy. In the earliest levels dating to 9000-8200 B.C., 3670 unworked malachite pieces were found. In the level dating to 8200-8000 B.C. beads and small objects made out of native copper and malachite were discovered. A total of 113 copper object dated to 8200-7500 B.C. were brought to day light. Among these objects, 44 copper implements, 33 malachite samples, and 12 mineral samples were analyzed. The analysis are based on the microstuructural observations and statistical calculations of trace element content determined by neutron activation analysis, by proton microprobe and by atomic absorption spectroscopy. Microscopic examinations of the copper objects showed the characteristic markings produced by cold working (Maddin *et al*., 1991; Maddin *et al*., 1999). At least three of the analyzed items showed marks of cold working followed by annealing. Numerous cracks, strain markings, and small new grains produced by the beginning of recrystallization are the evidences of these copper objects being shaped by the process of hammering followed by annealing. Annealing is a process practiced by the ancient metalsmiths, altough it is still not yet clear if the ancient metal smiths have realized its mechanical effects (Özdoğan and Özdoğan, 1999). The possible source of these copper objects in Çayönü Tepesi is Ergani Maden, which is located at 20 km north of the settlement and is a major copper deposit (Palmieri *et al.* 1993: 578-579).

Aşıklı Höyük is another important Pre-pottery settlement located 25 km south-east of Aksaray in Central Anatolia. Fortyfive copper beads were found from the graves of Aşıklı Höyük from the eight millenium B.C. levels (Esin, 1999). 14 of the samples are analyzed by using lead isotope analysis, X-ray diffraction, optical metallography, atomic absorption spectroscopy and by neutron activation analysis (Yalçın and Pernicka, 1999). The results of the chemical and metallographic analysis showed that all of the samples are made out of native copper. According to the results of the optical metallographic analyses, 11 samples were annealed. Beads were made out of native copper by hammering. The copper was first hammered into sheets and then rolled to form the beads (Yalçın and Pernicka, 1999). A set of four beads were also analyzed by using optical metallography and by neutron activation analysis. According to the analytical results, these beads were also made out of native copper and were annealed (Yalçın and Pernicka, 1999). These chemical and metallographic analyses showed that early stages of metallurgy and pyrotechnology were practiced in Aşıklı during eight the millenium B.C. (Esin, 1999).

Çatalhöyük is also an important settlement where metallurgical activity is observed. Copper and galena (PbS) based beads were found in the level dating to 7310-6400 B.C., suggesting that some slag pieces might be the first signs of extractive metallurgy (Yalçın, 2000) and that these slags might be the results of the copper smelting process (Sperl, 1997).

Can Hasan is located 13 km northeast of Karaman and is one of the Chalcolithic settlements of Anatolia. In Can Hasan, many copper based objects were found (ca. 6000 B.C.). Among these a mace head is especially important. This mace head is also dated to ca. 6000 B.C. For years, it is cited as the earliest cast copper object (French, 1967; Esin, 1976; Pernicka 1990), however, the latest metallographic and chemical analysis showed that the it is not cast but shaped by hammering native copper (Yalçın, 1998). From the metallographic analysis the marks of hammering are easily observed. The most important evidence for this conclusion is provided by the silver crystals observed in the metallographical analysis. Had the mace head been made by casting, it would not have been possible to see the silver crystals. The trace element analysis and the comparison of the analytical results with the results of Aşıklı Höyük proved that the mace head was made out of native copper (Table 2.1). The possible origin of the copper could be the Çamardı Region of Bolkar Dağ, which is nearly 80 km southeast of the Can Hasan (Wagner *et al.*1989).

Table 2.1. Trace elements of Can Hasan mace head and Aşıklı Höyük copper beads

	Can Hasan Mace head	Aşıklı Höyük Copper beads
Sn	<50 ppm	26 ppm
As	6 ppm	43 ppm
Sb	<1 ppm	1 ppm
Co	0.6 ppm	6 ppm
Ni	<30 ppm	10 ppm
Ag	550 ppm	340 ppm
Au	<0.03 ppm	<1 ppm
Fe	1920 ppm	313 ppm
Zn	1160 ppm	<10 ppm
Se	<2 ppm	1 ppm
Hg	1.5 ppm	32 ppm
Te	<37 ppm	<10 ppm
Cr	94 ppm	20 ppm
Ir	<0.006 ppm	<1 ppm

2.1.2. 5000-4000 B.C.

Mersin-Yumuktepe is an important prehistoric settlement dating back to Neolithic times. Excavations in Yumuktepe yielded several copper objects from the Chalcolithic Period. Among these, two needles from layer XXI, five needles from layer XVI, two chisels and an axe are of special importance. The analytical and metallographic analysis showed that the copper objects from Mersin-Yumuktepe were made by casting and smelted copper. Small slag particles in these objects are the evidence of smelting. The final shape has. been given by hammering. These objects found in Mersin are dated between 4930-4730 B.C. and are among of the earliest cast objects made out from smelted copper. In Table 2.2, the trace element distribution of Mersin samples are given. Since the levels of trace elements are so low, it can be concluded that highly rich pure secondary ores must have been smelted. In addition, the axe has some slag particles, which are easily observed during the metallographic analysis. (Yalçın, 2000).

Table 2.2. Trace element distribution of objects from Mersin-Yumuktepe (Esin, 1969).

Object	**Fe**	**Sn**	**As**	**Sb**	**Pb**	**Ni**	**Ag**	**Bi**
Needle	<0.01%	0	<0.01%	0.36%	0	<0.01%	0.02%	<0.01%
Needle	<0.1%	0	0	<0.01%	0	0	0.11%	0
Needle	<1%	0.75%	0.11%	0.58%	0.18%	0.19%	0.04%	0
Needle	<0.01%	0	0	<0.01%	<0.01%	<0.01%	0.18%	0
Needle	<0.01%	0	0.30%	0.62%	0.01%	<0.01%	0.04%	0.005%
Chiesel	<0.01%	0	<0.01%	<0.01%	0	0.02%	0.03%	0
Chiesel	<0.01%	0	0	0.09%	0	0	0.018%	0
Axe	<0.01%	0	<0.01%	0.39%	0	<0.01%	0.26%	0.007%

2.1.3. Late Chalcolithic and Earliest Alloys (4000-2700 B.C.)

During the fourth millenium B.C. the metallurgical activity is increased in the whole of Anatolia. Archeological excavations proved contacts with Uruk cultures of Mesopotamia. Mesopotamian cultures which lacked any metal sources established extensive trade systems to obtain metal. Thus, metals became one of the most important commercial raw material. Evidences of metallurgical activities are observed in most of the Chalcolithic settlements of Eastern Anatolian (Yalçın, 2000), (Stein *et al* ,1997).

Alloys of copper started to replace the use of pure copper, as a result of the increase in metallurgical knowledge. Ancient metal smiths have started to realize the superior properties of the alloys, so as to improve the metal technology.

During the Early Chalcolithic period arsenical copper were rare. However, some of the earliest examples of arsenical copper are found in Late Chalcolithic site of Ilıpınar in northwestern Turkey (Begemann *et al.*, 1994) and Late Chalcolithic levels of Arslantepe in eastern Anatolia (Palmieri *et al.*, 1993). Late Chalcolithic samples of İkiztepe analyzed by Kunç in 1986 also had arsenic concentration over one percent.

Excavations in Arslantepe-Malatya yielded the most sophisticated metallurgical activity during Chalcolithic Period. Many metal objects, slags, ores, crucible fragments, hammerstones and casting moulds are found. Chemical analysis of archaeometallurgical material showed that different types of copper ores have been utilized (Hauptmann and Palmieri, 2000). Nine swords, twelve spearheads and a plaque are some of the important metal artifacts dated ca. 3400 B.C. that were made out of arsenical copper. The arsenic contents are above 5.8 percent. Three of the swords had silver inlay decoration. The metal artifacts found in a “Royal Tomb” dated ca. 3000 B.C. were also made out of arsenical copper, some of them with high nickel content while some metal objects were made out of copper-silver alloy with a silver content between 23-65 percent (Hauptmann and Palmieri, 2000).

İkiztepe is a prehistoric settlement along the Black Sea coast in northcentral Anatolia. This site was inhabited during the Late Chalcolithic and Early Bronze Ages. Metallurgy was actively practised in İkiztepe (Özbal *et al*, 2002). Many metal objects, slags and crucible fragments from İkiztepe were analyzed (Özbal *et al*, 2002). The metal objects were mainly classified as weapons, tools, jewellery and symbols. 280 of the objects are from the EBIII period, 61 of them are from EBII, 14 are from MBI, while the remaining are from EBI, Late Chalcolithic, and Hellenistic periods. The chemical analyses showed that the İkiztepe metallurgy was based on exclusive use of the arsenical copper. Out of 360 samples, 91.6% had arsenic concentration over 1% (Özbal *et al*, 2002). In one sample, which is a ceremonial spearhead with male and female figurines on the blade, had an arsenic concentration over 9%, causing a silvery color. İkiztepe is very close to northcentral Anatolian copper sources. It is also possible that they had local sources of arsenic or arsenic containing copper ores such as tennantite and energite. Archeological excavations supported with the chemical analysis prove, that İkiztepe metal smiths had learned the arsenical copper technology and used it since EBI. İkiztepe study also showed that İkiztepe metallurgiest did not known bronze technology, or they had not had an easy access to tin (Özbal *et al*, 2002). During the fourth millenium B.C., arsenical copper was also practiced in Anatolia together with unalloyed copper.

2.1.4. Bronze Technology during the Bronze Ages (2700-1200 B.C.)

Bronze is an alloy of copper and tin. Cu-Sn alloys started to appear during the end of EBI period in Anatolia. The early examples of bronze were found in Kusura and Alişar (Esin, 1969). They, however, contained low levels of tin. An exception to these examples is the six bronze stattuettes from Tell Cüdeyde in Amuq dated to 3100-2800 B.C. These stattuettes are composed of bronze with a tin content more than 10 percent (Braidwood *et al.*, 1951). The helmets of the three male stattuettes and the collars of the three female stattuettes were made out of the ternary alloy of copper, silver and gold. Lead isotope studies of the silver metal, which is used in the helmets and collars of the stattuettes, showed that the source of the ore was somewhere in the Bolkardağ or Aladağ massifs (Yener *et al.*, 1991).

Between 2700-2000 B.C., known as EBII and EB III periods, the metallurgical activity is increased and diversified significantly both in Anatolia and throughout the whole of Near East. The number and the type of metal artifacts found is also increased. In addition, the development in the metallurgy can easily be observed from the many examples of complex metalworkings.

Alacahöyük and Horoztepe are the settlements, located on the main trade route from the Black Sea. Different types of precious metal artifacts were found from the royal graves of Alacahöyük and Horoztepe. The analysis showed that the copper-based artifacts are bronze (Esin, 1969).

The treasures of Troy , dated to EBII and EBIII periods contain different types of gold and copper objects. The analysis of copper objects from Troy dated to EB II showed that they were made out of good quality bronze (Bittel, 1959). The analysis of the metal objects from Amuq dated EB II and EB III periods were also made out of medium to high grade bronze. (Braidwood and Braidwood, 1960).

While the earliest examples of bronze objects are found in Anatolian sites, the source of tin used to manufacture these bronze objects are quite contradictory. There were many copper deposits in Anatolia but there were no known tin deposit.

The source of tin used during Early Bronze Age in Anatolia was a dilemma among archaeologists for a long time. Muhly suggested that the Afghan tin was brought to Anatolia through long distance trade (Muhly, 1973, 1980). While Stech argued that Troy served as an entrepot for the Afghan tin (Stech, 1999). According to her, the Afghan tin could reach Troy either from north via Black Sea or from south via the Mediterranean Sea. If these were the trade routes of tin, the cultures in between, must also have known bronze. There are also other inconsistencies in the Stech theory. Stech suggests that the Troy tin originated most likely from some port in Syria or Palestine through the Mediterrenian and Aegean route (Stech, 1999). If this was the route, the bronze technology must also have arrived to Cyprus, Syria and Palestine. Yet these settlements did not have bronze technology until EB IV or at the very end of the third millenium (Muhly 1985, 1999).

Archeological and analytical data does not support the idea of tin trade during the Early Bronze Ages. On the other hand, there are evidence that Anatolia had a centrally located tin mine (Yener *et al* .,1989; Earl & Özbal, 1996, Özbal *et al*., 2002). An ancient tin mine was discovered at Kestel/Göltepe about four km. west of the Çamardı in the province of Niğde. The mine is dated to ca. 2800-2200 B.C. Extensive underground and surface mining activity were observed at Kestel (Yener, 2000). Göltepe excavations yielded many crucibles, furnaces, tuyeres and storage pits. Kestel tin deposits and Göltepe workshop were likely to be a major tin source for Early Bronze Age metalsmiths of Anatolia.

Alacahöyük and Horoztepe are less than 200 km south of İkiztepe, but the typology and technology of metal artifacts from these sites are very different. Especially the use of alloying element with copper. 38 % of the copper based artifacts from Alacahöyük and 55 % of copper based artifacts from Horoztepe contain over 2 % tin (Esin, 1967). On the other hand, at İkiztepe there was not single metal object with tin content over 1%. It is confusing to see such a contradiction in alloying practices between two contemporary sites so close to each other. At the beginning of the second millennium B.C., bronze began to replace arsenical copper.

Iron appears for the first time during the third millenium B.C. in Anatolia. The earliest examples are a bracelet from the early third millenium B.C. context of Tilmen

Höyük, a gold-handled dagger, two gold-headed pins, a necklace, a disc, a knife fragment from Alacahöyük and a mace head from Troy II (Yalçın, 1999).

By 2000 B.C. Anatolia enters historical age. Over 16.000 cuneiform tablets were recovered from the Kültepe (Kanesh) excavations near Kayseri. These tablets were written in Assyrian cuneiform in Akkadian language. They were the records of an extensive trade network from northern Iraq to Central Anatolia during the first two centuries of the second millenium B.C. (Yener, 1982). The trade depends on the exchange of Anatolian silver and gold for textiles and a metal “Anaku” from Assur (Yener, 1982). The metal “Anaku” is generally identified as tin and traded in large quantities. Documents showed that tin was imported to Anatolia during the first centuries of the second millenium B.C. The important Bronze Ages sites of this period are shown in Figure 2.1. (Yener, 2000).

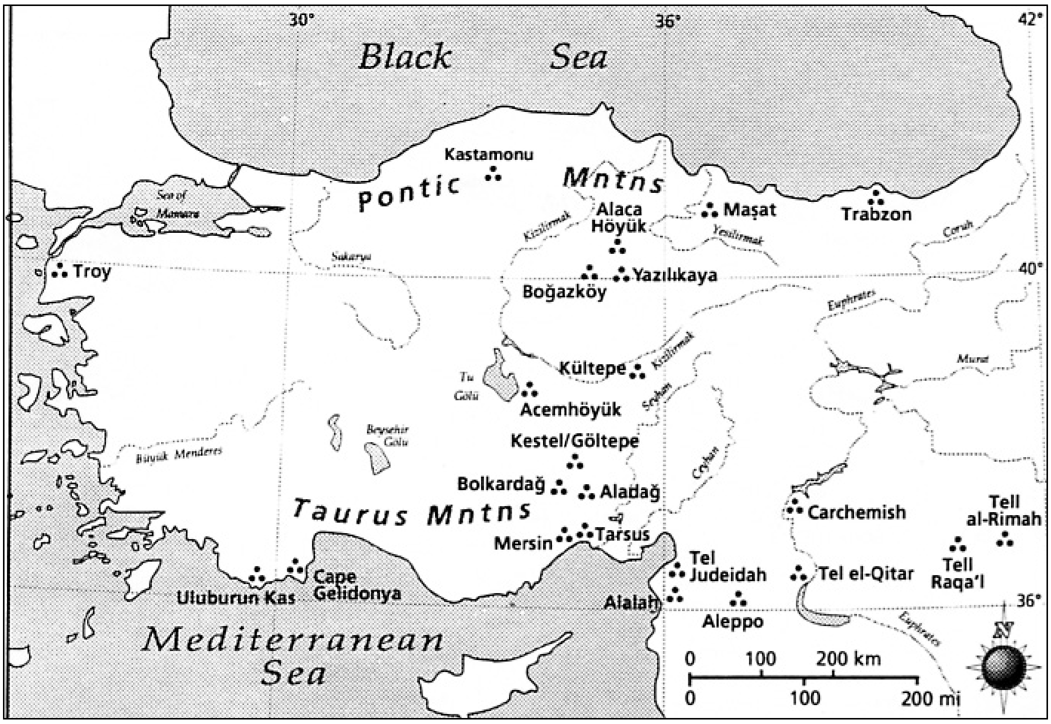


Figure 2.1. Important Bronze Age sites in Anatolia (Yener, 2000)

In the later part of the second millenium B.C., Hittites dominated the Anatolian central plato. The royal archives from Hattuşaş, the capital city of the Hittites, contained many documents about metals and metallurgy. Iron appears to have been an important metal at this Pre- Iron Age society.

The best documentation of large scale metal production and shipment came from two shipwrecks found on the Southwest Coast of Anatolia. The Uluburun ship wreck near Kaş dated from 1300 B.C.contained 9 tons of copper and one ton of tin ingots. Total of, 354 ox-hide and 121 bun-shaped copper ingots and also ox-hide, bun and disc shaped tin ingots were recovered from the ship wreck (Pulak, 1999).

The other shipwreck dated to about 1200 B.C. was found at Cape Gelidonya south of Antalya. With copper ingots as its cargo (Pulak, 1999). Furthermore, the lead isotope analysis of the two jugs that were also found in the shipwreck have been identified to come from the Cyprus ore sources (Stos-Gale *et al*., 1998).

2.2. Metallurgy at Tarsus/Gözlükule

2.2.1. Neolithic and Chalcolithic Period

Tarsus/Gözlükule is located in Cilicia, between Mersin and Adana (Goldman, 1956). Tarsus/Gözlükule had an important role in metal trade between Central Anatolia and the Mediterranien Coast as it is strategically located exactly at the southern enterance of the Cilician pass.

In antiquity, it was also an important sea port. Thus, the contacts with Cyprus, the Eastern Mediterranean and Western Anatolia via sea route also helps control trade. The settlements of Cilicia region probably had control over the rich ore deposits of the Central Taurus range (Kuruçayırlı & Özbal, 2005). Bolkar Mountains in the region, contain rich argenteferous galena and gold deposits, while tin, which is very crucial for bronze technology, can be found at Kestel-Göltepe tin mine north of Tarsus.

Archeological excavations at Tarsus Gözlükule during the late 30’s and late 40’s by Hetty Goldman revealed cultural deposits from the Neolithic to Islamic Period

(Goldman,1956). Numerous copper and copper based metal artifacts were found from EB I to Hellenistic Roman Periods. Goldman had identified and published 512 of the metal artifacts. 276 of the artifacts belong to the Bronze ages, 121 to Iron Age and 115 to the Hellenistic-Roman period. In addition to these, 215 unpublished metal artifacts are found in the museum with no inventory number and date.

From Chalcolithic period, only two metal artifacts were published. These objects were made out of lead and were found in a Late Chalcolithic Cemetery in connection with the burials. One of the object is an open link ring with overlapping ends (37.556, Goldman, 1956). The other object is a small cylindirical piece, closed at one end (37.757, Goldman, 1956). These objects were thought to be a cap for a rod. The lead isotope ratio of the link overlapped with the ore sources in the Central Taurus (Yener *et al.*, 1991).

2.2.2. Bronze Ages

Most of the copper samples of Tarsus belongs to the Early Bronze Ages. During the EB II, when the contacts with Cyprus were known to be intensified, Tarsus became a fortified urban town and probably the seat of a local king. This paralellism can also be observed in the metal artifacts styles between Tarsus and Cyprus. Cyprus adapted some of the metal forms of Tarsus, eventhrough the arsenical copper technology appeared in Cyprus at much later time (Mellink, 1991). The EB III period in Tarsus ended with a series of earthquakes. During LBA, the settlement became a major Hittite settlement with administrative buildings and abundant Hittite seals.

Most of the Early Bronze Age copper based artifacts from Tarsus and other Cilician settlements are made out of unalloyed copper. For example, 34 of 70 Tarsus Early Bronze Age samples analyzed by Esin (1969) were made out of unalloyed copper. 23 of them were arsenical copper but the concentration of the arsenic was low. Furthermore, eight objects contained both, arsenic and tin. Only five out of 70 samples were bronze.

Kuruçayırlı analyzed 87 copper based samples from Tarsus (2003). Out of 42 samples dated to EB and MB periods 32 were made out of arsenical copper with arsenic concentrations greater than1%. Only one sample with the excavation number 38.1595 has a arsenic concentration of 6.11% and it was the only weapon among the objects. The rest of the samples are classified as bronze with tin content between 2-3%. 13 out of 21 analyzed samples dated to the Late Bronze Age were made out of bronze. Four of the bronze objects also contain arsenic.

3. ANCIENT COPPER METALLURGY

3.1. Copper Ores

Ores are defined as metal-bearing minerals (Thrush, 1968). They are classified as primary and secondary. Primary ores are deposited when the original ore body was formed. They are sulfides and they exist at the lowest levels of mineral formations (Figure 3.1). Secondary ores are formed by the alteration of primary minerals by weathering or action of rain and ground waters. Secondary ores are sulfates, chlorides, carbonates, oxides, native metals and sulfides. Native copper is also a secondary ore constituent and formed by the reduction of copper sulfides and copper oxides. Some of the common copper ores and their chemical formulas are listed in Table 3.1.

Table 3.1. Copper Minerals and their chemical formulas

Copper Mineral	Chemical Formula
Cuprite	Cu_2O
Malachite	$CuCO_3Cu(OH)_2$
Azurite	$Cu_3(CO_3)_2(OH)_2$
Olivenite	Cu_2AsO_4OH
Chrysocolla	$CuSiO_3$
Covellite	CuS
Chalcocite	Cu_2S
Bornite	$Cu_5Fe_2S_4$
Chalcopyrite	$Cu_2SFe_2S_3$
Enargite	Cu_3AsS_4
Tetrahedrite	$Cu_{12}Sb_4S_{13}$
Tennantite	$Cu_{12}As_4S_{13}$

There are also primary native copper originating from magmatic sources. The cross section of a copper ore deposit is shown in the Figure 3.1.

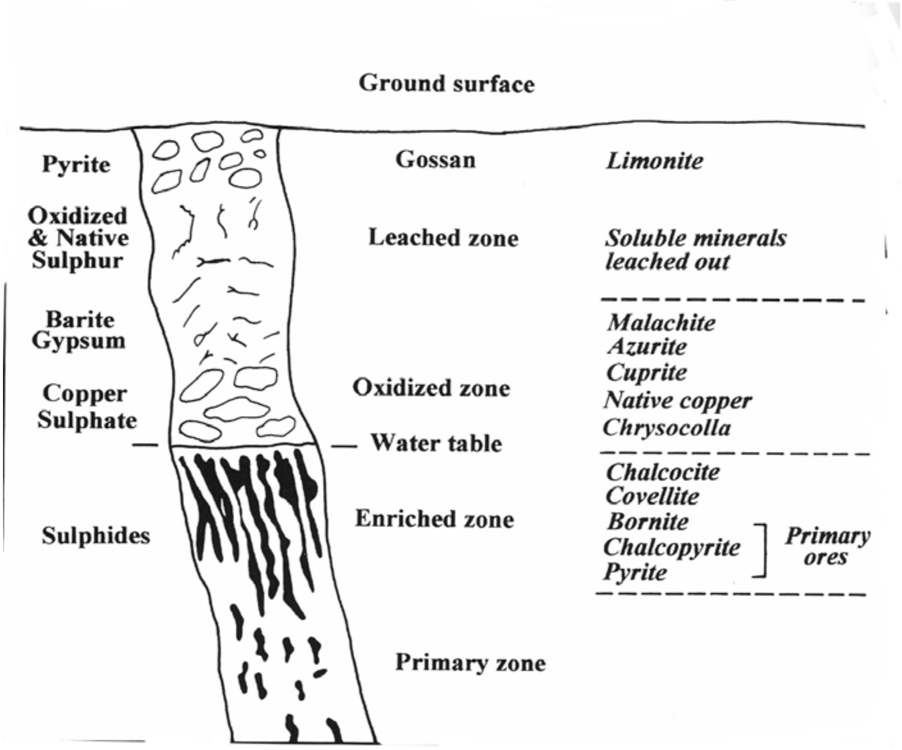


Figure 3.1. Cross section of a copper ore deposit

The ground surface of a copper deposits are generally covered by ore deposits known as Gossan. Because iron oxides are the major constituents at these layer, this part of the deposit is also called an “Iron hat” or “Iron cap”. The gossan is easily recognized by its yellow-orange color resulting from the presence of limonite. Gossan may also contain small amounts of copper minerals, native copper and precious metals.

Copper ores are leached from the upper layers to the secondary enrichment zone by the action of rainwater. Because of that reason, the concentration of copper at the enrichment zone is higher than the upper zones and primary zone. The secondary enrichment zone is also rich in Fe, As, Sb, Pb, Zn, Ni and native copper. As a result copper-arsenic and antimony sulfides are found in these zone, known as Fahlerz type ores.

3.2. Ancient Unalloyed Copper Metallurgy

3.2.1. Copper Utilization before Extractive Metallurgy

The first metal utilized in human history is native copper. The earliest evidence that is recorded at the Pre-pottery Neolithic site of Çayönü Tepesi in Eastern Anatolia (Özdoğan and Özdoğan, 1999). There are other Neolithic sites such as Aşıklı Höyük in Central Anatolia that, also yielded examples of early copper metallurgy. (Yalçın,2000).

These early objects are shaped by hammering native copper. Hammering increases the tension in copper during shaping process which may cause cracks in copper. On the other hand, heating copper below its melting point causes recrystallization and softening of the metal. This process is called annealing and this has been known since the Pre-pottery Neolithic periods. Annealing and hammering was repeated until final shape is reached. Microstructural analysis of some of the copper objects from Çayönü Tepesi has shown twinning, which occurs during annealing like boundries between atom regions. These annealing twins also shows that annealing was practised during the pre-pottery Neolithic period (Maddin *et al*., 1999).

3.2.2. Exractive Metallurgy

The steps of the metal production consist of mining, ore dressing, smelting, refining, and finally shaping of the artifact. Smelting is the process of extracting the metal from its ore by reduction.The earliest evidence of copper smelting in Anatolia was documented at the Early Chalcolithic levels of Mersin Yumuktepe (Level XVI, 4930-4730 B.C.), (Yalçın, 2000).

3.2.2.1. Ancient Mining. Early miners dug out the ore from where it outcropped onto the surface and the removal continued until the ore was finished or until ground water, rock instability or ventillation problems has occured. To extract the ores, stone hammers were used during the early times, as revealed by the marks they left on the walls. Bone tools were also used in removing the ores. Bronze chisels were used in the later times during the Bronze Ages (Craddock, 1995).

Fire setting was also practised to make mining easier. In this operation, a fire was set in front of the rock. Heat weakens the rock and causes it to fracture. A layer can be peeled away by simple hammering. At the end the surfaces become very smooth. The smoothness and blackened roof of the galleries are the evidence of fire setting (Craddock, 1995).

During the Middle Bronze Ages the mining techniques developed further. Galleries were widened, strengthened by wood supports to prevent collapse. With the drainage technique during this period, ancient miners could work below ground water.

3.2.2.2. Ore Dressing. Ores are never pure. They almost always contain impurities known as gangue minerals. The most common impurity is silicates. To increase the purity of the ore, mechanical and chemical processes are applied known as ore dressing. Ore dressing methods applied in antiquity are classified as hand picking, grinding, sieving or hydrotechnology.

First, the ore is crushed. Rich minerals are picked up by hand and the gangue is discarded. Grinding is necessary, if the ore is dispersed in the host rock. Seperation is achieved by the use of hydrotechnology. In hydrotechnological method, the lighter gangue minerals float away by water where as the heavier metal part remains behind. Enrichment eliminates impurities as well as increases metal yield during smelting.

3.2.2.3. The Chemisty of Smelting. Metals are obtained from its ores by reduction. The reduction requires high temperatures, generally between 1000-1200^{0}C as well as a reducing atmosphere. Charcoal used both as fuel and as the reducing agent. The reductant is carbon monoxide that is formed when the combustion temperatures are above 710^{0}C. The general reaction where metal is reduced by CO is shown in Reaction 3.1.

$$MO + CO \rightarrow M + CO_2 \qquad (3.1)$$

Where M = Metal

MO = Metal oxide

The carbonmonoxide is formed at temperatures above 710^{0}C by the combustion of charcoal with oxygen according to Reactions 3.2, 3.3, and 3.4 (Cottrell, 1967).

$$C + O_2 \rightarrow CO_2 \quad (3.2)$$

$$\underline{CO_2 + C \rightarrow 2\,CO} \quad (3.3)$$

$$2C + O_2 \rightarrow 2\,CO \quad (3.4)$$

Formation of CO above 710 ^{0}C is spontaneous because of enthalpy (heat content) and entropy (disorder) of the system (Figure 3.2). Reduction of a metal from its ores however is a very endothermic process. Endothermic reactions are generally non-spontaneous and requires excessive energy.

The Ellingham diagram (Figure 3.2) represents the relative stability of the metal oxides with respect to temperature. The lower the position of the metal oxide on the free energy axis (ΔG), the greater affinity of that metal to oxygen. If the free energy of a metal oxide is higher on the free energy axis above that of carbonmonoxide at a specific temperature it can be reduced by carbonmonoxide (Cottrell, 1967).

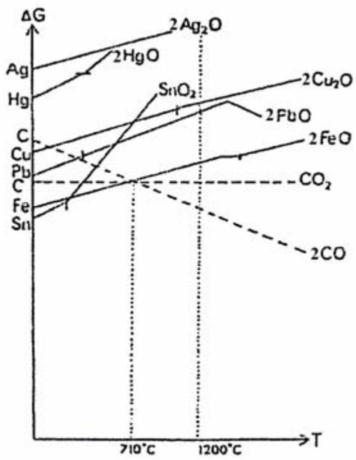


Figure 3.2. Ellingham diagram of metal oxides (Cottrell, 1967)

High temperatures are also necessary for the formation of slag, a viscous material that forms when the gangue minerals react with the fluxing agents. The reduced liquid metal is denser than the slag so it accumulates at the bottom of the furnace. Both the slag and the metal can be tapped separetely from the smelting furnace (Figure 3.3), (Tylecote, 1976).

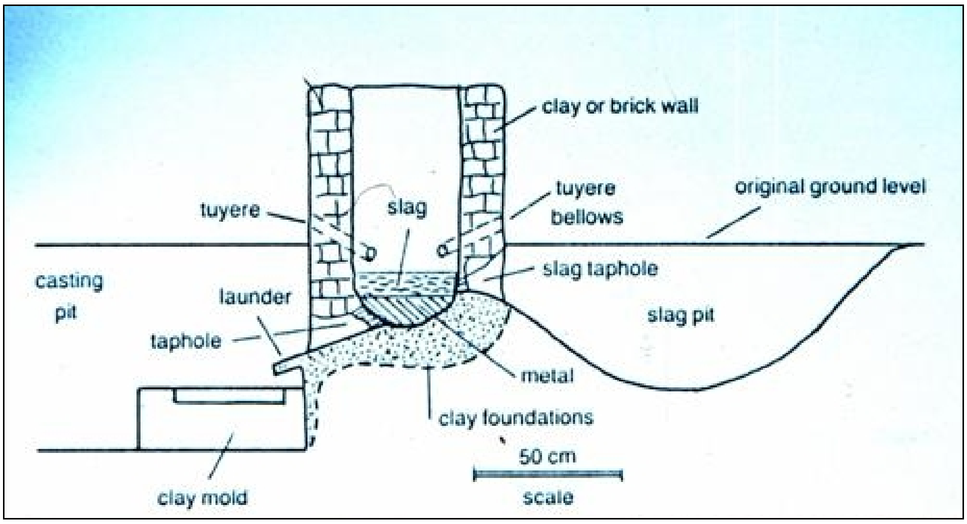


Figure 3.3. Ancient smelting furnace (Tylecote, 1976)

<u>3.2.2.4. Fluxing Agents and Slags.</u> The impurities in ore are called the gangue minerals and are mostly silicates. They can not be totally removed by ore dressing. The remaining impurities are removed in the form of slag during smelting. Since silicates have very high melting points, some fluxing agents are generally used to reduce the melting point and obtain liquid slag. Fluxing agents are usually the oxides of Fe, Ca, Mn, Mg, Zn, Pb, and Na. If the ore contains excess amount of silica, generally iron oxide is added. If, on the other hand, iron is in excess, silica is added as a fluxing agent. The main idea behind this application is to get the formation of fayalite ($2FeO.SiO_2$), which is the major component of smelting slags. Some ores of copper contain both silica and iron in proper amounts so they are called self-fluxing. This type of ores does not need extra addition of fluxing agents during smelting (de Jesus, 1980).

Smelting slags are classified by de Jesus into three catagories according to their composition (de Jesus, 1980). The first type is the glassy slag, which is black and resembles obsidian. It has high silica content. The second type is ripple slag, the color of which vary from gray to black. The third type is the chunky slag, which is the most heterogeneous one. It contains both ore, charcoal, copper and iron oxides together.

3.2.2.5. Smelting Copper Ores. Earliest miners utilized the most enriched and pure secondary copper ores at the upper levels of ore deposits. At the oxidized zone generally copper oxides and copper carbonates are found which are rich in copper content and poor in iron. Nearly pure copper oxides and copper carbonates were the first ores smelted (Craddock and Meeks, 1988). Because these ores are pure and contain no silicate gangue minerals, they do not require any addition of fluxing agents, thus no slag is produced. This type of smelting process is called slagless process. Figure 3.4. shows the slagless procedure.

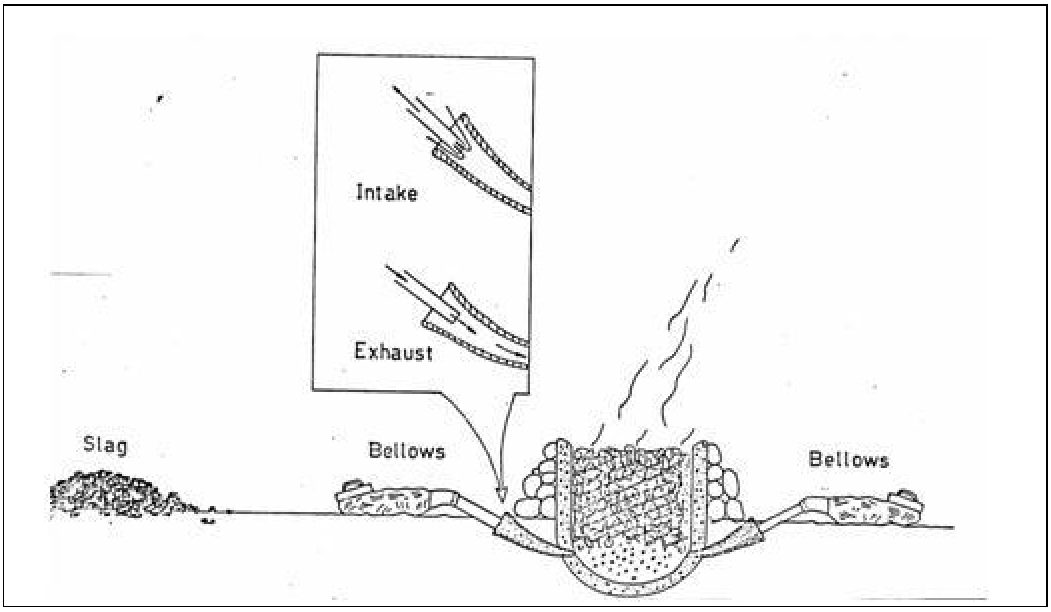


Figure 3.4. Slagless smelting

When rich secondary ores of copper ore are consumed, smelters had to use primary copper sulfide ores. Copper sulfide ores are found at the lower primary zone of the ore deposit (see Figure 3.1.). These ores contain higher amount of impurities, therefore their reduction is more difficult. Iron is the most important impurity in sulfide ores. Eliminating sulfur before smelting is especially important. The copper sulfide ores are therefore first roasted. This method involves the exposition of the ore concentrate to air at temperatures between 500-700^{0}C as shown in Reaction 3.5. If roasting is complete, all the sulfur will be converted to the gaseous SO_2 and so it is eliminated. Iron and copper will be converted to their oxides.

$$CuS + FeS + 3O_2 \rightarrow CuO + FeO + 2SO_{2\,(g)} \qquad (3.5)$$

The oxides of copper and iron is smelted by using charcoal.

The smelting of copper sulfide ores can also be accomplished by partial roasting of ore concentrate under controlled temperature (Reaction 3.6).

$$4CuFeS_2 + 7O_2 \rightarrow 2Fe_2O_3 + 4CuS + 4SO_2 \qquad (3.6)$$

To remove iron oxides, excess silica is used so that fayalite slag can form. The unchanged ore and copper sulfide forms a solid product known as matte (Reaction 3.7).

$$CuFeS_2 + 5O_2 + 2FeS_2 \rightarrow \underbrace{\underline{CuS + FeS}}_{\text{“matte”}} + FeO + 4SO_2 \qquad (3.7)$$

The iron oxides are again removed with excess silica as fluxing agent and matte can be roasted and smelted (Reaction 3.5., Reaction 3.8), (Craddock, 1995).

$$SiO_2 + 2\,FeO \rightarrow Fe_2SiO_4 \qquad (3.8)$$

3.2.3. Distrubition of Trace Elements During Smelting

Ancient copper based metals almost always contain elements like Ni, Sb, As, Pb, Co, Fe, Zn and Au at trace amounts. The origins of these trace elements can be the fluxing agents, fuel, furnace lining, alloying element if used and the ore itself. The distrubition of the trace elements depends on the affinitiy of trace elements to the metal and the slag as well as the smelting temperature.

Trace elements in the copper ores can vary considerably depending on the type of the ore and fluxing agent used. While copper oxides and copper carbonate ores usually do not have iron, copper sulfide ores may contain Fe, As, Sb, Zn, Pb, Ag, Ni and Bi.

Earliest copper objects have low iron content because they were produced from relatively pure copper ores (Craddock and Meeks, 1987). Copper artifacts produced from pure secondary copper ores contain about 0.03% iron. High iron content is the evidence for the smelting copper sulfide ores, because copper sulfides usually contain iron sulfide also. Matte smelting of copper sulfide ores may also require iron ores as fluxing agents. As a result final copper artifact has higher concentration of iron in the range of about 0.3-0.4% (Craddock and Meeks, 1987). As, Ag, Ni and Sb have high tendency to accumulate in the copper metal during smelting.

Roasting and matting processes have also important effects on the trace element distrubition. Roasting may result in the enrichment of Fe, Co, Zn, As, Se, Ag, Au and Pb if they are present in the ore (Germani *et al.*, 1981). On the other hand, Tylecote *et al.* (1977), state that volatile elements such as As, Zn and Sb are partially lost during the roasting of copper sulfides. Smelting temperature is also an important variable. Higher smelting temperatures cause volatilization of elements such as As, Zn, Sb and Bi (Tylecote *et al.*, 1977).

Nickel is one of the most important impurities in copper ores. During smelting Ni accumulates in the copper. It has been observed that copper-arsenic ores in ophiolithic rocks also contain high levels of nickel (Hauptmann, Palmieri; 2000). Thus, nickel can be an important trace element for source analysis. If no roasting and matting is applied, but low smelting temperatures are used, arsenic and antimony will have high tendency to accumulate in the metal. Because arsenic is commonly used in the ancient copper-based artifacts as an alloying element, it is an important impurity.

3.3. Copper Alloys

Pure copper is a soft metal, therefore it can only be used for the simple tools and decorative objects. Hammering copper metal, increases its internal stress which also increases hardness. But cold hammering can not provide the necessary hardness for many tools and weapons. Ancient metallurgiests soon discovered that mechanical properties of copper can be improved by adding various alloying elements.

An alloy is a metallic substance that contains at least two elements. The major or base element should be a metal. The alloying part can be a metal or a non-metal. The atoms of the alloying element can substitute in the place of the base metal in crystal lattice Another possibility is that the alloying atoms can fill between the base metal atoms.

Pure copper is a very soft and mellable metal. Improving the mechanical properties and hardness of the alloys is due to deformation of slip planes in the metal. When force is applied on pure copper metal, its atoms can slide within the slip planes rather easily (Figure 3.5., 1-2). When an alloying element is introduced, however, the slip planes are distorted. As a result the resistance of the atoms against the applied force is increased (Figure 3.5., 3), (Hodges, 1964). This type of mixing of base metal and alloying element may form a single homogenous phase and is called primary solid solution.

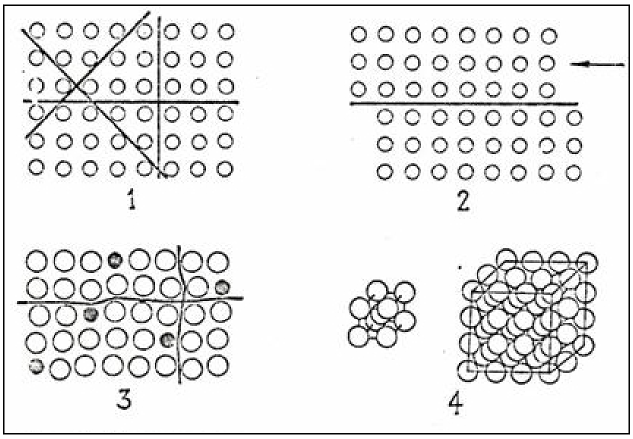


Figure 3.5. Slip planes in an unalloyed metal (1-2), (Hodges,1964); Distortion of slip planes in an alloy (3), (Hodges,1964)

An alloying element can be totally soluable, totally insoluable or partially soluable in the base metal. The composition of binary alloys are presented by phase diagrams. These diagrams shows the behaviour of binary alloy phases at various compositions and temperatures.

Nickel forms a solid solution with copper at all compositions. If Ni containing copper ores are smelted, Ni will be displace copper atoms in the crystal matrix and there will be a single phase.

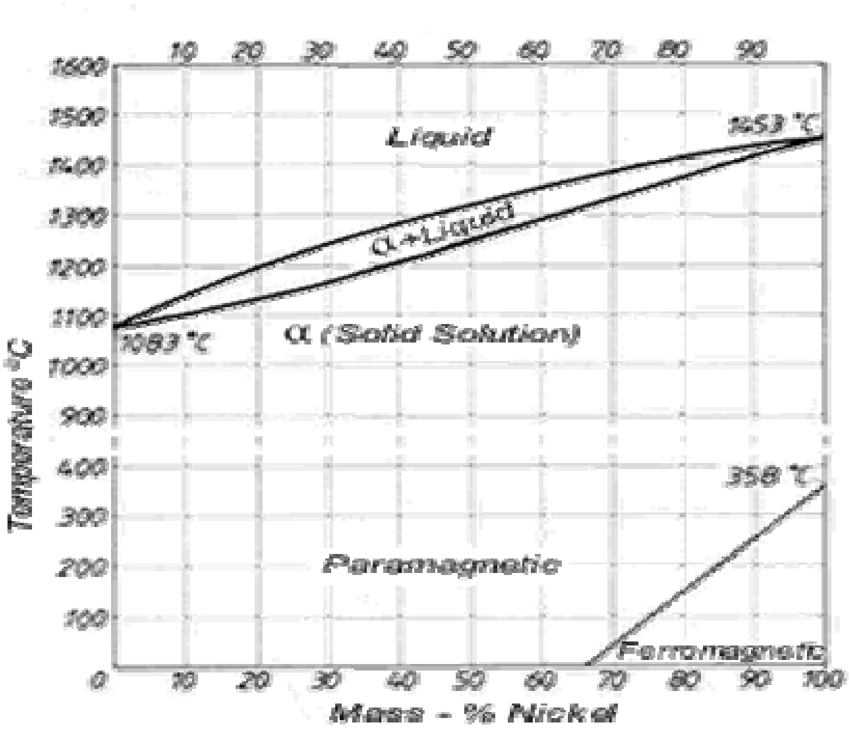


Figure 3.6.Copper-Nickel phase diagram

Solubility of lead in copper, however, is very low. When a molten mixture of Pb-Cu is allowed to solidify, each metal will crystallize separately and a solid mixture will form. Pb will separate out as a second phase in copper matrix. Phase diagram of Cu-Pb binary mixture is shown in Figure 3.7.

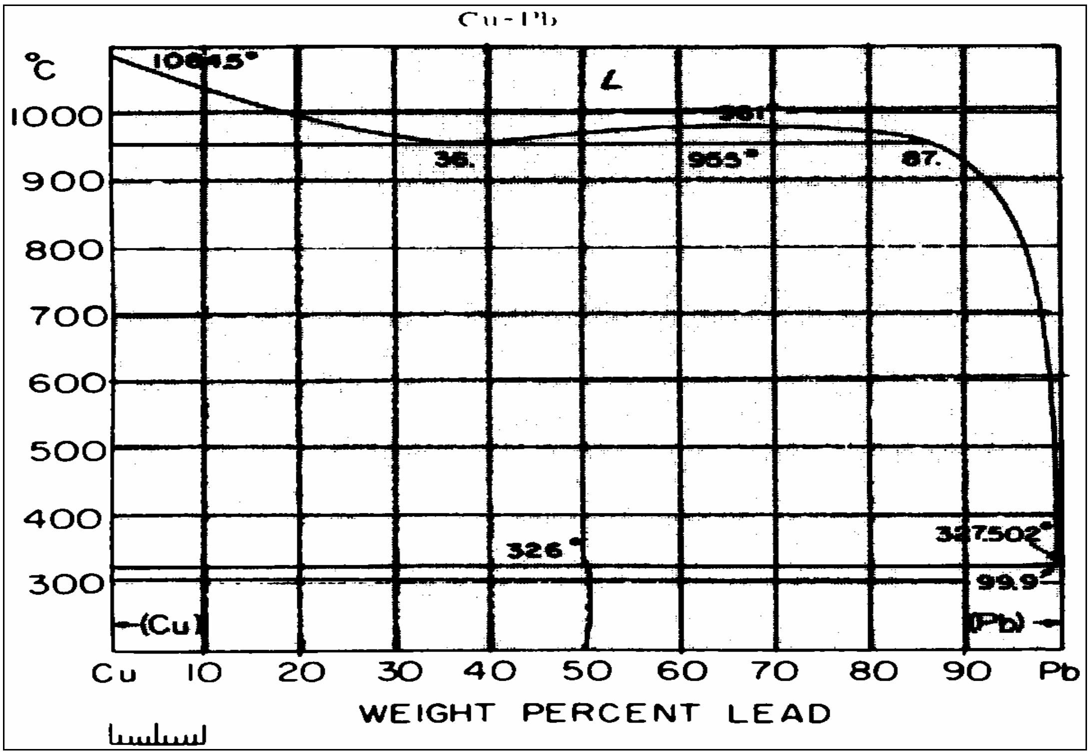


Figure 3.7. Copper-Lead phase diagram (R. Hultgren, and P. D. Desai; 1971)

Arsenic, tin and zinc are partially soluable in copper. The phase diagram that represents these alloys are shown in Figure 3.9., 3.10., 3.11 respectively. As can be seen in these phase diagrams the solubility of arsenic in copper is about 7%, that of tin is about 10% and that of zinc is about 30%. Ancient metallurgiests had determined by trial-and-error method the limits of solubility of arsenic, tin and zinc in copper and produced alloys with proper ratios.

Addition of alloying element into copper reduces its melting point and thus improves its casting properties. The addition of an alloying element also increases the hardness. Increase in the hardness of copper with the addition of arsenic and different amounts of tin is shown in the Figure 3.8.

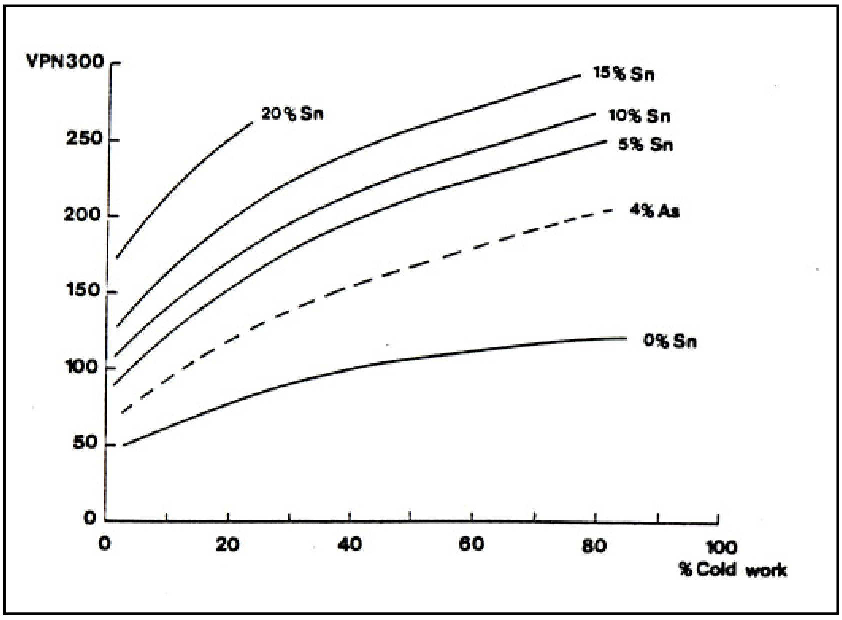


Figure 3.8. Hardness of copper and copper alloys (Northover, 1984)

3.3.1. Copper-Arsenic Alloy (Arsenical Copper)

The earliest alloy in human history is the copper-arsenic alloy. According to archeological evidences, it first appear during the fourth millenium B.C. in the Near East. It is believed that the early examples of arsenical copper was produced accidentally, because arsenic is a volatile element and it is not found in metallic form in nature. During smelting of arsenic containing copper ores like tennantite and enargite, ancient metallurgist must have realized the improved properties of the new metal.

The arsenic containing ores, such as tennantite and enargite, are blackish-gray in color, metallic lustre and quite a different appearence from the other copper minerals except chalcosite. Thus, it is not difficult to recognize arsenic containing copper ores. These ores are copper sulfides, therefore they require roasting and matting before smelting. Roasting and matting process causes some lose of arsenic in form of volatile oxides because of high temperatures (Charles, 1967).

Copper-arsenic alloy can also be produced by co-smelting copper and arsenic ores together. During co-smelting, when arsenic is reduced, it dissolves in molten copper and thus its oxidation is prevented.

Cementation is another method to make copper-arsenic alloy. In cementation, a mixture of arsenic ore and charcoal is added to molten copper in a crucible. Arsenic is quickly reduced and absorbed by the liquid copper.

The production of copper-arsenic alloy and its utilization became widespread in the Near East because of the improved mechanical properties. The melting point is also lowered. Lower melting temperatures makes casting easier with needs less energy and requirement.

From the phase diagram of Cu-As binary system, it can be seen that copper and arsenic form a solid solution (α-phase) up to about seven percent arsenic (Figure 3.9). If the concentration of the arsenic is increased (Scott, 1991) beyond seven percent, an intermetallic compound domeykite (Cu_3As) forms, which has about 27 wt% arsenic.

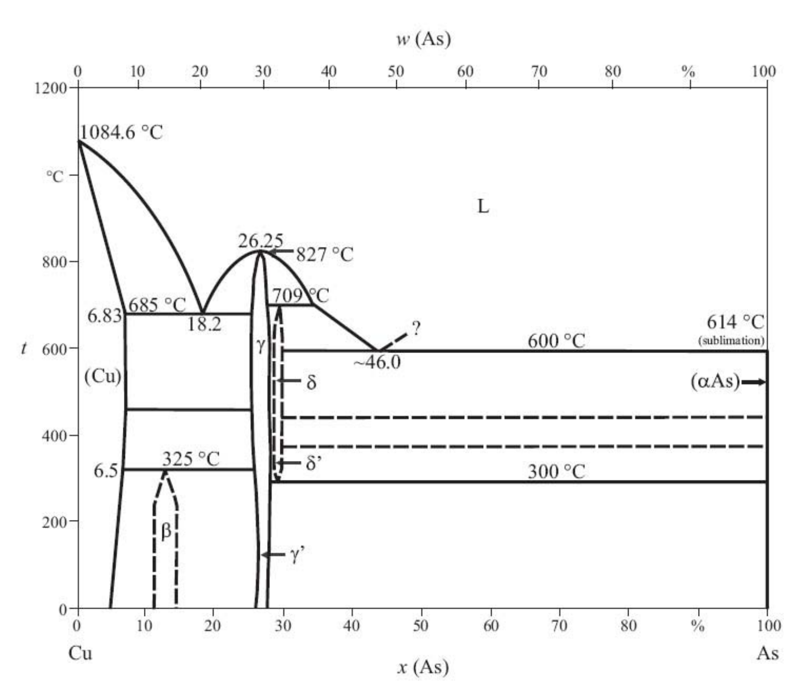


Figure 3.9. Phase diagram of the Cu-As binary system (Scott, 1991)

Domeykite has silvery color and may form at the surface of Cu-As alloys by reverse segredation.

Arsenic is usefull for increasing the hardness and strength of copper. In addition to these properties, arsenic also acts as a deoxidizing agent in copper. During the smelting process arsenic reacts with the oxygen in the medium to form arseneous oxide, which is insoluable in copper. Because oxygen is used by arsenic, copper do not produce copper oxide. This is also an advantage, because copper oxides are brittle and have low ductilitity (Charles, 1967).

Arsenic causes an increase in the recrystallization temperature of the copper. Recrstallization temperature is the temperature at which the metal retains its strength obtained by cold working. Thus, copper becomes more suitable for hard working (Charles, 1967).

Arsenical copper is used until the first half of the second millenium B.C. It is then slowly substituted by bronze (Cu-Sn alloy). The mechanical properties of arsenical copper and bronze are nearly the same. The main reason of this replacement is the difficulty of controlling arsenic content in the alloy. It is not possible to produce copper-arsenic alloy at an exact percantage by the ancient metallurgists without knowing the arsenic concentrations in the ore.

Arsenic minerals are also toxic. This disadvantage may also be the reason for its replacement by bronze. Anyone smelting arsenic containing ores to produce arsenical copper would run the risk of health problems by poisoning. A new material, having the same properties and does not have any health risks must be replace the other one (Charles, 1967).

3.3.2. Copper-Tin Alloy (Bronze)

Bronze objects began to appear in Anatolia and Near East at the beginning of the third millenium B.C. At this period arsenical copper was also in use. During the first half of the second millenium B.C. bronze became the dominant metal. During the second half of the second millenium bronze almost completely replaced the use of copper-arsenic alloy.

Bronze is an alloy of copper and tin. Tin is a silvery metal with a low melting point (238^{0}C). Its major mineral is cassiterite (SnO_2), which is found in the magmatic rocks. Cassiterite is usally found together with hematite, pyrite, arsenopyrite and chalcopyrite. It can be easily reduced by using charcoal, unless it contains high amounts of iron (Pearce, 1979). It is easy to produce bronze by melting proper amounts of copper and tin metals in a crucible. Bronze can also be produced by co-smelting proper amounts of copper and tin ores. Another bronze production method is cementation. In this case, cassiterite ore is mixed with charcoal and added on to the molten copper metal.

In Figure 3.10., the phase diagram of copper tin binary system is shown. Copper and tin form a solid solution (α-phase) with tin concentration up to 13.5 percent (Scott, 1991). Tin concentration above two percent increases the mechanical properties of copper. On the other hand, good quality bronzes have tin content between 8-10 percent.

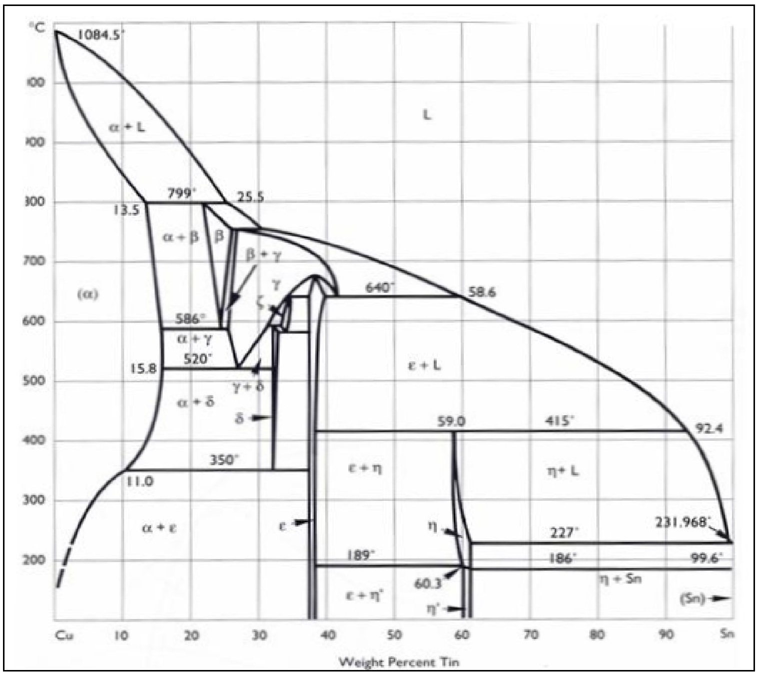


Figure 3.10. Phase diagram of Cu-Sn binary system (Scott, 1991)

Copper which contains roughly 10 percent tin and arsenical copper which contains 5-6 percent arsenic are nearly the same in hardness property.

3.3.3. Cu-As-Sn Ternary Alloy

The ternary alloy of Cu, As and Sn is sometimes found in ancient copper based artifacts. This alloy does not have better mechanical and hardness properties than bronze or arsenical copper. Therefore, there is uncertainity in the reason for its utilization. It is possible that high contents of both alloying elements in a copper based artifact may result from the remelting of the scrap metal. Another possibility could be the addition of arsenic to bronze during smelting in order to increase its casting ability (Charles, 1967). It may also be used when tin was not available.

3.3.4. Other Alloys of Copper

Brass is another important alloy of copper, which is composed of copper and zinc. Zinc can dissolve in copper and form a solid solution up to 30 percent (Figure 3.10), (Northover, 1998). If the zinc level is between 15-20 percent, the alloy will have the highest ductility. Zinc metal has a low boiling point (907^0C) and thus during smelting it vaporizes and forms zinc oxide. The first reduction of zinc from its ores was achieved in the 13th century A.D. However, during the Bronze Ages high zinc containing copper objects was quite common. Its production was made either by cementation method or co-smelting copper and zinc ores. Brass, zinc alloy, was mainly used for coinage and decorative purposes.

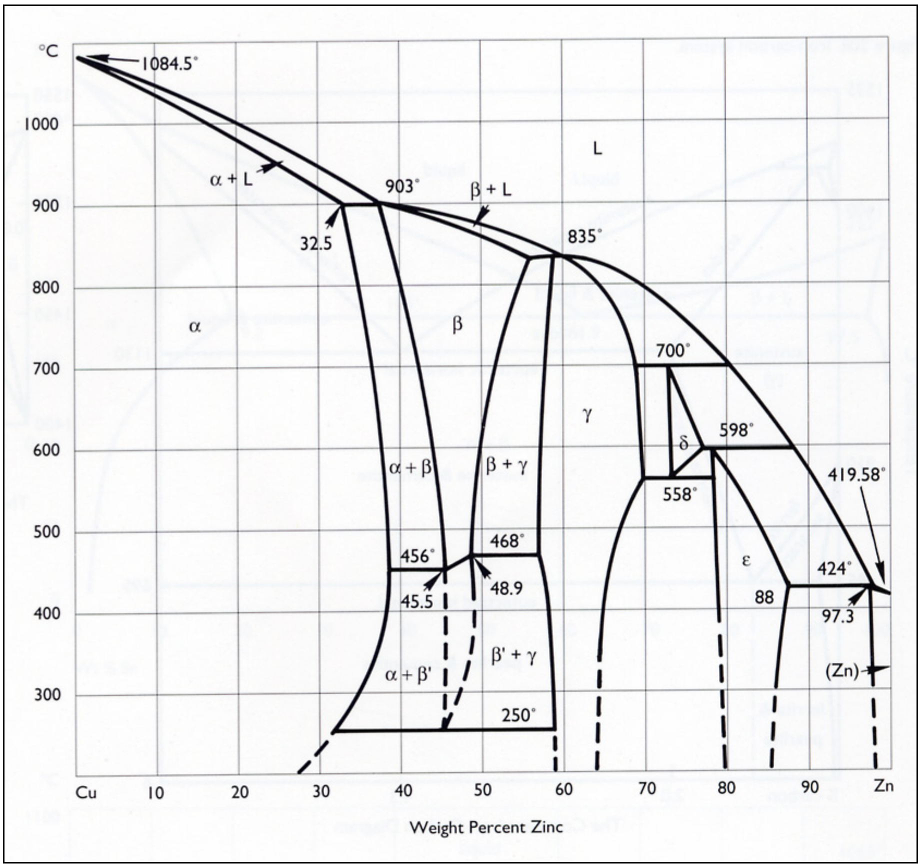


Figure 3.11. Phase diagram of Cu-Zn binary system (Scott, 1991)

Copper-antimony alloy is a rare copper based alloy generally was used in the production of ornamental, cult and prestigious objects during antiquity. During the Bronze Ages, few copper-antimony objects are found. Like arsenic, antimony is also partially soluable in copper and forms solid solution up to 5.8 percent (Figure 3.12), (Scott, 1991). At the eutectic composition the melting point of the alloy drops to 645^0C. The viscosity also decreases and copper-antimony alloy becomes an ideal material for casting. Another property of this alloy is its color when it contains ten percent antimony. At this composition copper-antimony alloy looks like gold. If the percent of antimony increases above 20 percent, its color becomes silvery gray . Copper- Antimony alloys are extremely brittle and can not be shaped by hammering.

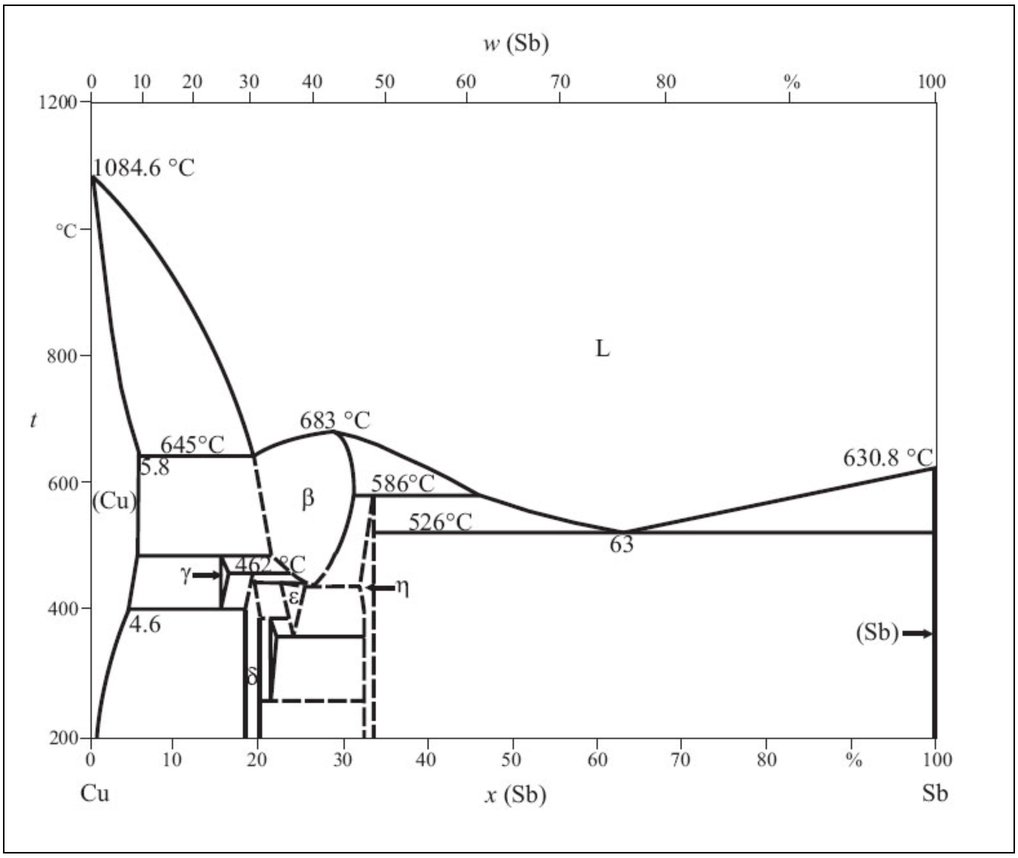


Figure 3.12. Phase diagram of Cu-Sb binary system

3.4. Ore Sources around Tarsus

3.4.1. Central Taurus Range

Central Taurus Mountain Range and especially Bolkardağ region has major deposits of argentefereous lead and gold .There are extensive evidence that these deposits have been exploited during antiquity (Yener *et al*., 1989). On the other hand, Central Taurus Range has limited copper ore deposits. Some copper deposits are reported near Namrun, Kızılca, Sarıkavak, Nergizlik and Sarıhısır-Hasançiftliği. However, there is no information about ancient workings (Ryan, 1957).

MB/LB copper pin from Mersin and EB III lead coil from Tarsus have lead isotope ratios with high probability to originate from Central Taurus ore sources (Yener *et al.*, 1991).

Similarly, lead isotope ratios of several lead and silver artifacts from the third millenium B.C. context of Troy and Mesopotamian settlements like Tello, Assur and Knaferje also overlap with the Central Taurus ore sources indicating active metal trade between Cilicia and Mesopotamia during the third millenium B.C. (Yener *et al.*, 1991). It is obvious that the rich Central Taurus ore sources were used since the beginning of ancient metallurgy.

3.4.2. Amanos Range

Amonos mountain range along the Amuq plain has rich copper ore deposits. These are located at Güvenç, Domuzdamı, Karacaören, near Hassa, Akarca near Iskenderun and Kisecik near Antakya. Only region with evidence of ancient metal working is Kisecik (Ryan, 1957).

3.4.3. Kestel Tin Mine

For a long time there was no documented source of cassiterite in Anatolia and Near East region which is necessary for bronze production. Recently an ancient tin mining and smelting site was discovered at Kestel/Göltepe which is located about 170 km. North of Tarsus (Figure 1.1).

Kestel tin mine is located 4 km. west of the town of Çamardı. It is an important cassiterite source. Cassiterite was mined and metallic tin was produced at the Göltepe workshop between 2800-2200 B.C. Simple stone tools and fire setting marks are the evidences of the surface and underground mining activity. (Yener, 1989; Willies, 1995; Earl and Özbal, 1996; Yener, 2000).

Kestel/Göltepe has a strategic location, thus it could easily supply tin for bronze utilization through the Anatolian sites during the third millenium B.C. Any shipment of tin to south must have passed through Taurus via Cilician Gates. It is, however, very difficult to document the role of Tarsus for tin trade during the third millenium B.C. at this time.

4. METHODS USED

In this study two different atomic absorption spectroscopy methods were used to determine the elemental composition of the samples. Cu, Sn, Pb, Sb, Ni, Fe, Co, Ag and Zn contents of the samples were determined by flame atomization method. Au and As contents were determined by carbon rod atomization.

4.1. Atomic Absorption Spectroscopy

4.1.1. Principles

Atomic absorption spectroscopy is based on the principle of determining the absorption of the electromagnetic radiation by the analyte atoms.

The radiation interacts with the atomized gasous analyte atoms. Light absorption is a function of concentration which is known as Beer-Lambert Law (Formula 4.1).

$$A= \log I^0/I = \epsilon lc \qquad \text{(Formula 4.1)}$$

Where,
A = Absorption
I^0 = Intensity of the initial radiation
I = Intensity of unabsorbed radiation
ϵ = molar absorptivity (constant)
l = path length of the radiation in the analyte solution
c = concentration of the anayte (mole/liter)

Hollow cathode lamps are used as radiation sources. The cathode of the hollow cathode lamps are made out of the desired element. The lamp emits the radiation at some energy of the anayzed element. This radiation is specific for each element so the lamp emits narrow bands of radiation. The electrons of the analyte atom that are at the ground state absorb the radiation and exited to higher energy levels. By measuring the intensities of initial and transmitted radiation, the magnitude of the absorption is determined. To determine the concentration, the absorption value is plotted on a calibration graph, is made by measuring the absorption of three or four solutions of known concentration of the element.

4.1.2. Flame Atomic Absorption Spectroscopy

Flame atomization is most widely used atomic absorption technique. The analysis of one sample takes a few seconds. In this method a solution of analyte is first aspirated into a nebulizer that converts it into a “nebula” which is then sprayed into a flame. The flame creates a hot, gaseous medium where the metal ions are reduced to atomic state. These reduced atoms in the flame then absorbs the radiation emitted by the hallow cathode lamp. All elements use different flame temperatures and different conditions according to their melting point, boiling point, ionization potential and degree of interference by other elements and the matrix.

With different type of gases and different fuel to oxidant ratios various temperatures between 2500-3000^{0}C are achieved. The most common gas combination is air-acetylene. In this study only nitrous oxide acetylene combination is used to determine tin. This combination creates a reducing flame at a higher temperature and with higher atomization efficiency (Ingle and Crouch, 1988).

4.1.3. Graphite Furnace (Carbon Rod) Atomic Absorption Spectroscopy

In this method; 5-10 µl sample solution is injected in to a graphite tube that is heated electrothermally. The heating process consists of three steps. The first step is desolvation. Here the solvent is evaporated at 100-110 ^{0}C for 10-30 seconds. The second step is ashing. The sample is heated up to 350-1000 ^{0}C for 10-20 seconds in order to remove any organic residues. In the last step which is known as atomization, the temperature is raised up to 2500-3000 ^{0}C so the analyte is reduced to atomic state which is then vaporized. The characteristic lines emitted by the hollow cathode lamp absorbed by the atomic vapour.

During the atomization step an inert gas must be purged through the tube in order to prevent the oxidation of the graphite electrodes. In this study N_2 gas is used. For this purpose H_2 can be also used.

Graphite tube atomic absorption spectroscopy gives better results in detection limits than flame atomic absorption spectroscopy, because the residence time of the sample is longer. In this study, carbon rod method is used for the determination of arsenic and gold. A comparison of detection limits of flame and graphite furnace spectroscopies for the metals analyzed in this study is given in Table 4.1 (Hughes *et al.*,1976). The instrument parameters that are used in As and Au determination in this study are given in Table 4.2.

Table 4.1. Typical atomic absorption detection limits of the elements analyzed (Hughes *et al.*,1976)

ELEMENT	FLAME (ppm)	GRAPHITE (ppm)
Cu	2.50	0.1250
Sn	25.0	2.5000
As	250	0.2500
Ni	5.00	2.5000
Pb	25.0	0.1250
Fe	13.0	0.0500
Ag	50.0	0.0125
Zn	2.50	0.0025
Co	25.0	1.0000
Sb	100	0.5000
Au	25.0	0.2500

Table 4.2. Graphite furnace instrument parameters for As and Au analysis

Element	Wavelength	Lamp Current	Slid Width	Drying	Ashing	Atomization
As	193.7 nm	7 mA	0.5	100^0C 15 sec.	900 ^{0}C 10 sec.	2700^0C 2.5 sec.
Au	242.8 nm	5 mA	0.5	110^0C 10 sec	700 ^{0}C 20 sec.	2100^0C 1.0 sec.

4.2. Experimental Methods

4.2.1. Instruments Used

- Varian SpectraAA 250-Plus atomic absrption spectrometer
- Varian CRA-90 carbon rod atomizer

4.2.2. Sample Preparation

From each metal artifact roughly 5-20 mg sample is taken by drilling. The samples are dissolved in 5 ml of aqua regia and diluted to 25 ml in volumetric flask using 6N HNO_3. From the original sample solution further dilutions are made to 100 ml. The dilutions are made with diionized water. For the analysis of Sn, Ni, Pb, Fe, Ag ,Zn, Co, As and Sb mostly the original sample solution is used but if needed diluted ones are also used. For the analysis of Cu diluted samples are used.

Gold is present in most of the samples at very low levels. Because of this reason a preconcentration step is applied to the sample solution. The gold ions are first converted to gold chloride complex by addition of 2.5 ml. of concentrated (37 % by volume) hydrochloric acid. The gold chloride is soluable in organic solvent. It is extracted from the aqueous medium by 5 ml. of water saturated methyl isobuthyl ketone (MIBK). The organic layer with gold complex is taken as analyte (Haddon and Pantory, 1980).

5. MATERIAL

5.1. Definition and Classification of the Arrowheads

An arrow is a missile shot from a bow. The technology was invented by our distant ancestor in Africa during the later Acheulean period, circa 400,000-200,000 B.P. This technology involved knocking bits of stone off a hunk of rock to create sharp points. Archaeologists call this technique the Levallois technique or Levalloisian flaking industry.

During Middle Paleolithic Age beginning around 166,000 years ago, Levalloisian flake tools were refined and became quite abundant. It is during this period that stone tools were probably first attached to spears. They were almost certainly used at the end of a long shaft, and were used to help hunt big mammals for food, either by hurling the spear at the animal, or by thrusting it into the animal at close range.

The bow and arrow, dates to the Paleolithic Ages. All types of hunting, the spear, the bow and arrow, were used today around the world, reminicent of what our ancestors were using on daily basis.

The parts of an arrow are the head, the barb-piece, fore shaft or stele, and feathering.

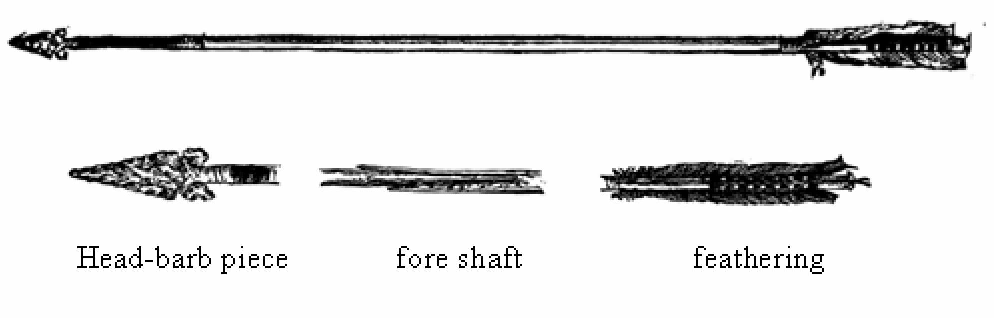


Figure 5.1. Parts of an arrow (Mason, 1891)

An arrowhead is the pointed striking end of an arrow. It is made out of a different types of material, such as flint, obsidian, copper, bronze or iron, depending the materials available. An arrowhead is composed of a blade, stem or butt, and tang (Figure 5.1.), (Mason *at al.*,1891).

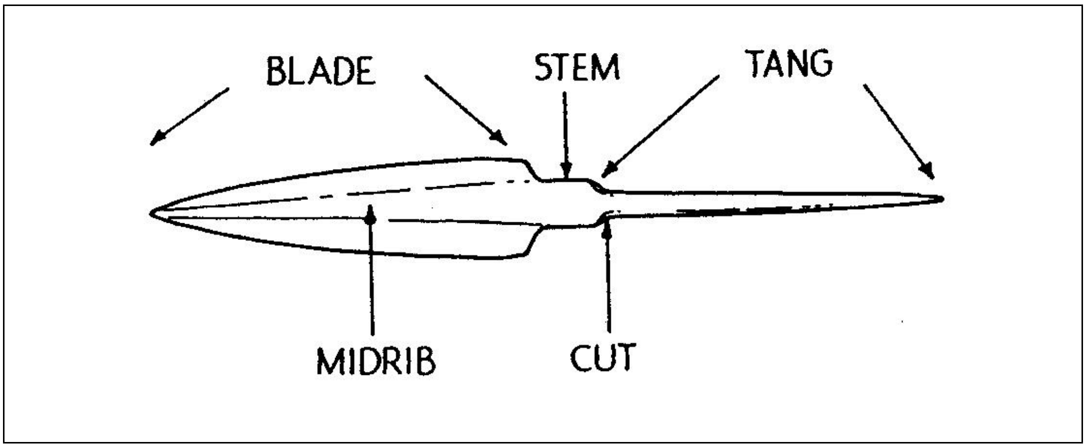


Figure 5.2. Arrowhead components (Moorey, 1971)

In this study, the arrowheads are first classified according to their tang. Further classification was made according to the blade and other morphological variations of the blade.

5.2. Classification of the Arrowheads According to Tang

The arrowheads in this study are classified into three main groups depending on how they are attached to the fore shaft. The arrowheads can be attached to the fore shaft either by a socket or by a tang which may be straight or butted.

5.2.1. Socketted Arrowheads

In socketted arrowheads the shaft is inserted to a socket at the back of the arrowhead (Figure 5.3). Some examples of socketted arrowheads are shown in Figures 5.3, 5.4, 5.5.

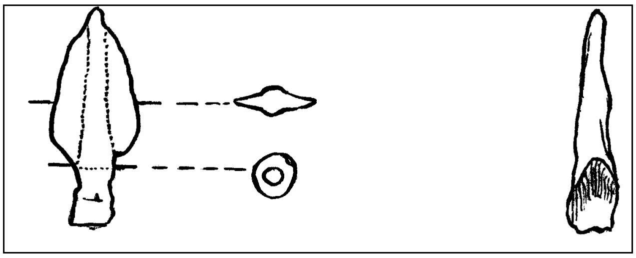


Figure 5.3. Cross-section of a socketted arrowhead

Spur, which is commonly observed with the socketted arrowheads is a small hook attached near the socket of the arrowhead (Figure 5.4)

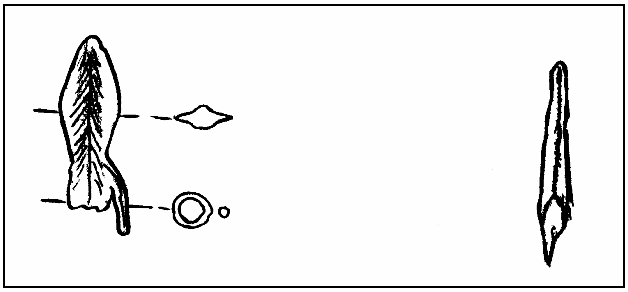


Figure 5.4. Socketted arrowhead with spur

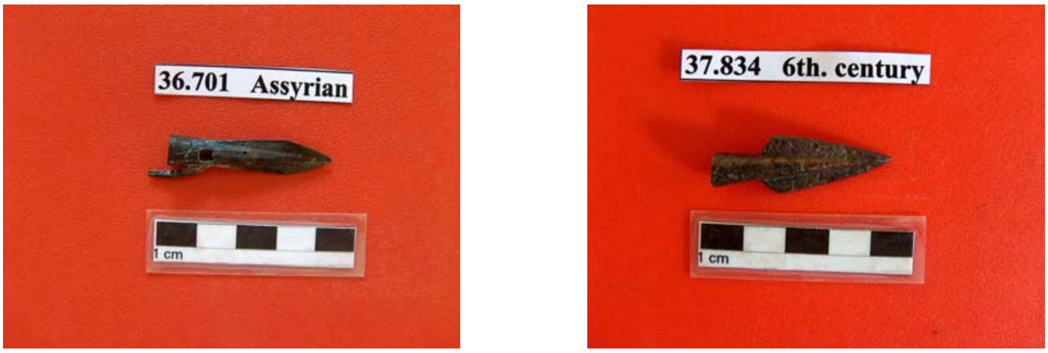


Figure 5.5. Pictures of socketted arrowheads

5.2.2. Straight Pin Arrowheads

Straight pin arrowheads have a thin, straight tang (Figures 5.6, 5.7).

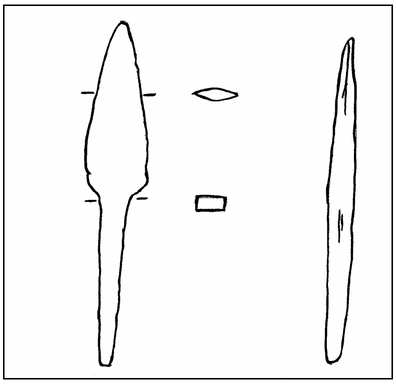


Figure 5.6. Cross-section of a straight pin arrowhead

Figure 5.7. Pictures of straight pin arrowheads

5.2.3. Butted Pin Arrowheads

Arrowheads that are classified in this group also has a straight tang. The difference is a wider butt between the blade and the tang (Figures 5.8, 5.9).

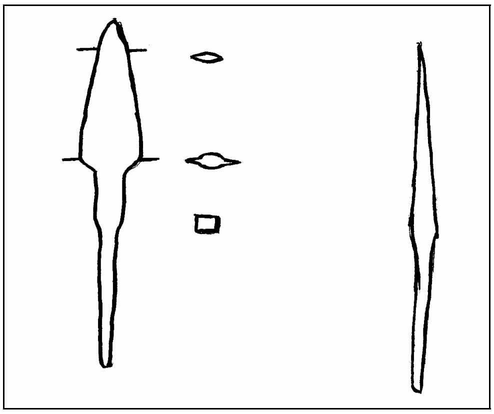


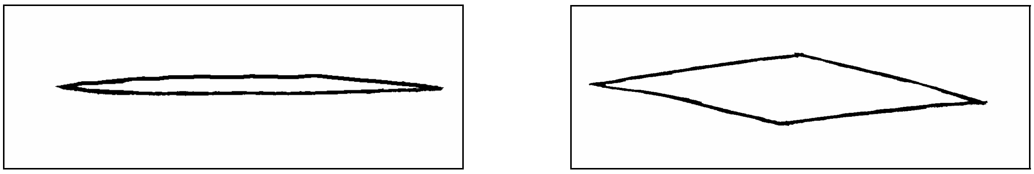
Figure 5.8. Cross-section of a butted pin arrowhead

Figure 5.9. Pictures of of butted pin arrowheads

5.3. Subclassification of Arrowheads According to Blade

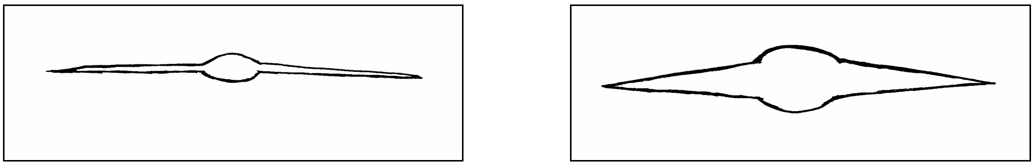
5.3.1. Cross Section of the Blade

The cross section of the blade is another important parameter. The cross section of the blade can be flat, flat with midrib, rhombic or rhombic with midrib. Examples of blade cross-sections are shown in Figure 5.10 and Figure 5.11.



flat

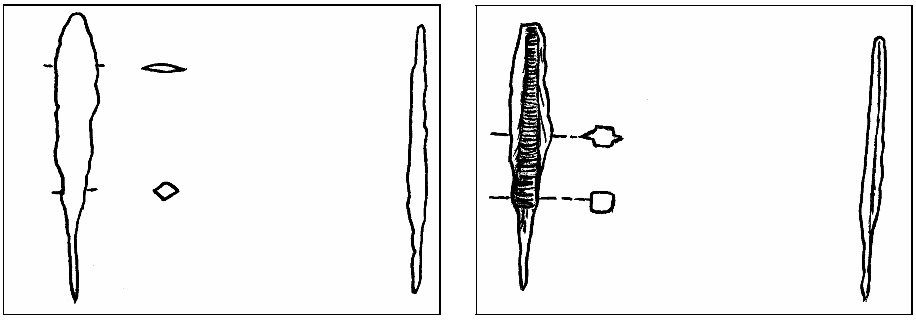
rhombic



flat with midrib

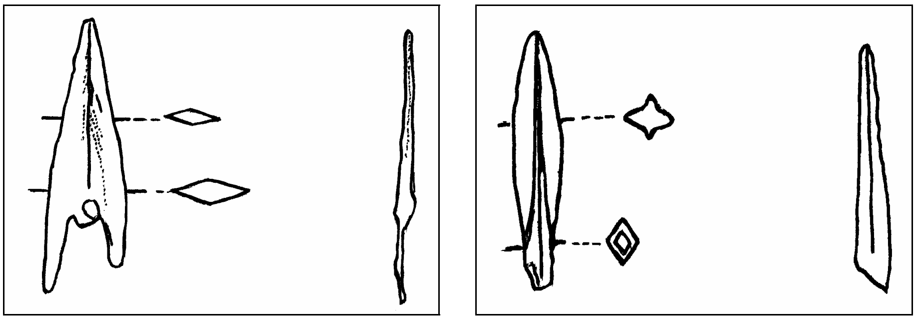
rhombic with midrib

Figure 5.10. Blade morphologies



flat

flat with midrib



rhombic

rhombic with midrib

Figure 5.11. Variations in the cross section of arrowhead blades

Tribolated arrowheads are another group where the blade has three section. They are only observed in socketted arrowheads.

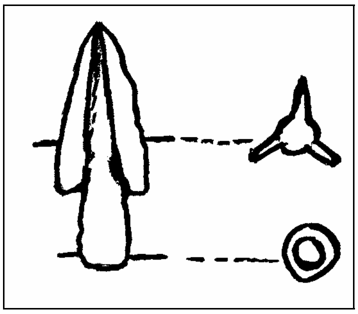


Figure 5.12. Socketted tribolated arrowheads

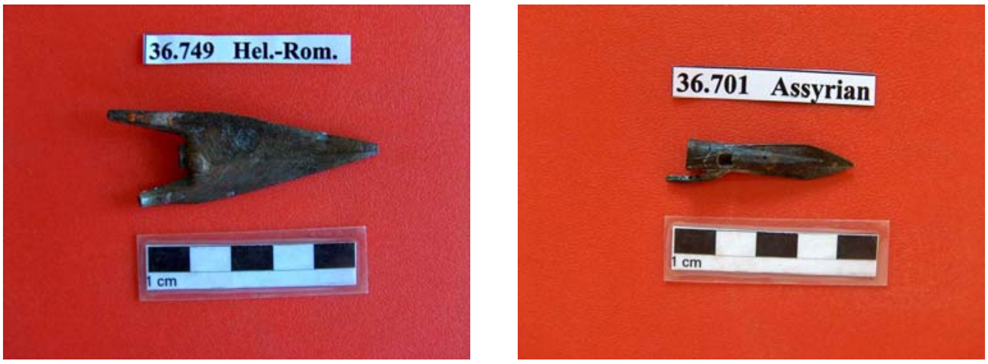
5.3.2. Shape of the Blade and Other Morphological Features

Shape of the blade and other morphological features that are also helpful in classifying the blades of arrowheads which include the point, the edge and the shoulder. The end (point) is subclassified as pointed or round. The edge (stem) is subclassified as sloping or angular. Finally, the shoulder (cut) can also be sloping or angular. Arrowhead can also have a wing or spur or both. Examples of the features of arrowheads are shown in Figure 5.13.

1-pointed end
2-rounded end

3-sloping edge
4-straight edge

5-sloping shoulder
6-angular shoulder



7-wings
8-spur

Figure 5.13. Arrowhead blade morphologies

The type codes assigned to the arrowheads in this study are listed in Table 5.1.

Table 5.1. Type codes of arrowheads

Arrowhead Codes	Arrowhead Classification
180	Socketted, flat blade
181	Socketted, flat blade with midrib
182	Socketted, rhombic blade
183	Socketted, rhombic with midrib
184	Socketted, tribolated
185	Socketted, unclassified
190	Straight pin, flat blade
191	Straight pin, flat blade with midrib
192	Straight pin, rhombic blade
193	Straight pin, rhombic blade with
194	Straight pin, unclassified
195	Butted pin, flat blade
196	Butted pin, flat blade with midrib
197	Butted pin, rhombic blade
198	Butted pin, rhombic blade with
199	Butted pin, unclassified
1	Pointed end
2	Rounded end
3	Sloping edge
4	Straight edge
5	Sloping shoulder
6	Angular shoulder
7	Wings
s	Spur

5.4. Classification and Distrubituon of Tarsus Arrowheads

In this study, a total of 82 copper and copper alloy arrowheads from different periods of Tarsus/Gözlükule is investigated.

Percent distribution of arrowheads according to their tang in the three different periods, namely LBII, IA and H-R are shown in Figure 5.14.

There were only 14 arrowheads from the Late Bronze II. Goldman has classified the Iron Age arrowheads from Tarsus into several groups such as Assyrian, Early Iron, Middle Iron, and sixth century Iron Age. In this study, they are all collected as a single group named as Iron Age. The same method is used for arrowheads from Middle Hellenistic, and Hellenistic Roman periods and are reported as one group.

There were also 30 unpublished arrowheads from Goldman's excavations without any excavation code. Since no definite time period could be assigned to these arrowheads, they are classified as unpublished group.

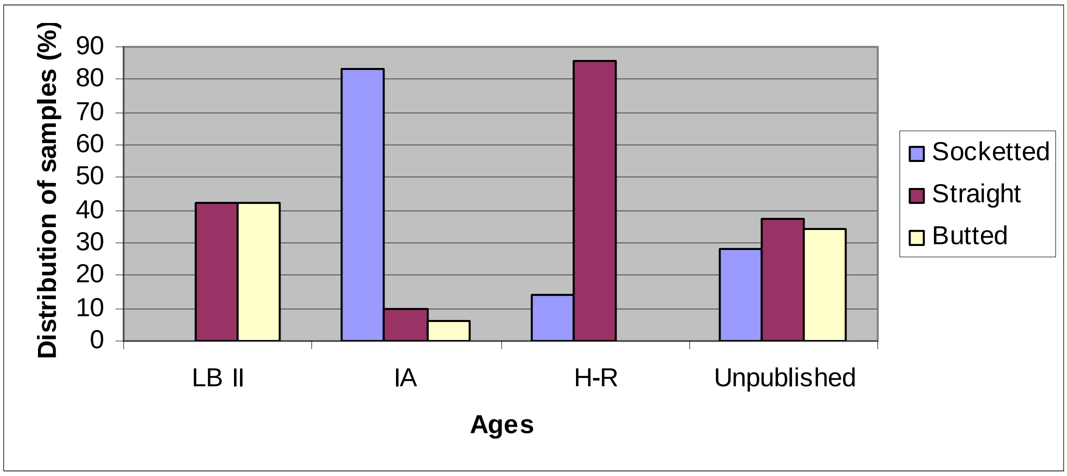


Figure 5.14. Percent distribution of arrowheads versus periods

5.4.1. LB II Arrowheads

In LBII Period, there were no socketted arrowheads. The percentage of butted pin arrowheads and straight pin arrowheads are equal and their percentages are 42%. These percentages does not sum up to 100%, because the rest of the LBII period arrowheads can not be classified typologically, since they are highly corroded (Appendix A, Table A.1). The total classification of the 14 LB II samples are summarized in Appendix A., Table A.1, from item number 2 to 15.

5.4.2. IA Arrowheads

Just the opposite distribution is observed for the IA arrowheads. Socketted arrowheads composites 83% of this period. Straight pin and butted pin arrowheads have very low percentages, 10% and 6%, respectively. 24 of the 28 arrowheads were socketted, two were straight pinned and two were butted. Having a spur is also a characteristic of these group of arrowheads. The samples with item numbers "17" and "34" have butted pin and they are rhombic. In Appendix B and, in Table A.1., items from 16 to 43 shows the IA samples.

5.4.3. Hellenistic-Roman Period Arrowheads

In Hellenistic-Roman period, the straight pin arrowheads became popular once again. The straight pin arrowheads constituting the 85% of the arrowheads in this group. The rest of the arrowheads in the group are socketted. In this period there were no butted pin arrowheads. Item 44 to 52 from Table A.1 belong to this period. There is only one Middle Hellenistic example that is classified as socketted. Nine samples belong to Hellenistic-Roman period. They are all sockketted arrowheads except item "49", which is flat with midrib, so they are all type 191. Out of nine HR period samples, six have wings. Wings seem to be a characteristics of HR period arrowheads.

5.4.4. Unpublished Arrowheads

There is a total number of 30 of unpublished arrowheads from Tarsus with no date assigned. The total collection of this group is summarized in Table A.1 from item number 53 to item number 82.

The unpublished arrowheads were distributed almost evenly in the three major styles. The socketted arrowheads could belong to Iron Age, because in Iron Age most of the samples are socketted. Again, by using the same logic, it can be concluded that the straight pin arrowheads belong to Hellenistic-Roman period and the butted pin arrowheads belong most probably to LBII period.

Among the socketted arrowheads, flat blade with midrib (type 181) is the most common one. The major subgroup in straight pin arrowheads is the flat blade with midrib (type 191). The two dominant subgroups of butted pin arrowheads are rhombic and rhombic with midrib.

5.5. A Comparative Classification System of Arrowheads in Anatolia

Erkanal (1977) has published a morphological study of 68 arrowheads dated to second millenium B.C., namely Middle and Late Bronze Ages. He has used different typological features to classify the arrowheads into various groups.

These second millenium B.C. arrowheads examined by Erkanal are reclassified according to system adopted in this study and is shown in Figure 5.15. The biggest group studied by Erkanal is straight pin arrowheads, nearly 60%, followed by butted pin 33%. The distribution of arrowheads in Erkanal study is similar to the distribution of LBII arrowheads from Tarsus. However, four socketted arrowheads were reported by Erkanal. There were no socketted arrowheads from the Bronze Age Period in Tarsus. The four socketted arrowhead in Erkanal study, however, were not made by casting. They are made by folding a sheet of copper metal into a socket.

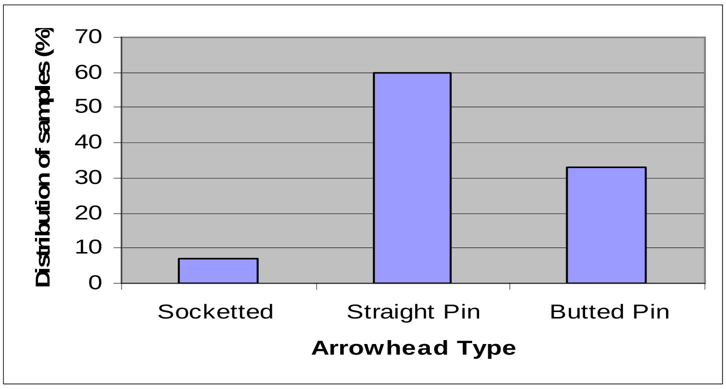


Figure 5.15. Reclassification of arrowhead types from Erkanal’s study

5.6. Arrowhead Technology

Ancient metalsmiths have used different methods to produce metal arrowheads. The earliest arrowheads had flat blades and were made out of sheet of copper by hammering. Later two piece molds are used to produce arrowheads that have especially rhombic or midrib blades.

Two different methods are used to produce socketted arrowheads. The earliest socketted arrowheads, as seen in Erkanal's study, are made by hammering the back end of the arrowhead in a flat sheet and then folding it to create a socket.

Casting socketted arrowheads appeared much later and require better precision. In Figure 5.16, a two piece mould for production of arrowhead is shown. In this method, a clay core is inserted in the cavity between the molds to create a socket.

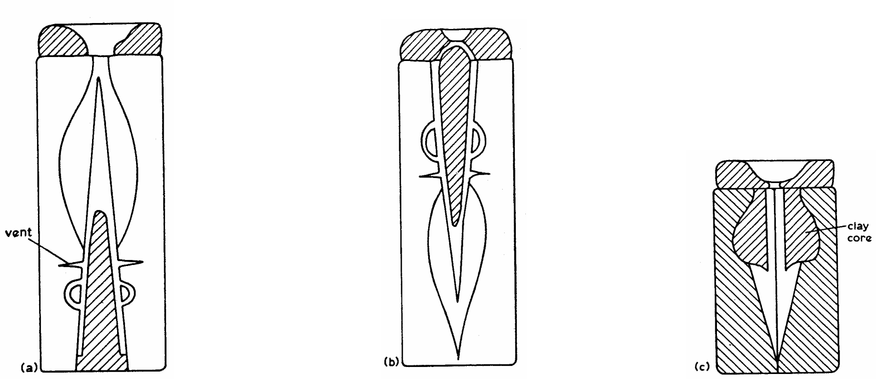
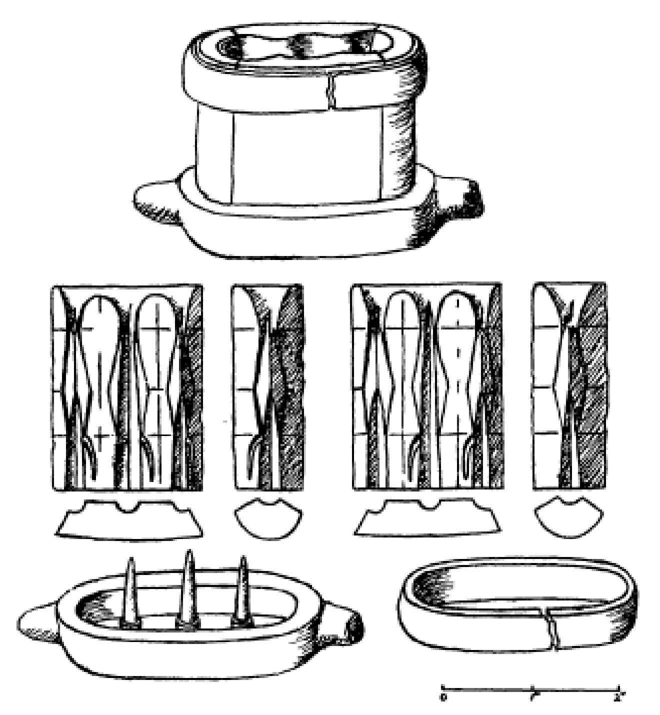


Figure 5.16. Two piece arrowhead mold

Bronze mould found at Mosul and kept in British Museum is shown in Figure 5.17. Three arrowheads can be produced in a single casting. The mold is made out of six sections. The base piece has metal prongs which create the socket.



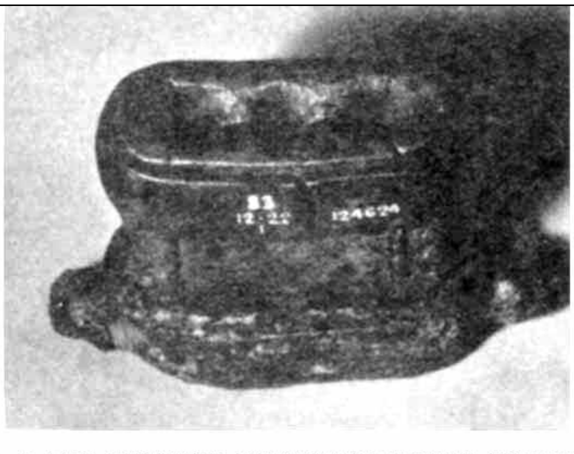


FIG. I. THE SCYTHIAN ARROWHEAD MOULD ASSEMBLED

Figure 5.17. Socketted bronze arrowhead mold of Mosul (Underwood, 1958)

6. RESULTS AND DISCUSSION

In this study 82 arrowhead samples from Tarsus/Gözlükule is examined. Their age, inventory number, weight and type codes are listed in Appendix A.1. The elemental composition of alloying and trace elements are determined by using different methods of AAS (Table 6.1). Eight of the samples were previously analyzed by Kuruçayırlı (2003). The elemental composition of the samples are given in percent. For most of the samples, the total of the elements does not sum up to 100 percent. Main reason is due to the highly oxidixed condition of the arrowheads. In some samples the sum is over 100 percent, due to experimental errors.

Table 6.1. Elemental composition of Tarsus Arrowheads

Item	**Date**	**Cu%**	**As%**	**Sn%**	**Pb%**	**Ni%**	**Fe%**	**Sb%**	**Zn%**	**Co%**	**Ag%**	**Au(ppm)**
1*	**EBIII**	85.16	6.11	0.16	0.05	0.01	0.12	0.13	Nd	0.01	0.05	
2	**LBII**	53.75	0.16	Nd	0.137	0.028	0.255	0.035	0.01	0	0.154	64.8
3	**LBII**	98.44	0.348	Nd	0.004	0.037	0.537	0.196	0.01	0.023	0.009	698
4	**LBII**	91.21	2.69	1.89	0.572	0.024	0.091	0.065	1,034	0.021	0.015	307
5	**LBII**	94.45	0.863	Nd	0.063	0.015	0.43	0.075	0.008	0.027	0.007	362
6	**LBII**	96.3	1.79	Nd	0.008	0.022	0.426	0.015	0.117	0.023	0.008	210
7	**LBII**	98.22	0.297	Nd	0.003	0.012	0.148	0.117	0.016	0.019	0.006	21
8	**LBII**	97.03	0.371	Nd	0.007	0.02	0.615	0.057	0.022	0.028	0.009	212
9	**LBII**	83.18	0.695	7.03	0.197	0.064	0.099	0.119	0.027	0.024	0.008	152
10	**LBII**	87	0.524	2.51	0.114	Nd	0.099	0.289	0.045	0.039	0.008	242
11	**LBII**	93.44	0.615	Nd	0.026	0.217	0.564	0.084	0.012	0.037	0.008	77
12	**LBII**	65.22	Nd	0.121	Nd	0.024	0.112	0.072	1,208	0.016	0.018	
13*	**LBII**	83.75	0.09	8.88	Nd	0.04	0.1	0.04	0.07	0.03	0.02	
14*	**LBII**	92.13	1.96	0.27	0.08	0.05	1.02	0.08	Nd	0.02	0.06	
15*	**LBII**	80.7	0.61	4.32	0.05	0.06	0.15	0.05	0.14	0.06	0.02	
16	**IA**	74.02	0.02	0.667	11.25	0.038	0.115	0.325	0.039	0	0.22	4.73
17	**IA**	88.52	Nd	0.778	0.187	0.079	0.161	0.019	0.015	0	0.102	23.50
18	**IA**	72.8	0.28	Nd	11.1	0.06	0.689	0.231	Nd	0	0.162	3.68
19	**IA**	67.18	0.31	0.446	21.88	0.054	0.058	0.904	Nd	0	0.306	89.80
20	**IA**	64.26	5.99	0.017	0.062	0.027	0.124	0.82	0.059	0.022	0.042	
21	**IA**	46.43	0.06	Nd	15.9	0.062	0.769	0.321	0.009	0	0.214	14.1
22	**IA**	86.9	Nd	1,638	Nd	0.088	Nd	0.089	0.043	0.026	0.028	

Item	Date	Cu%	As%	Sn%	Pb%	Ni%	Fe%	Sb%	Zn%	Co%	Ag%	Au(ppm)
23	**IA**	69.7	Nd	5,495	Nd	0.017	0.071	0.048	2,189	0.018	Nd	**
24	**IA**	56.93	0.03	0.272	8.88	0.023	0.21	Nd	0.047	0	0.101	4.97
25	**IA**	96.13	1.48	1	0.268	0.067	0.567	0.085	0.005	0	0.134	75.1
26	**IA**	57.12	Nd	Nd	32.3	0.028	0.026	0.313	0.023	0	0.091	25.8
27	**IA**	82.93	1.25	3,171	Nd	0.015	Nd	0.594	5,183	0.024	0.089	**
28	**IA**	74.27	Nd	3,682	Nd	Nd	0.026	0.066	1,971	0.016	0.019	**
29	**IA**	64.07	0.22	5.76	0.015	0.046	0.046	0.082	0.045	0.042	0.002	22
30	**IA**	110	0.31	2.85	2	0.033	0.139	0.054	0.08	0.046	0.002	39
31	**IA**	56.93	0.182	Nd	22.69	0.052	0.096	0.527	0.03	0	0.162	20
32	**IA**	80.11	0.02	2	11.25	0.028	0.058	0.253	0.023	0	0.18	16.8
33	**IA**	83.44	0.03	0.414	10.4	0.041	0.222	0.518	0.03	0	0.28	20.3
34	**IA**	96.41	0.02	0.598	0.179	0.034	0.179	0.001	0.004	0	0.101	10.4
35	**IA**	90.6	0.75	1	8.4	0.048	0.712	0.11	0.03	0	0.132	19.6
36	**IA**	60.29	1.89	Nd	25	0.169	0.691	0.308	Nd	0	0.382	18.9
37	**IA**	72.52	0.4	1	14.44	0.047	0.624	0.957	0.079	0	0.252	16.0
38	**IA**	97.3	3.31	Nd	0.023	0.172	0.496	0.143	Nd	0	0.09	15.0
39	**IA**	76.76	Nd	3,342	Nd	Nd	0.021	0.092	0.033	0.024	0.02	**
40	**IA**	82.89	Nd	3,980	Nd	Nd	0.102	0.079	1,092	0.021	0.016	**
41	**IA**	76.71	2.5	2,515	0.037	0.02	Nd	2,109	0.039	0.011	0.015	**
42*	**IA**	125.8	0.32	3.74	4.11	0.04	0.04	0.09	0.15	Nd	0.16	**
43*	**IA**	71.3	2.62	0.19	11.01	0.02	1.01	0.21	0.06	Nd	0.05	**
44	**HR**	69.34	0.04	5	19.06	0.045	0.083	Nd	0.014	0	0.138	52.3
45	**HR**	72.52	Nd	0.128	20.39	0.054	0.119	0.099	0.007	0	0.124	25.7
46	**HR**	69.41	0.86	1	23.92	0.055	0.131	0.025	0.016	0	0.124	42.5
47	**HR**	92.07	0.188	3.06	22.56	0.04	0.189	0.046	0.021	0.034	0.017	27
48	**HR**	68.78	Nd	4,749	Nd	Nd	0.212	0.082	1,587	0.019	0.016	**
49	**HR**	70.91	Nd	2,802	0.016	Nd	0.041	0.055	2,614	0.014	0.015	**
50	**HR**	91.8	Nd	5.14	Nd	0.026	0.07	0.12	0.052	0.042	0.01	**
51	**HR**	62.5	0.37	7.78	21.94	0.04	0.093	0.159	0.019	0.042	0.002	48
52	**HR**	89.53	0.37	1.71	0.253	0.028	0.341	0.058	0.024	0.033	0.002	21
53	**UnPub**	95.69	0.03	Nd	Nd	0.02	0.501	Nd	Nd	0	0.095	3.32
54	**UnPub**	77.54	0.03	0.435	13.2	0.047	0.522	0.623	0.067	0	0.306	8.67
55	**UnPub**	104.95	0.6	7.51	0.085	0.044	0.165	0.01	1,653	0.031	0.014	17
56	**UnPub**	96.15	0.04	Nd	0.088	0.182	0.429	Nd	0.016	0	0.123	7.91
57	**UnPub**	88.87	1.66	0.976	0.026	0.039	0.168	0.002	0.007	0	0.11	13.5
58	**UnPub**	92.21	1.24	0.579	0.386	0.163	0.159	0.005	0.013	0	0.254	368
59	**UnPub**	59.25	Nd	0.108	0.042	0.016	0.156	0.035	Nd	0	0.052	3.49
60	**UnPub**	91.96	0.68	0.87	0.073	0.04	0.274	0.005	0.049	0	0.075	3.47
61	**UnPub**	89.06	0.3	0.923	0.064	0.068	0.351	0.054	Nd	0	0.071	9.74
62	**UnPub**	91.23	0.42	Nd	0.008	0.018	0.328	0.066	0.003	0	0.074	8.90
63	**UnPub**	94.08	0.953	Nd	0.072	0.018	0.135	0.209	0.025	0.025	0.008	77
64	**UnPub**	92.69	1.02	Nd	0.299	0.045	0.123	0.213	0.029	0.028	0.006	74

Item	Date	Cu%	As%	Sn%	Pb%	Ni%	Fe%	Sb%	Zn%	Co%	Ag%	Au(ppm)
65	**UnPub**	88.35	0.666	2.94	0.07	0.036	0.289	0.129	0.056	0.061	0.007	26
66	**UnPub**	72.58	0.383	4.46	20.53	0.054	0.074	0.166	0.046	0.038	0.004	31
67	**UnPub**	74.25	0.154	7.3	0.466	0.052	0.116	0.59	0.041	0.052	0.011	46
68	**UnPub**	37.86	0.13	Nd	0.985	0.029	0.815	Nd	0.061	0.046	0.002	Nd
69	**UnPub**	94.33	0.562	Nd	Nd	0.035	0.264	0.16	0.016	0.02	0.008	12
70	**UnPub**	88.71	0.499	3.78	0.394	0.096	0.106	0.202	0.011	0.021	0.003	77
71	**UnPub**	69.42	0.3	8.05	0.891	0.06	0.324	0.237	0.06	0.076	0.007	34
72	**UnPub**	86.86	0.21	Nd	0.064	Nd	0.311	0.131	0.272	0.051	0.01	23
73	**UnPub**	79.88	0.163	10.48	2	0.098	0.672	0.049	0.072	0.063	0.006	21
74	**UnPub**	0.53	0.16	Nd	0.003	0.032	?	0.071	0.055	0.066	0.003	Nd
75	**UnPub**	74.57	0.479	9.87	2	0.026	0.304	0.226	0.04	0.029	0.009	43
76	**UnPub**	77.99	0.277	10.17	2	0.022	0.127	0.53	0.021	0.036	0.008	42
77	**UnPub**	101.4	Nd	Nd	Nd	0.04	0.253	0.147	0.033	0.025	0.096	**
78	**UnPub**	85.6	Nd	7,588	Nd	0.03	0.009	0.084	0.03	0.03	0.083	**
79	**UnPub**	65.51	Nd	5,158	Nd	Nd	0.089	0.123	0.351	0.022	0.057	**
80	**UnPub**	89.38	0.69	8,717	Nd	0.058	0.058	0.135	0.08	0.051	0.013	**
81	**UnPub**	71.5	0.49	6.591	Nd	0.095	0.248	0.078	1,515	0.02	0.036	**
82*	**UnPub**	92.5	1.19	2.88	0.03	0.03	0.08	0.02	5.78	0.03	0.04	**

* Analyzed by Kuruçayırlı (2003)

** Not analyzed

6.1. Distribution of Alloying Elements of Tarsus Arrowheads

Copper based artifacts that contain over 1% As and over 2% Sn are considered to be an intentional alloy. If an arrowhead has both As concentration above 1% As and 2% Sn, it is considered as a ternary Cu-As-Sn alloy.

6.1.1. LB II Arrowheads

Distribution of the arrowheads from the LBII according to the presence of alloying elements are shown in Figure 6.1. A single arrowhead from the EBIII is also incleded in this group.

In this period almost half of the arrowheads were made out of pure copper (Figure 6.1). It is suprizing to see the use of copper-arsenic alloys in LBII. In this period, no Cu-As-Sn alloy is observed.

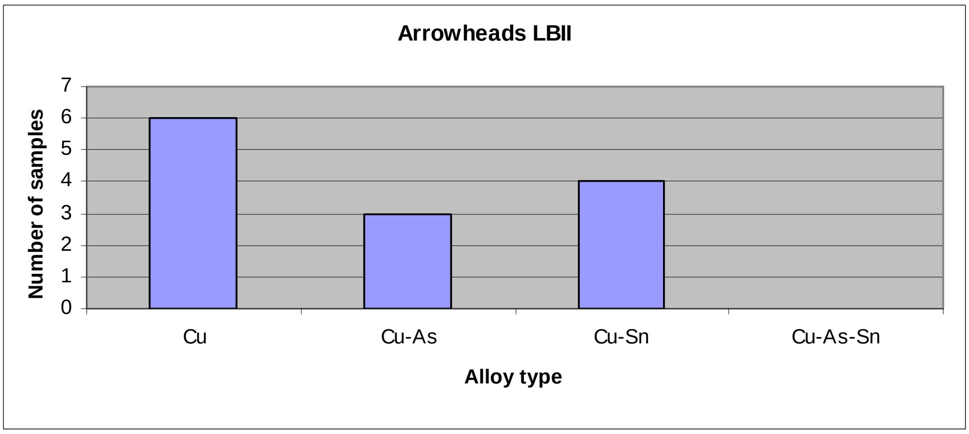


Figure 6.1. Distribution of alloy type of LB II arrowheads

The samples with item numbers “4” and “14” (Appendix A.1) have As concentrations 2.69% and 1.96 % respectively, which are the highest As concentrations in this group.

The samples with item numbers “9” and “13” have Sn concentrations 7.03% and 8.88 % respectively. The Sn concentration in item “13” is the highest in all LBII arrowheads. It is interesting to see that arsenic is used as an alloying element during the LBII, despite at quite low levels. Among the 14 arrowheads only two (items “9” and “13”) can be classified as the bronze.

6.1.2. IA Arrowheads

The distribution of alloy types for the Iron Age arrowheads is shown in Figure 6.2. It is interesting to see that there is hardly any difference in alloying preference when compared to LBII arrowheads. Again pure copper arrowheads constitute the biggest group among the IA samples. Similarly, bronze arrowheads are slightly more than arsenical copper arrowheads.

It is intresting to see arsenic containing, copper object during the Iron Age. In fact, the sample with item number ”20” has an As content of 5.99 %. High tin content was seen in sample “29” with 5.76 % of Sn. There were also couple of Cu-As-Sn ternary alloyed arrowheads.

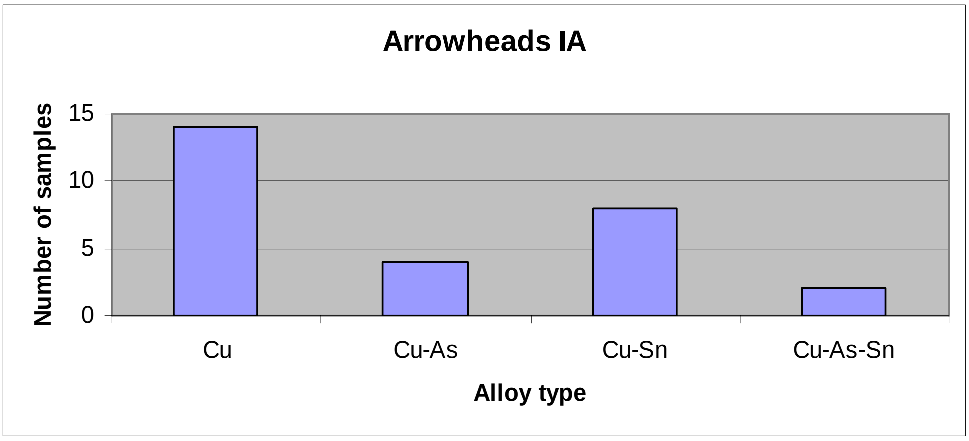


Figure 6.2. Distribution of alloy type of IA arrowheads

6.1.3. Hellenistic-Roman Arrowheads

There is a sharp increase in bronze arrowheads among the Hellenistic-Roman samples (Figure 6.3). Out of nine samples, six were made out of bronze and the rest is pure copper. As was not used as an alloying element. In addition to that, the Sn content of the samples has also increased. The highest Sn content in this group is 7.79 % (sample with item number 51). In Hellenistic- Roman samples, arsenical copper or Cu-As-Sn type of alloys is not observed.

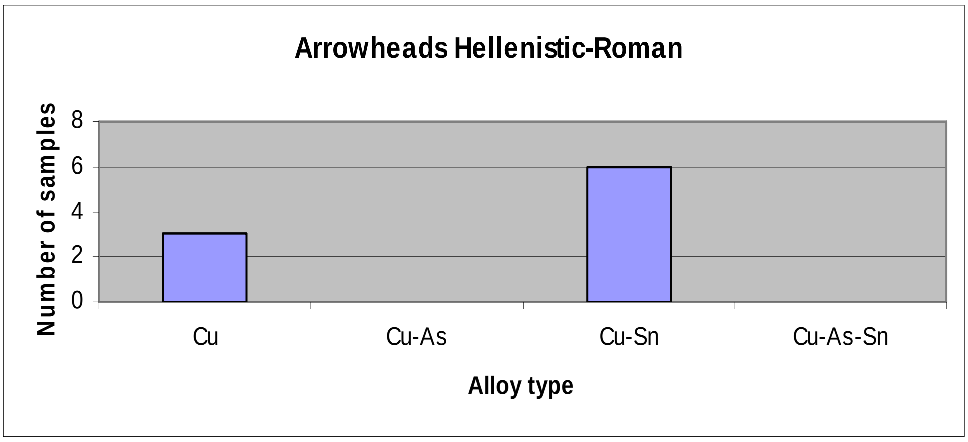


Figure 6.3. Distribution of alloy type of Hellenistic-Roman arrowheads

6.1.4. Unpublished Arrowheads

The distribution of alloying elements in the 30 unpublished arrowheads are shown in Figure 6.4. The most striking feature of Figure 6.4 is the high number of bronze arrowheads. There are also the same number of unalloyed copper arrowheads. The highest value of Sn, among these samples is observed in sample with item number "73" with 10.48% Sn. The sample "76" has also a high Sn% which is 10.17. There are only three arrowheads that were classified as arsenical copper. Among these highest arsenic content was only 1.66% (sample "57").

If one tries to assign possible dates to these unpublished arrowheads with respect to percent alloying elements, pure copper arrowheads can belong to all these periods, however, bronze arrowheads could be from IA or Hellenistic-Roman periods.

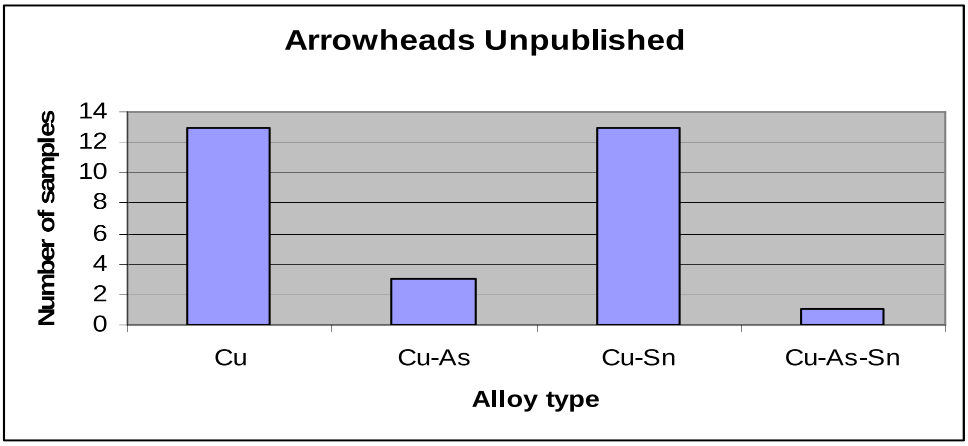


Figure 6.4. Distribution of alloy type of unpublished arrowheads

6.1.5. Comparative Distribution of Alloying Elements among the Periods

A comparative distribution of alloying elements of all arrowheads from the LBII, IA and Hellenistic-Roman periods is shown in Figure 6.5. The percent distribution of pure copper arrowheads in all three periods seem to be almost the same with a slight decrease during Hellenistic-Roman period. Also similar percentage is observed for Cu-As and bronze alloys in both LBII and IA. The percentage of bronze objects has a sharp increase in Hellenistic-Roman period. The ternary alloy of copper is only observed with a small percentage in IA

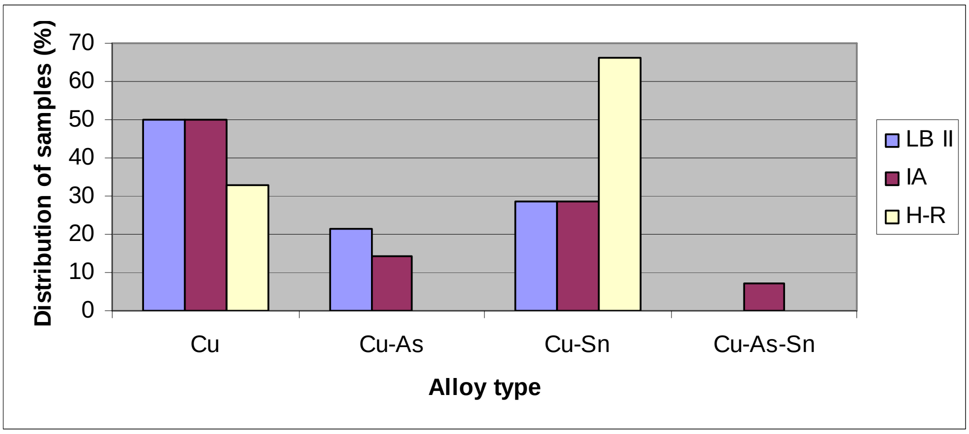


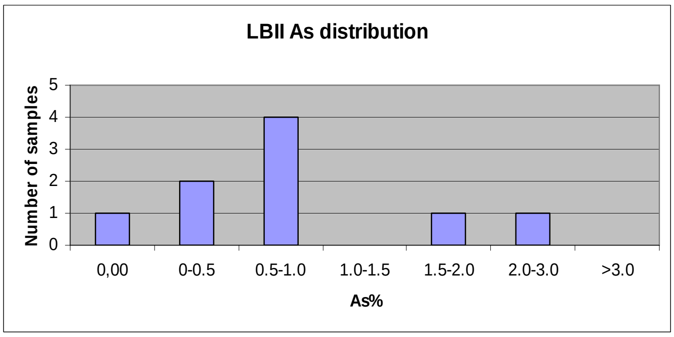
Figure 6.5. The distribution of alloy types versus the periods

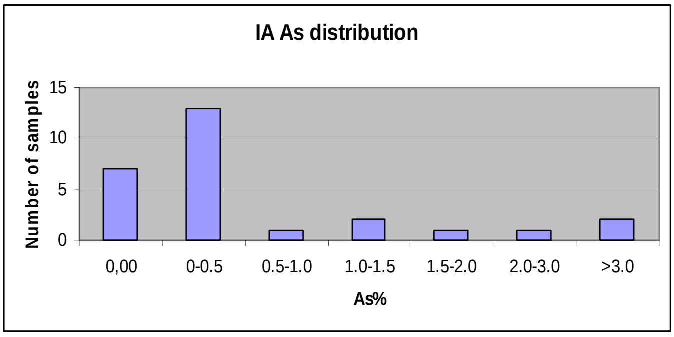
6.1.6. Distribution of Arsenic and Tin Concentrations

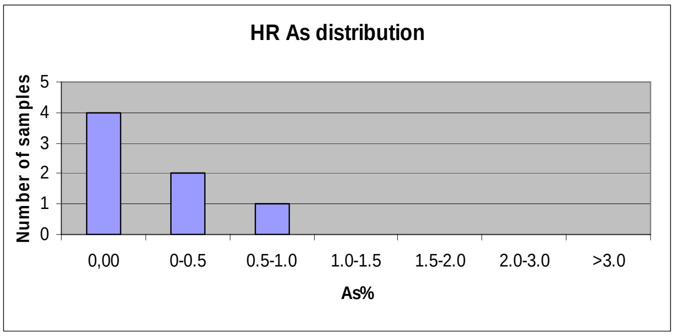
The distribution of As and Sn as alloying elements in the arrowheads studied seem to follow similar trend which is observed in alloys of all copper objects analyzed from the Cilicia region (Kuruçayırlı and Özbal, 2005).

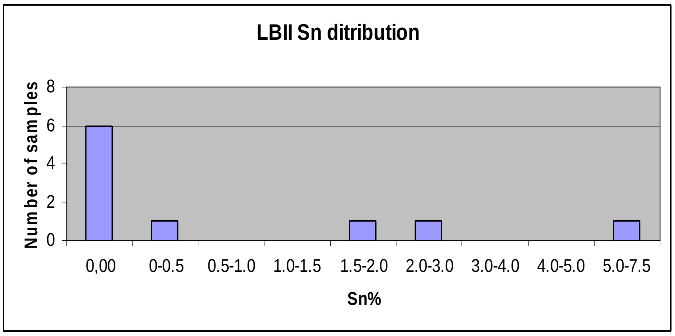
In LBII period, As concentration is mostly, between 0.5-1.0 %. In IA, As concentration in arrowheads is decrased to about 0.0-0.5 %. Trend in decrease in the concentrations of arsenic starting from IA is very clear. Arsenic is at trace element levels in the arrowheads dated to H-R period.

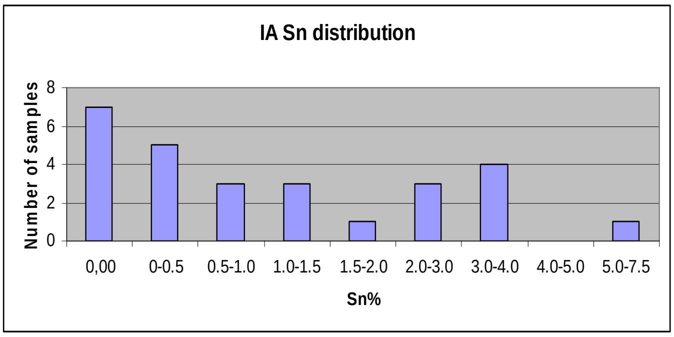
There is an opposite trend in the usage of Sn as an alloying element. Among the LBII arrowheads only one sample can be classified as a true bronze with 5.75% Sn. There is a definite increase in use of Sn in IA arrowheads. The trend becomes much clear with the H-R Period arrowheads (Figure 6.6). Majority of arrowheads belonging to H-R period have Sn levels between 2-7.5%.











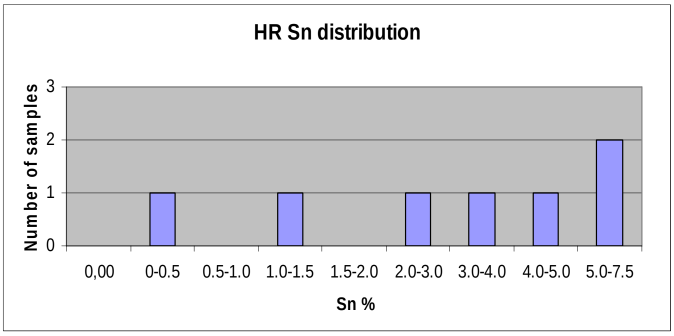


Figure 6.6. Distribution of As and Sn concentration at different periods

6.2. Trace Element Distributions

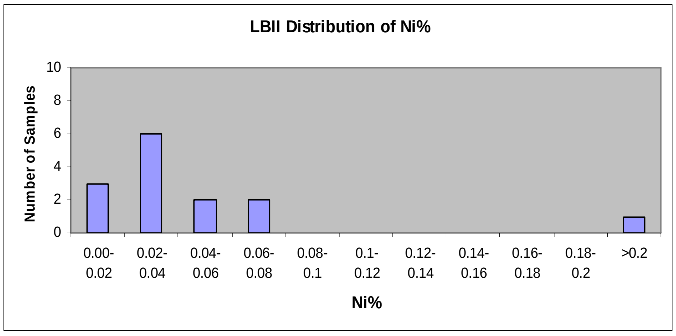
The trace element distributions of the arrowheads examined in this study are listed in Table 6.2. Trace element such as Ni, Sb, Ag, Au, Zn, Pb, Co, and Fe in ancient copper and copper based artifacts are routinely determined. The objective is to see if there is any variation in the concentration of these trace elements between different types of copper objects or between different periods. Trace elements are contaminations that are incorporated into copper objects when copper ores containing these elements at trace levels are smelted. Some trace elements may show considerable variations with respect to ore sources as well as the smelting technology applied. Such work cannot be used to identify the possible ore source, however it is possible to see any change in copper ore utilization within a settlement between different time periods.

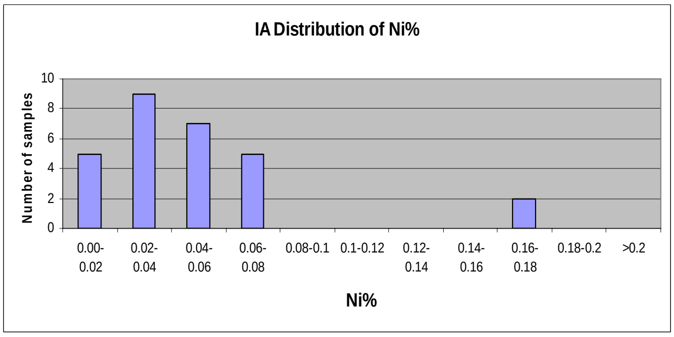
6.2.1. Distribution of Nickel and Antimony as Trace Elements

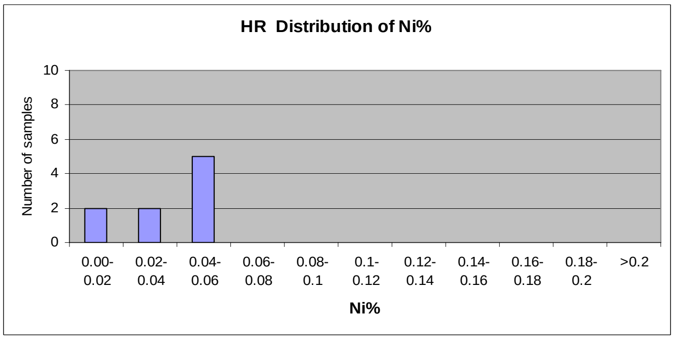
In the copper based artifacts, nickel and antimony are the most important impurities. These two elements accumulate in the metal during smelting. As a result, nickel and antimony have an important role to provide better information about the ore types and sources.

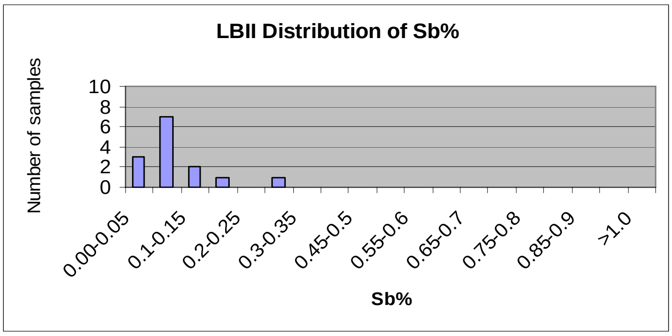
Examination of the distribution of Ni content of arrowhead in Figure 6.7, from the three periods show a very similar pattern. There are couple of sample in LBII and IA with high Ni content. On the other hand higher levels of antimony is observed in the IA arrowheads when compared to LBII and H-R periods. Lowest levels of Sb are seen with the H-R arrowheads.

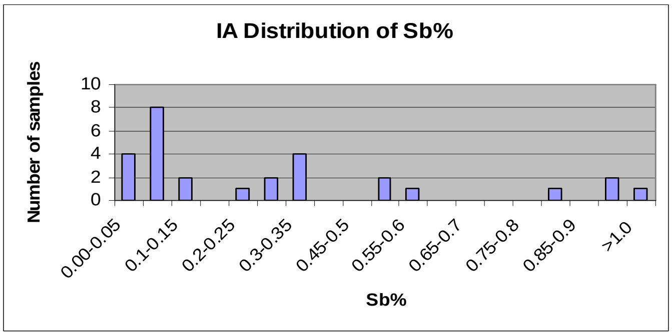
Nickel is a nonvolatile element and during smelting it is incorparated in copper. Since nickel distribution in all three periods are similar, one can conclude that probably same ore sources are utilized. Antimony on the other hand is a volatile element and also highly soluable in copper. Its accumulation in copper, however, is more sensitive to smelting conditions and can show greater variability. This is probably what is observed in the antimony variation among the three periods.


LBII Distribution of Ni%
Number of Samples
0
2
4
6
8
10
0.00-0.02
0.02-0.04
0.04-0.06
0.06-0.08
0.08-0.1
0.1-0.12
0.12-0.14
0.14-0.16
0.16-0.18
0.18-0.2
>0.2
Ni%


IA Distribution of Ni%
Number of samples
0
2
4
6
8
10
0.00-0.02
0.02-0.04
0.04-0.06
0.06-0.08
0.08-0.1
0.1-0.12
0.12-0.14
0.14-0.16
0.16-0.18
0.18-0.2
>0.2
Ni%


HR Distribution of Ni%
Number of samples
0
2
4
6
8
10
0.00-0.02
0.02-0.04
0.04-0.06
0.06-0.08
0.08-0.1
0.1-0.12
0.12-0.14
0.14-0.16
0.16-0.18
0.18-0.2
>0.2
Ni%


LBII Distribution of Sb%
Number of samples
0
2
4
6
8
10
0.00-0.05
0.1-0.15
0.2-0.25
0.3-0.35
0.45-0.5
0.55-0.6
0.65-0.7
0.75-0.8
0.85-0.9
>1.0
Sb%



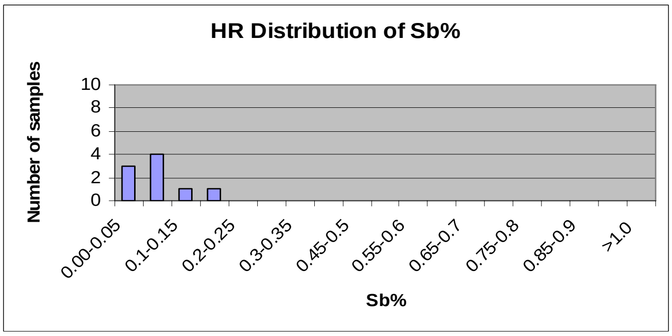


Figure 6.7. Distribution of Ni and Sb concentrations at different periods

6.2.2. Lead in Arrowhead

Among the trace elements determined in this study, lead concentrations were the most surprizing to observe. Lead is almost totally insoluble in copper and generally occurs in ancient copper less then 0.05%. During the Roman Period, it is well known that cheap lead was added to copper as high as 30% to increase volume. In such cases lead solidifies separately as lakes in the copper matrix and causes severe decrease in hardness and other mechanical properties of copper. Generally such mixtures cannot be hammered because they easily crack. However, when lead is added into copper over 2%, it increases the fluidity and makes it much easier to handle during casting.

It was interesting to see that number of arrowheads analyzed in this study had lead levels as over 20% (Table 6.1). It is inconceivable to think that arrowheads with such high levels of lead will have the necessary hardness to penetrate the target upon impact. A total of 25 arrowheads had lead concentrations over 1%. It was realized that arrowheads with high levels of lead were all socketted style. It was soon realized that to increase the mass of these small socketted arrowheads, much denser lead metal has been cast into the small cavity at the center of the blade. While sampling the arrowheads by drilling some of the lead present in the center was contaminating the copper turnings.

Recently a highly deformed piece of metal from Acemhöyük was studied at Boğaziçi University. Originally it was not possible to identify the nature of this objects. Chemical analysis yielded together with copper high levels of Pb and Ni. To understand the nature of this object, a small section was cut, polished and studied under both SEM and Optical Microscope.

Epoxy imbedded picture of the sample is shown in Figure 6.8. In Figure 6.9, the Optical Microscope image of the cross section is shown (50 magnification). The semi curved light colored outer section is the copper casing. The grainy center section is lead. There is a thin corrosion layer between the outer copper casing and the lead at the center.

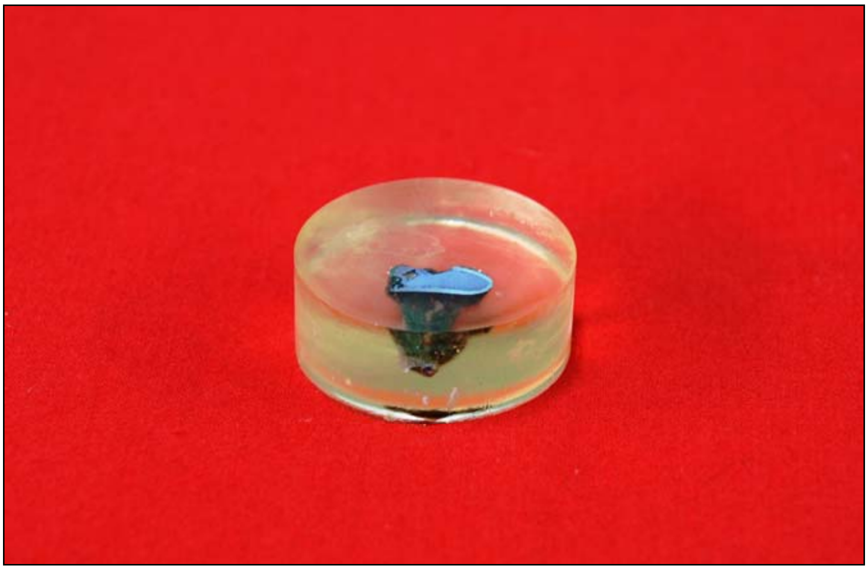


Figure 6.8. Epoxy imbeded picture of Acemhöyük arrowhead

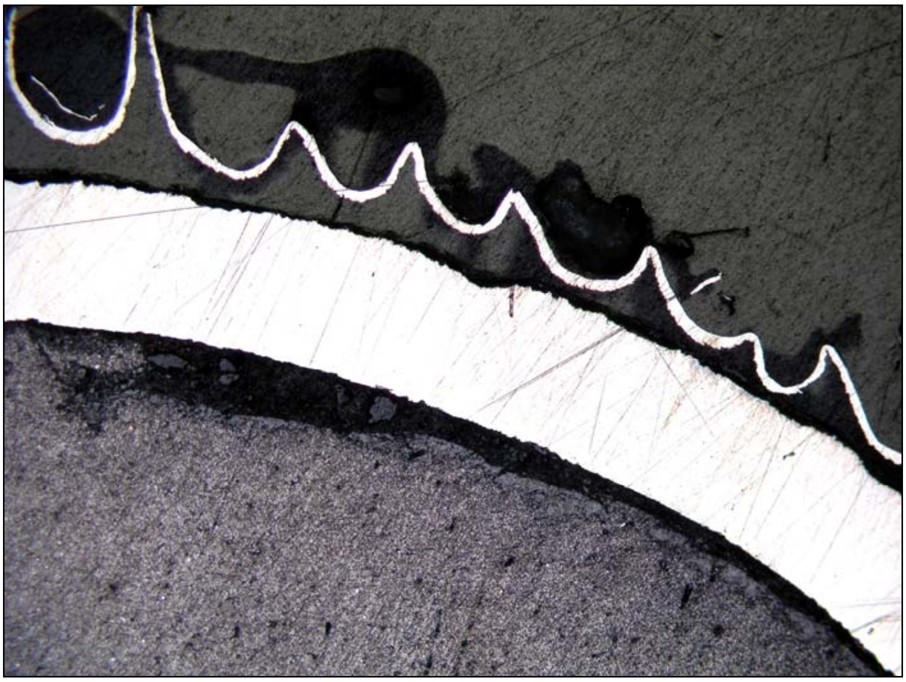


Figure 6.9. Optical microscope image of Acemhöyük arrowhead

Scanning electron microscope images of the same cross section is shown in Figure 6.10. Semiquantitative EDX analysis of the three different layers is summarized in Table 6.2.

Table 6.2. Semiquantitative EDX anaysis of Acemhöyük arrowhead

	Cu%	Pb%	Ni%	Sb%
Outer Cu Layer	64.9	Nd	18	0.14
Corrosion Layer *	23.6	3.16	9.39	0.35
Inner Core	0.35	51.1	Nd	2.58

* Determined as oxides

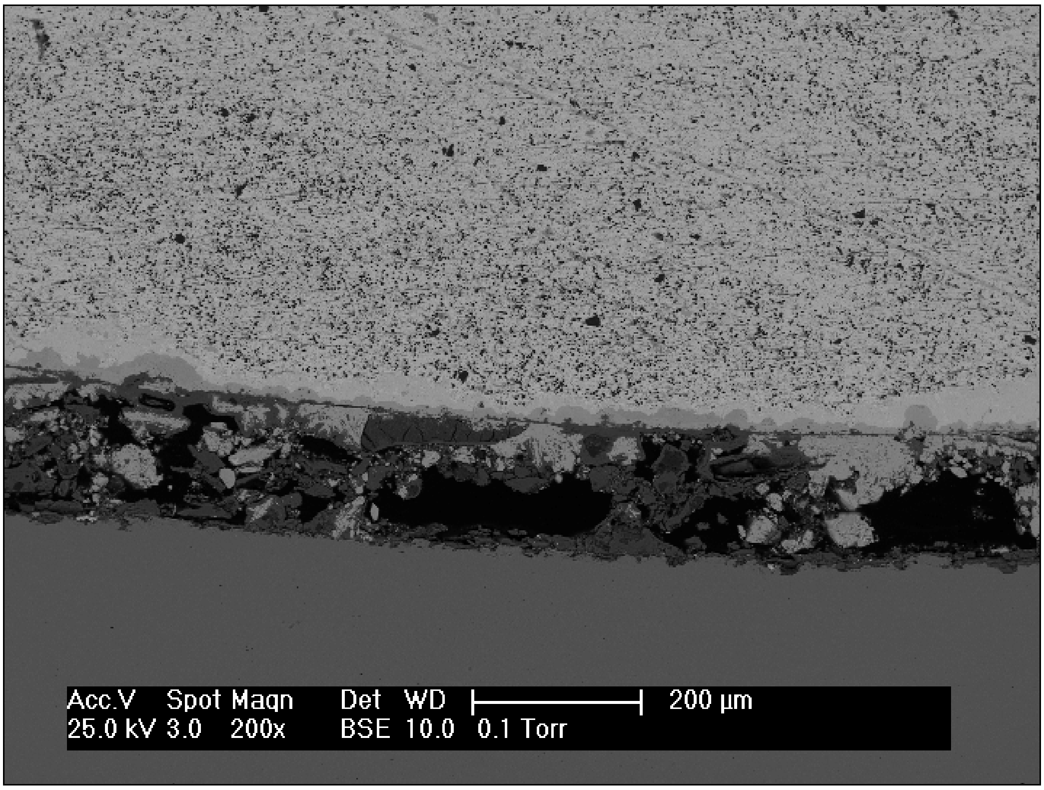


Figure 6.10. SEM of Acemhöyük sample

It eventually became evident that this highly deformed object was a socketted arrowhead that had similar typology as the socketted Iron Age arrowheads from Tarsus. It is thus confirmed that the Scythian style socketted arrowheads traditionally contain lead in the center to increase their mass. The bullets of handguns that are used today have the same technology, i.e. the projectile has a copper alloy case filled with lead metal. Fig 6.11.

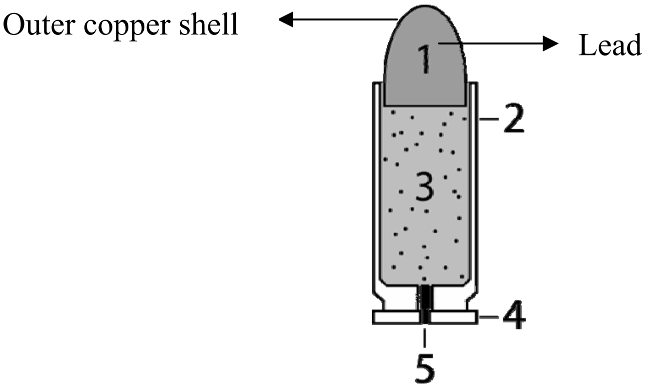


Figure 6.11. Cross section of a modern handgun bullet

The second unique feature of Acemhöyük arrowhead is that it is dated to the beginning of the second the millennium B.C., i.e. the Assyrian Colonial Period. Private communication with the archaeologist responsible at Acemhöyük excavations confirmed that the arrowhead was found in a secure context at the area known as Hatipler Sarayı and belonged to the Assyrian Colonial Period. However, the similar arrowheads from Tarsus are all from the first millennium BC Iron Age. None of the Bronze Age arrowheads studied by Erkanal contained such an arrowhead. If the date of the Acemhöyük arrowhead is correct, tradition of adding lead to increase the mass of arrowheads extends further back by about 800 years.

The final unusual aspect of Acemhöyük arrowhead is the high nickel content of the outer copper casing. Nickel is almost always found in ancient copper objects at trace levels. Recently, analysis of arsenic containing copper objects from the beginning of the third millennium royal grave from Arslantepe showed a linear bimodal correlation in samples that have greater than two percent arsenic and one percent nickel (Hauptmann and Palmieri, 2000). Such metals are believed to have been produced from copper-arsenic ores thought to occur in ophiolithic rocks in the Near East.

Nickel forms a solid solution with copper at all composition (Figure 3.6). Northover (1998), calls such alloys exotic and gives another example from Anatolia. Analysis of a Hittite style Bull from the second millennium BC context of Anatolia contained 17.7 % nickel and 2.1 % cobalt. Further study is needed to determine the source and possible production technology of high nickel containing ancient copper objects. Copper-Nickel alloy was also used as a coinage metal in Bachria, Iran.

6.3. Mass of Arrowheads

One of the important parameter in constructing of an arrow is the balance of the projectile. Generally the lighter the arrowhead the further it can travel (Cotterell and Kamminga, 1990). Depending on particular use such as hunting or warfare, different types of arrowheads with different masses were probably used.

There were considerable difference in the mass of the arrowheads from the three different periods. The avarage, the minimum and maximum mass of the arrowheads are shown in Table 6.3.

Table 6.3. Mass of Arrowheads

Period	Weight (min)	Weight (max)	Weight (avg)	Std. Deviation
LBII	5.3g	16.8g	10.9g	3.7
IA	3.7g	8.0g*	6.0g	1.1
HR	3.4g	18.2g	10.8g	2.8

*IA item “23” not included

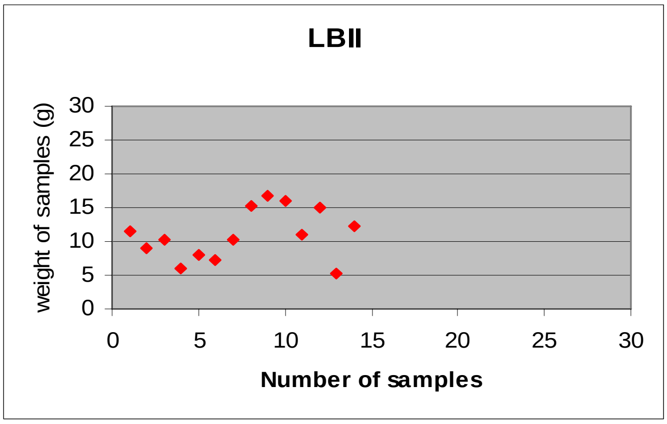
It can be seen that there is a noticible decrease in the avarage mass of arrowheads during the Iron Age. During this period small socketted arrowheads were dominant. There is a straight pin arrowhead (item “23”), that has a mass of 19.6g which is not incueded in this discussion.

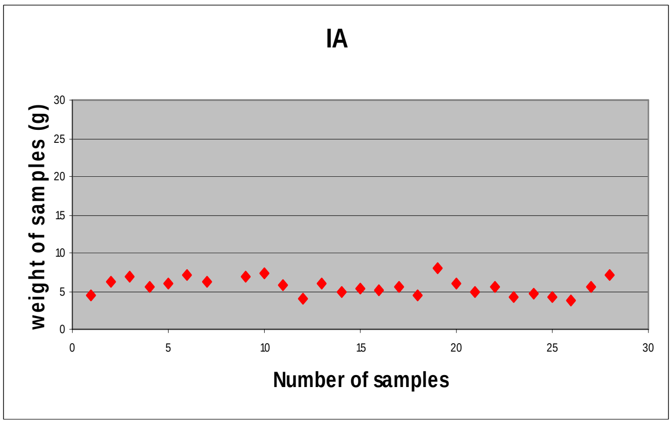
The avarage masses and variations of arrowheads from the LBII and H-R periods are very similar.

6.3.1. Mass Distribution According to Periods

The correlations of the masses of the arrowhead among the periods are shown in Figure 6.12. There seems to be no standardization in the LBII arrowheads. The mass vary between 5.3-16.8 grams. The distribution of mass of arrowheads from the IA, however, is very similar. Except one straight pinned arrowhead in this period, they were all around 6g with a standard deviation of 1.1g.

Mass of H-R period arrowheads have a wide range between 3.4g to 18.2g, as was the case in the LBII period (Figure 6.12).





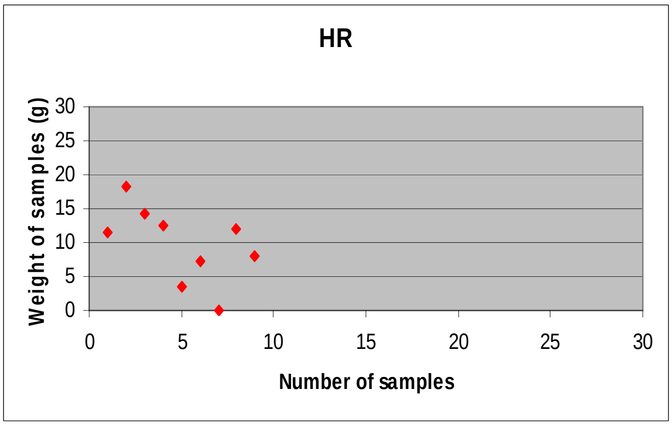


Figure 6.12. Mass Distribution of Arrowheads at different periods

7. CONCLUSION

The distribution of different types of arrowheads from the LBII Period was very similar to the distribution observed with the arrowheads studied by Erkanal from the MB and LB ages. In Erkanal's study the arrowheads with straight pin were slightly more than the butted pin type. The sockets of the four arrowheads in Erkanal's study were made by folding the extended flat sheet of copper at the back end of the arrowhead into a tube.

The earliest socketted arrowheads in this study were from the Iron Age, namely the beginning of the first millennium BC. However, the IA socketted arrowheads of Tarsus were made by casting, most likely by using two-piece mold with a proper core to obtain the necessary socket for the shaft. There was again a dramatic shift in the H-R Period arrowhead styles where the straight pin arrowheads become dominant with little socketted style.

The type and quantity of alloying elements determined by chemical analysis also showed wide variations between the three periods. Arrowheads made out of pure copper were a common practice in all three periods. However, there was a definite decrease in the use of arsenical copper from LBII to H-R where there was none in the H-R period. The use of bronze however was similar in both the LBII and IA. On the other hand a significant increase during the H-R period. These variations seen with the arrowheads are all in accordance of alloying traditions in most of the Near East cultures.

The distribution of nickel at trace levels among the three periods was very similar which may indicate that there was not a major change in the exploitation of ore sources. Antimony concentrations of the IA arrowheads were significantly higher that the other two periods. This may indicate a possible ore site changes. However, it may also be due to the high levels of lead detected for almost all of the socketted arrowheads. Since lead and antimony ores sometimes occur together, the excess antimony may come from the lead metal filled into the cavities of the blades of socketted arrowheads. Bimodal Pb-Sb correlation however did not show any significant trend.

Almost all of the socketted arrowheads had lead levels over 1%. Such high levels of lead do not originate from the copper but from the lead filled cavity of the blade. During sampling for analysis, the lead from the core was contaminating the copper metal. Once the technology of lead filled socketted arrowheads was recognized from the IA arrowheads, a problem with an unidentified object studied at the center dating to the Assyrian Colony Period (beginning of second millennium BC) from Acemhöyük was clarified. The object now turned out to be a highly deformed arrowhead. Back scattered electron image of a cross section of this arrowhead lead filled elliptical copper ring. If the date of this arrowhead is correct, the technology of adding lead to increase the mass of arrowheads may extend further back as much as 800 years.

Another interesting feature observed in this study was the very small variation in the mass of lead filled socketted arrowheads. The average mass was 6.0 gram (st. dev. 1.1). During the Iron Age a very standard production technology must have been practiced. The arrowheads from the LBII and H-R periods, however, had a wide difference in their mass somewhere between about three grams to about 18 grams.

APPENDIX A: CLASSIFICATION OF THE ARROWHEAD SAMPLES

Table A.1. Arrowhead samples

Item	Date	Inventory#	Reference	Analysis #	Weight(g)	Type
1**	EBIII	38.1595	291/77,427	02/230	4.3	190-135
2	LBII	35.1699		05/189	11.4	*
3	LBII	36.947		05/195	9.1	198-135
4	LBII	36.930	291/83, 427	05/196	10.3	191-137
5	LBII	38.1614	291/89, 427	05/197	5.9	198-135
6	LBII	38.21	291/87, 427	05/198	7.9	197-146
7	LBII	38.1619	291/91, 427	05/199	7.3	197-135
8	LBII	38.1601	291/90, 427	05/200	10.3	192-146
9	LBII	36.734	291/84, 427	05/201	15.2	197-136
10	LBII	38.1611	291/80, 427	05/202	16.8	198-237
11	LBII	37.181	291/86, 427	05/203	16.0	191-145
12	LBII	36.695	291/79, 427	06/126	11.0	*
13**	LBII	36.735	292/92, 427	01/206	15.1	192-235
14**	LBII	36.1120	291/88, 427	01/211	5.3	198-135
15**	LBII	36.732	291/85, 427	01/213	12.3	194-235
16	IA	36.702	373/18, 174	05/172	4.5	181-136s
17	IA	38.23	373/4	05/178	6.2	198-135
18	IA	38.281	373/19, 174	05/185	6.9	181-146s
19	IA	36.713	373/21, 174	05/191	5.6	181-146s
20	IA	36.704	373/20, 174	06/129	5.9	181-000s
21	IA	38.1450	373/10, 174	05/164	7.1	181-146s
22	IA	38.510	373/11, 174	06/132	6.2	183-145s
23	IA	36.746	372/1, 174	06/133	19.6	193-145
24	IA	36.903	373/1,13	05/169	6.8	181-135s
25	IA	38.638	373/3, 174	05/179	7.4	191-137
26	IA	36.874	373/13	05/188	5.7	181-135s
27	IA	36.878	373/12	06/131	4.1	181-135s
28	IA	36.879	373/16	06/135	6.1	181-135
29	IA	37.834	373/29, 174	02/286	4.9	181-146
30	IA	37.847	374/30	02/287	5.4	181-146
31	IA	38.276	373/26	05/163	5.2	181-146s
32	IA	36.708		05/166	5.5	181-135s
33	IA	36.899	373/24	05/173	4.5	181-136s
34	IA	38.277	373/6, 174	05/174	8.0	197-235
35	IA	38.123	374/32	05/176	5.9	181-146
36	IA	38.261	373/27, 174	05/184	5.0	181-135s

Item	Date	Inventory#	Reference	Analysis #	Weight(g)	Type
37	IA	36.876	374/34, 174	05/187	5.6	184-146
38	IA	38.532	373/8, 174	05/190	4.3	191-146
39	IA	38.282	373/25	06/128	4.6	181-235
40	IA	38.14	374/31, 171	06/130	4.2	181-135
41	IA	38.117	373/28	06/122	3.7	181-135s
42**	IA	36.716	373/17, 171	01/203	5.6	181-146s
43**	IA	36.705	373/15, 174	01/204	7.1	181-146s
44	HR	36.752	389/4, 264	05/165	11.4	191-147
45	HR	37.804	389/7, 264	05/170	18.2	191-137
46	HR	37.803	389/6, 264	05/171	14.2	191-147
47	HR	36.749	389/3, 264	05/193	12.5	191-147
48	HR	36.855	389/8, 264	06/125	3.4	191-140*
49	HR	35.703	389/1, 264	06/134	7.2	183-145
50	HR	37.852	391/42, 264	06/137	-	191-000
51	HR	No Tag #8		05/218	12.1	191-137
52	HR	No Tag #10		05/219	8.1	191-137
53	Unpub	37.849	373/9	05/167	5.3	198-136
54	Unpub	36.859	374/35	05/180	7.6	181-135s
55	Unpub	36.745		05/194	8.9	197-136
56	Unpub	38.1620		05/168	7.9	191-135
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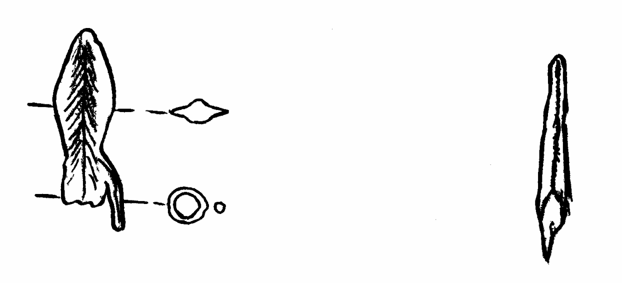
58	Unpub	38.1616		05/177	19.8	191-235
59	Unpub	38.1468		05/181	13.5	197-147
60	Unpub	38.1471		05/182	18.4	197-135
61	Unpub	38.306		05/183	10.5	197-135
62	Unpub	38.25		05/186	8.4	197-135
63	Unpub	No Tag #		05/204	5.7	197-146
64	Unpub	No Tag #		05/205	5.6	195-000
65	Unpub	No Tag #		05/206	5.5	195-000
66	Unpub	No Tag #9		05/207	15.1	191-137
67	Unpub	No Tag #7		05/208	3.7	184-137
68	Unpub	No Tag #6		05/209	4.6	184-135
69	Unpub	No Tag #116		05/210	12.0	192-000
70	Unpub	No Tag #120		05/211	26.4	191-146
71	Unpub	No Tag #1		05/212	5.0	184-135
72	Unpub	No Tag #5		05/213	6.4	184-135s
73	Unpub	No Tag #3		05/214	5.7	184-135s
74	Unpub	No Tag #121		05/215	3.6	190-146
75	Unpub	No Tag #4		05/216	6.1	182-135s
76	Unpub	No Tag #2		05/217	4.8	181-135
77	Unpub	35.1718	291/78, 427	06/121	3.5	*
78	Unpub	No Tag #		06/123	4.0	*
79	Unpub	36.729		06/124	9.6	191-135
80	Unpub	36.912	291/82, 127	06/127	11.5	*
81	Unpub	38.1627	291/81, 427	06/136	11.0	*
82**	Unpub	36.744		01/210	23.9	194-135

* typology is not exact.

** Analyzed by Kuruçayırlı (2003)

[Reference: Goldman, 1956]

APPENDIX B: CATALOG OF ARROWHEAD DRAWINGS



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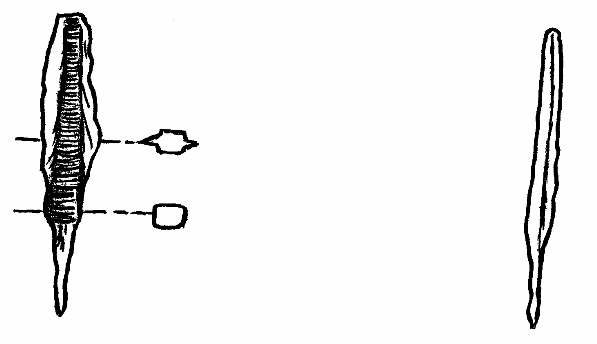

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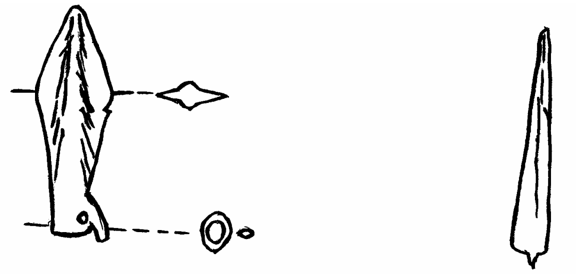

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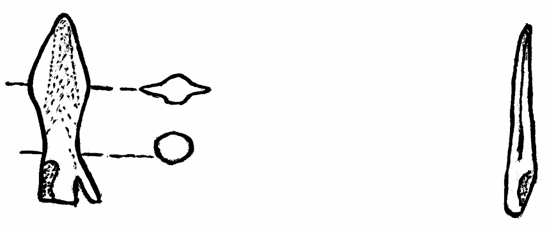

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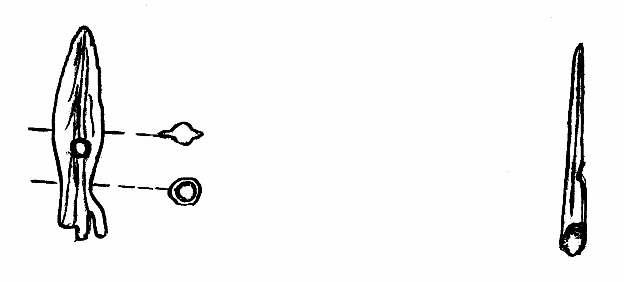

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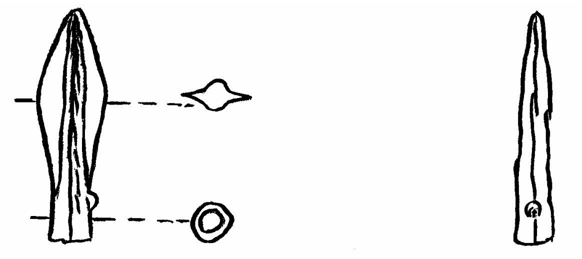

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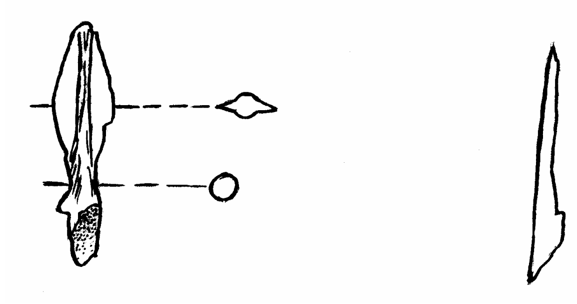

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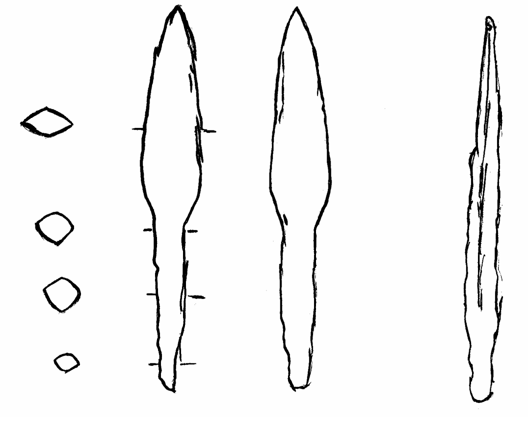

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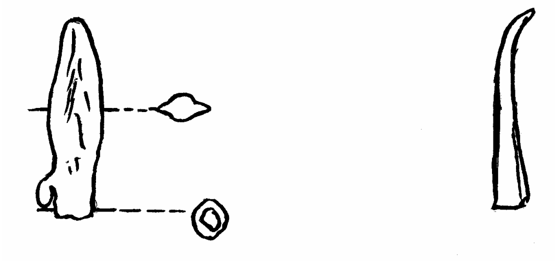

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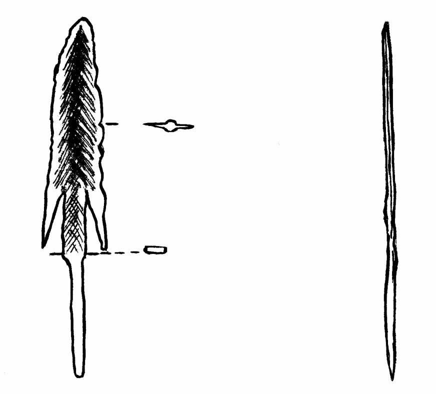

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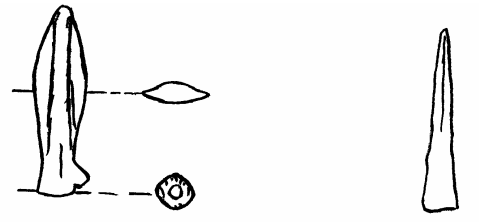

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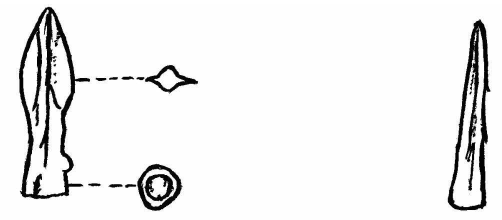

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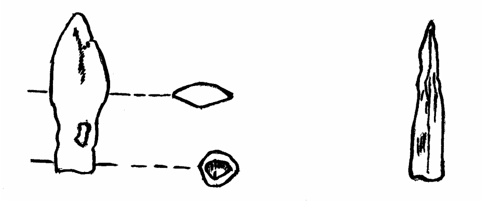

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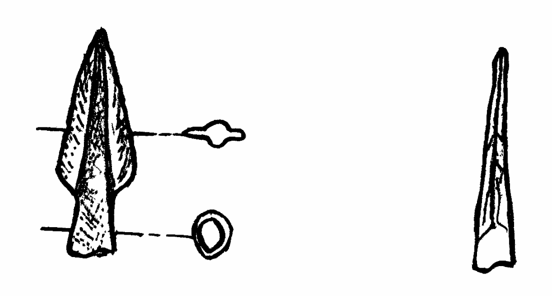

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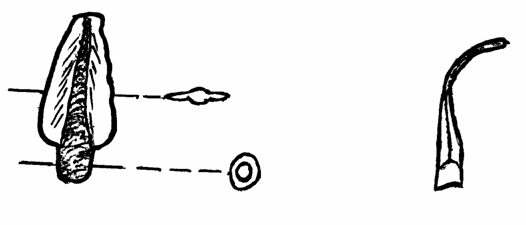

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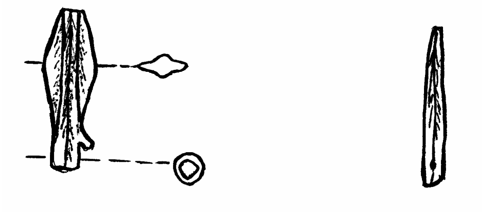

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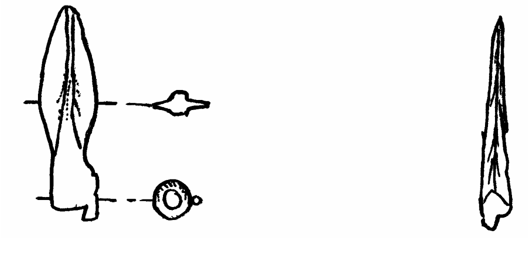

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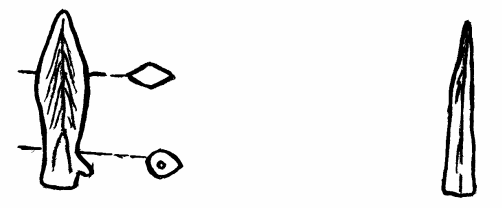

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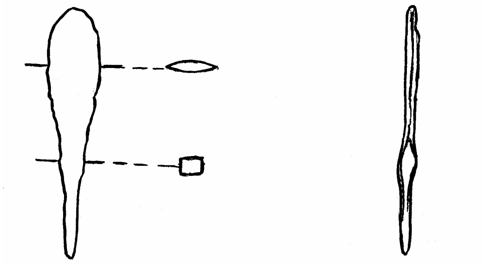

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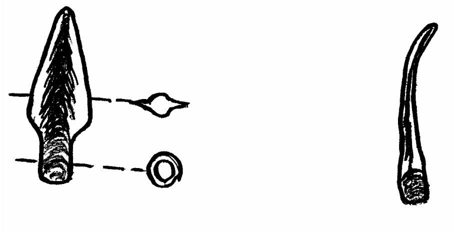

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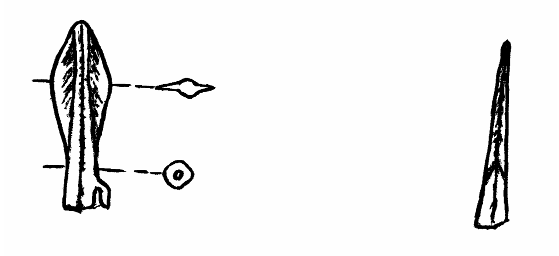

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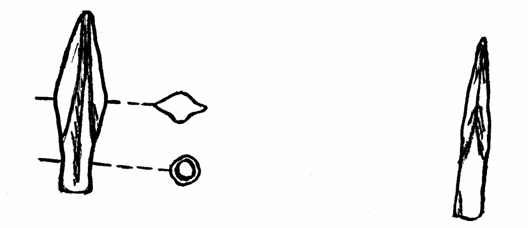

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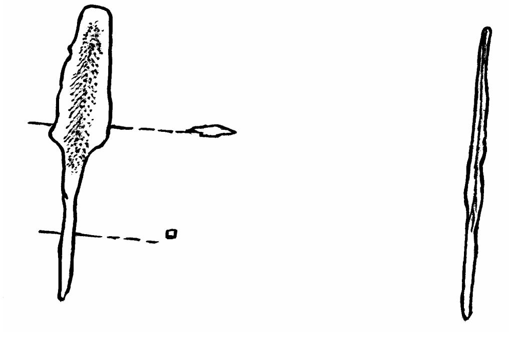

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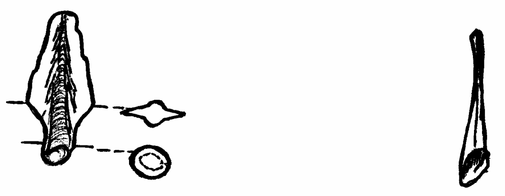

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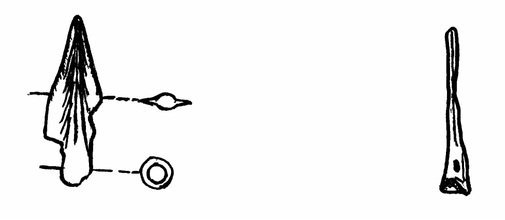

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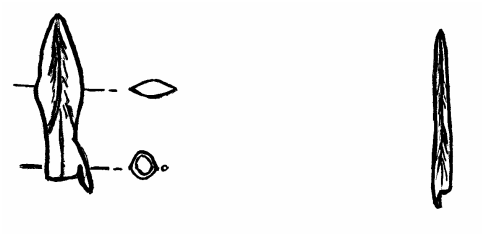

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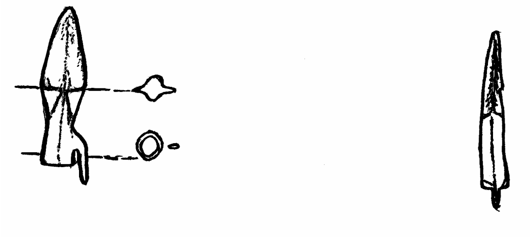

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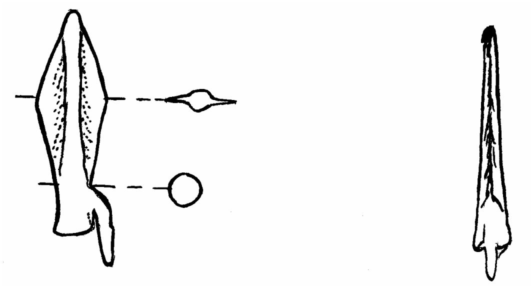

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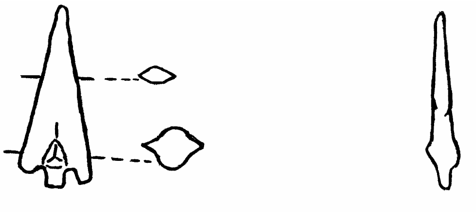
Figure B.1. IA samples



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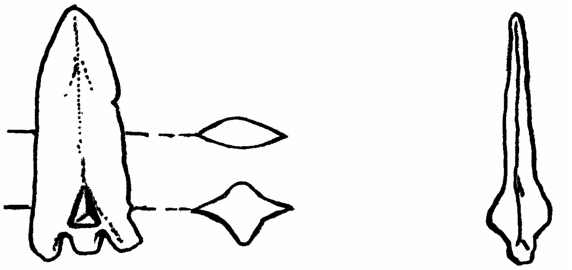

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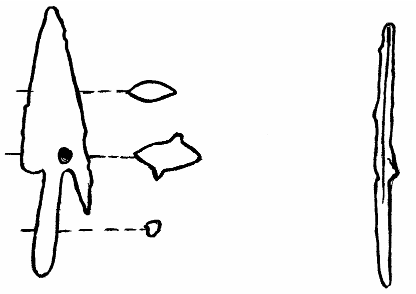

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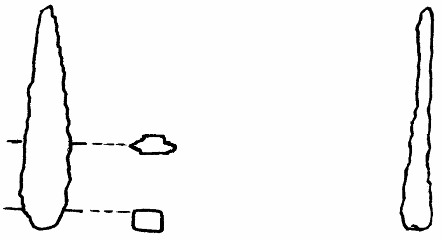

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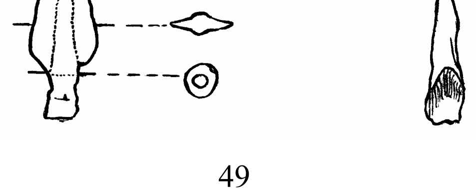

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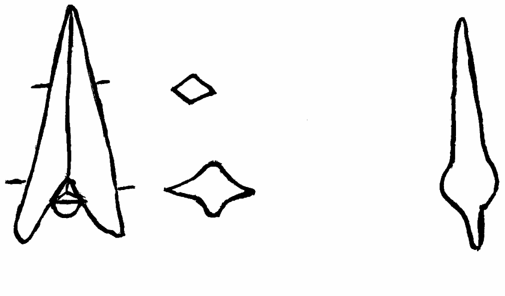

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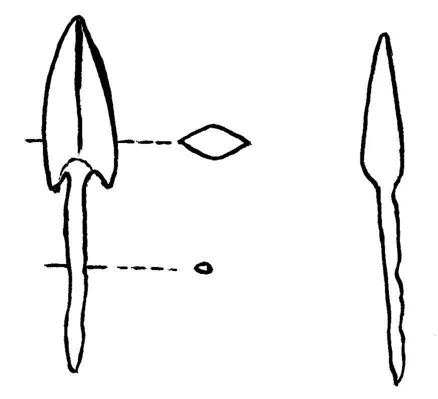

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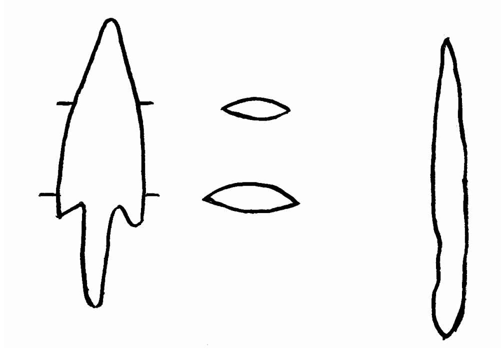
Figure B.2. Hellenistic-Roman period samples



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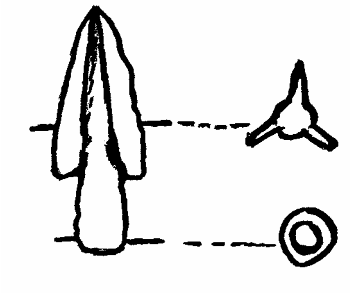

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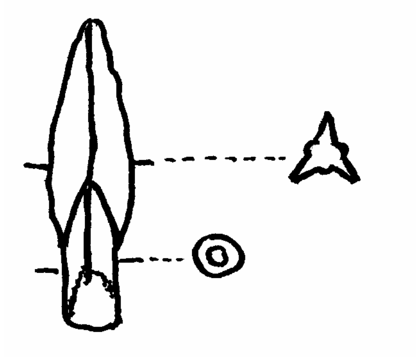

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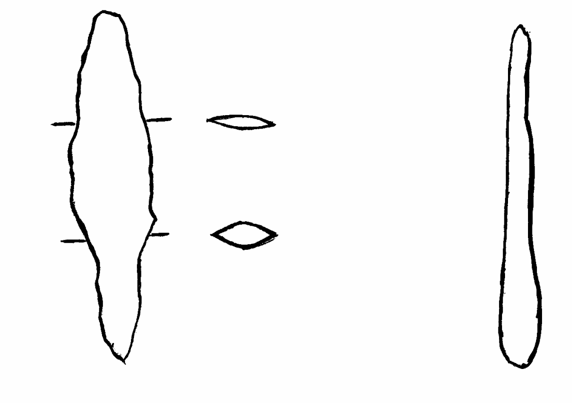

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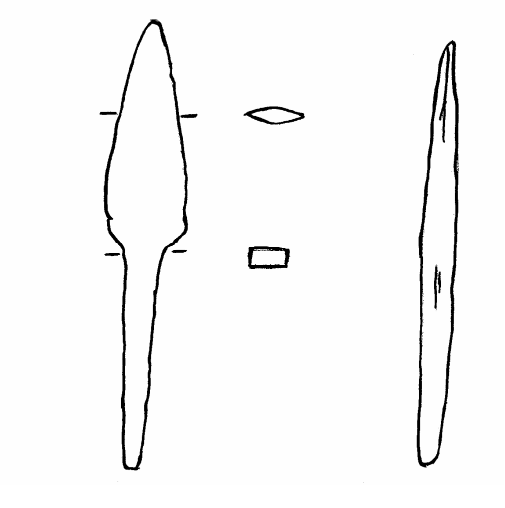

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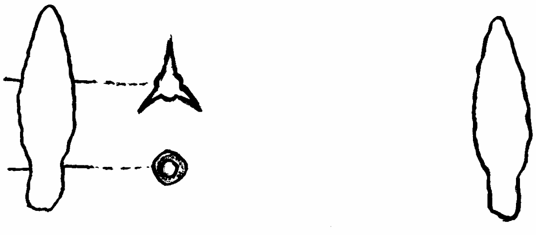

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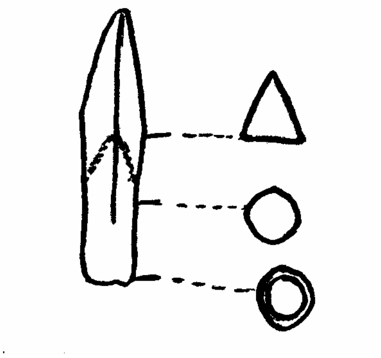

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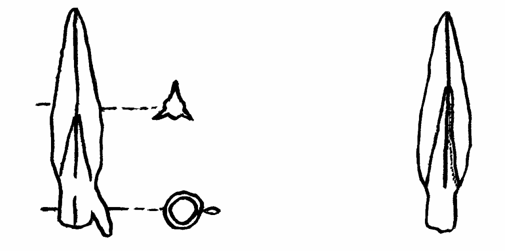

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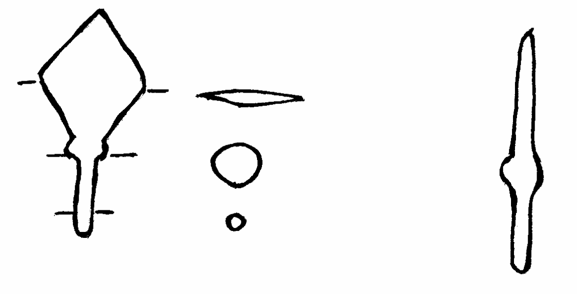

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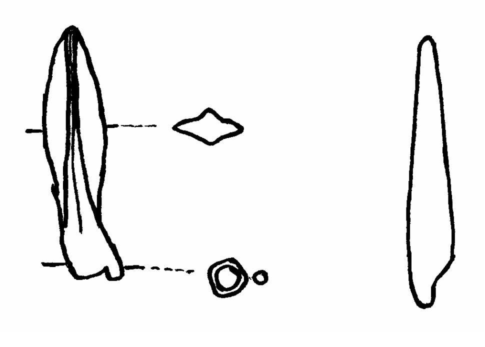

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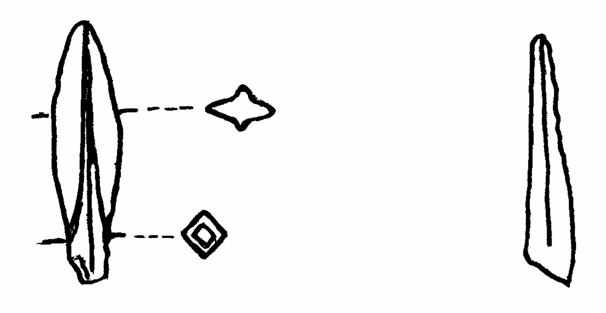

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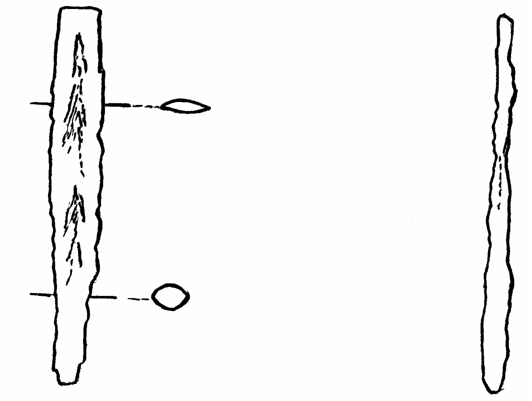

79

Figure B.3. Unpublished samples

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